

**Carbon Aerogel Supported Pure Pt and
Bimetallic Pt-Cu Alloy Nanoparticles by
Supercritical Deposition as Electrocatalysts for
Polymer Electrolyte Membrane Fuel Cells**

By

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to my beloved sister...

ABSTRACT

Supercritical deposition method was used to synthesize carbon aerogel supported Pt, Pt-Cu and carbon black supported Pt-Cu nanoparticles. CAs with average pore diameters of 6, 8 and 19 nm (CA6, CA8 and CA19, respectively) were synthesized and impregnated with Pt(cod)me₂ precursor using supercritical carbon dioxide followed by the thermal conversion at various temperatures between 200-1000 °C. All of the prepared CAs have high surface areas with very sharp pore size distributions. XRD and TEM results show increased Pt particle size with increasing conversion temperature with a homogenous distribution of nanoparticles on the CA supports. Cyclic voltammetry was used to determine the effect of CA pore properties on electrocatalytic activity. At a conversion temperature of 400 °C, the highest electrochemical surface area value were obtained for the CAs with higher average mesopore size (Pt/CA19). Furthermore, Pt/CA19 showed good mass activity whereas Pt/CA6 and Pt/CA8 had lower activity values towards ORR. The mass activity values for Pt/CA19 increased with increasing conversion temperature, except for the sample converted at 1000 °C which exhibited the lowest mass activity. The specific activity increased significantly with the conversion temperature up to 600 °C which gave a value six times that obtained at 200 °C. At 800 °C, the specific activity decreased slightly, probably due to a change in the CA structure at this elevated conversion temperature.

The adsorption isotherms of Cu(tfa)₂ on CA19 were measured in 35 °C and 10.7 MPa in scCO₂ and fitted to Langmuir adsorption model. Both simultaneous and sequential SCD methods were applied for the preparation of preliminary Pt-Cu/CA19 samples, however, simultaneous SCD resulted low Cu loadings due to competitive adsorption of Pt(cod)me₂ and Cu(tfa)₂ on CA19. Sequential SCD was used to prepare Pt-Cu/CA19 samples. Decomposition

of the precursors were carried out thermally under H_2 flow, followed by the annealing under N_2 at three different temperatures, 600 °C, 800 °C and 950 °C. The effects of deposition order, annealing temperature and metal composition on the average Pt-Cu particle size, dispersion, and particle morphology and electrocatalytic activity were investigated. Two sets of Pt-Cu/CA19 samples were prepared with different Pt:Cu mole ratios; first set was prepared with Pt:Cu mole ratio of 1:1 and the second set was prepared with Pt:Cu mole ratio of 1:3 using the single component adsorption isotherms of $Pt(cod)me_2$ and $Cu(tfa)_2$ in $scCO_2$ and changing the deposition order. XRD and EDX mapping showed that all prepared samples formed disordered Pt-Cu alloy nanoparticles on CA19. The metal composition did not have a significant effect on the average particle size or dispersion of Pt-Cu nanoparticles. XRD and TEM images showed homogenous distribution of Pt-Cu nanoparticles on CA19 with narrow particle size distributions for all samples. All prepared samples have average Pt-Cu nanoparticles sizes between 1.8 nm and 4.5 nm. Furthermore, increasing annealing temperatures found to promote alloying process without excessive growth of Pt-Cu nanoparticles. Adsorption of first $Cu(tfa)_2$ on CA19 resulted in low electrocatalytic activities for both 1:1 and 1:3 samples whereas the samples prepared by first adsorbing $Pt(cod)me_2$ on CA19 had promising electrocatalytic activities. Samples with Pt:Cu mole ratios of 1:3 showed better catalytic activities than the ones with 1:1. Enhanced catalytic activity as compared to pure Pt/CA19 was obtained for Pt-Cu/CA19 sample (0.123 A/mg_{Pt}) annealed at 800 °C, where $Pt(cod)me_2$ adsorbed firstly, with a Pt:Cu mole ratio of 1:3.

The effect of support was also investigated by impregnating CA19 and Vulcan (carbon black) with $Pt(cod)me_2$ and $Cu(tfa)_2$ via *in-situ* sequential SCD method with Pt:Cu mole ratios of 1:3. The average particle size of Pt-Cu on CA19 was significantly lower (2.8 nm) than the average particle size on carbon black (4.9). Mole ratios obtained from XRD and XRF were quite close to each other when compared to other Pt-Cu/CA19 samples. Moreover, Pt-

Cu/Vulcan sample resulted in higher electrocatalytic activity than the Pt-Cu/CA19 sample (0.09 A/mg_{Pt} and 0.04 A/mg_{Pt}).



ÖZET

Süperkritik depozisyon (SCD) yöntemi ile karbon aerogel destekli Pt, Pt-Cu ve karbon siyah destekli Pt-Cu ikili alaşım nanoparçacıkları başarıyla sentezlenmiştir. Gözenek çapları 6, 8 ve 19 nm olan karbon aerogeller (CA) $Pt(cod)me_2$ ile süperkritik karbondioksit ($scCO_2$) ortamında yüklenmiş ve metal öncülü değişik sıcaklıklarda (200-100 °C) N_2 akışında indirgenmiştir. Sentezlenen tüm karbon aerogellerin yüksek yüzey alanına ve dar bir gözenek dağılımına sahip olduğu görülmüştür. Pt parçacık boyutunun artan indirgenme sıcaklığıyla arttığı fakat bütün örneklerde Pt parçacıklarının homojen dağılımının ve dar parçacık boyutu dağılımının sağlandığı XRD ve TEM sonuçlarından görülmüştür. Destek maddesinin gözenek özelliklerinin elektrokatalitik aktivitesine olan etkileri çevrimli voltametri yöntemi ile belirlenmiştir. 400 °C’de indirgenen örnekler arasında, en yüksek elektrokimyasal aktif alan yüksek mezogözenek boyutuna sahip Pt/CA örneğinde (Pt/CA19) elde edilmiştir. Ayrıca, Pt/CA19 örneği oksijen indirgenme reaksiyonuna (ORR) karşı iyi bir aktivite gösterirken, Pt/CA6 ve Pt/CA8 örnekleri daha düşük aktivite göstermiştir. Pt/CA19 örneklerinin ORR’a karşı kütle aktivite değerlerinin, 1000 °C’de indirgenen örnek dışında, ortalama parçacık boyutu ile arttığı belirlenmiştir. Spesifik aktivite değerlerinin ise 600 °C’ye kadar önemli ölçüde arttıkları ve bu sıcaklıkta 200 °C’deki altı katı kadar arttığı gözlemlenmiştir. 800 °C’de spesifik aktivitenin, muhtemelen yüksek indirgenme sıcaklığında CA’nin yapısında oluşan değişim nedeniyle hafifçe azaldığı görülmüştür.

$Cu(tfa)_2$ ’ın CA19 üzerinde adsorpsiyon izotermi 35 °C’de ve 10,7 MPa’da $scCO_2$ içerisinde ölçülmüş ve Langmuir modeline uydurulmuştur. Öncül Pt-Cu/CA19 örnekleri eşzamanlı ve ardışık SCD yöntemleri kullanılarak sentezlenmiştir. Fakat eşzamanlı SCD yönteminde $Pt(cod)me_2$ ve $Cu(tfa)_2$ ’nin rekabetçi adsorpsiyonu örneklerde düşük Cu oranına neden olmuştur. Bu nedenle Pt-Cu/CA19 örneklerinin sentezine ardışık SCD ile devam

edilmiştir. Bakır öncülü 200 °C’de H₂ akış ortamında indirgenmiş ve takiben farklı sıcaklıklarda (600, 800 ve 950 °C) N₂ akış ortamında tavlantıya alınmışlardır. Adsorpsiyon sırasının, tavlantı sıcaklığının ve metal oranlarının ortalama parçacık boyutuna, parçacık dağılımına, alaşım sürecine ve elektrokatalitik aktiviteye etkileri incelenmiştir. Öncül maddelerin tekli adsorpsiyon izotermi kullanılarak, ilk set Pt:Cu mol oranı 1:1 olacak şekilde, ikinci set ise Pt:Cu mol oranı 1:3 olacak şekilde ve set içerisinde adsorpsiyon sırasını değiştirerek iki set Pt-Cu/CA19 örnekleri hazırlanmıştır. XRD ve EDX haritalaması, Pt ve Cu’nun her örnekte düzensiz alaşımlar oluşturduğunu göstermiştir. Metal oranının, ortalama parçacık boyutunda ya da parçacık dağılımında önemli bir farklılık yaratmadığı, bütün sentezlenen örneklerde Pt-Cu nanoparçacıklarının CA19 üzerinde homojen dağılımlarının ve dar parçacık boyutu dağılımının sağlandığı görülmüştür. Hazırlanan örneklerin tamamında Pt-Cu ortalama parçacık boyutunun 1,8 nm ve 4,5 nm arasında olduğu görülmüştür. Artan tavlantı sıcaklıklarının alaşım sürecine katkı sağlarken, parçacık boyutunu çok artırmadığı görülmüştür. CA19 üzerine ilk Cu(tfa)₂’nin adsorpsiyonu, mol oranları hem 1:1 hem de 1:3 olan örneklerde düşük elektrokatalitik aktiviteye sebep olmuştur, Pt(cod)me₂ ilk olarak adsorplandığında ise daha iyi aktivite elde edilmiştir. Pt:Cu mol oranları 1:3 olan örneklerin 1:1 olan örneklerden daha yüksek aktivite değerleri olduğu görülmüştür. 800 °C’de tavlantıya alınan, mol oranı 1:3 olan ve Pt(cod)me₂’nin ilk adsorbe edildiği örnekte geliştirilmiş aktivite (0,123 A/mg_{Pt}) elde edilmiştir.

Destek maddesinin etkisi, CA19 ve Vulcan (karbon siyah) üzerine, *in-situ* ardışık depozisyon yöntemi ile sentezlenen ve Pt:Cu mol oranı 1:3 olan iki örnek ile incelenmiştir. Ortalam parçacık boyutunun CA19 üzerinde (2,8 nm) karbon siyaha (4,9 nm) oranla çok daha küçük olduğu fakat her iki örnekte de homojen dağılımın sağlandığı görülmüştür. XRD ve XRF’den elde edilen Pt:Cu mol oranlarının, diğer örneklerle göre çok daha benzer olduğu belirlenmiştir. Ayrıca Pt-Cu/Vulcan örneğinin Pt-Cu/CA19 örneğine kıyasla daha iyi bir elektrokatalitik aktivite gösterdiği belirlenmiştir (sırasıyla 0,087 A/mg_{Pt} ve 0,044 A/mg_{Pt}).

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TABLE OF CONTENTS

Abstract	iv
List of Tables	xiv
List of Figures	xvi
Nomenclature	xxii
Chapter 1: Introduction	1
Chapter 2: Literature Review	7
2.1. Carbon Aerogels	7
2.2. Supercritical Fluids	8
2.3. Supercritical Deposition	10
2.3.1. Adsorption Isotherms	12
2.3.2. Conversion of Adsorbed Metal Complexes to Metallic Nanoparticles	14
2.4. Oxygen Reduction Reaction	15
2.4.1. The Volcano Plot	17
2.4.2. The d-band Theory	18
2.5. Hydrogen Oxidation Reaction	19
2.6. Cyclic Voltammetry	19
2.5. Platinum Nanoparticles on Carbonaceous Supports as Electrocatalysts	24
2.5.1. Effect of Support Properties on Electrocatalytic Activity	24
2.5.2. Effect of Pt Particle Size and Shape on Electrocatalytic Activity	26

2.6. Pt-Cu Bimetallic Nanoparticles on Carbonaceous Supports as Electrocatalysts	27
Chapter 3: Experimental Methods and Characterization Techniques	31
3.1. Materials	31
3.2. Synthesis of Resorcinol Formaldehyde Aerogels and Carbon Aerogels	31
3.4. Metal Complex Adsorption Measurements and Supercritical Deposition Experiments	33
3.4. Precursor Conversion and Annealing	35
3.5. Material Characterization	37
3.6. Electrochemical Characterization	39
Chapter 4: Results and Discussion	42
4.1. CA supported Pt Nanoparticles	42
4.1.1. Properties of CAs	42
4.1.2. CA Supported Pt Nanoparticles	45
4.1.3. Effect of Pore Properties of CA on the Electrocatalytic Properties	57
4.1.4. Effect of Pt Particle Size on Electrocatalytic Behavior	63
4.2. CA19 Supported Pt-Cu Bimetallic Alloy Nanoparticles	65
4.2.1. Single Adsorption Isotherms of Pt(cod)me ₂ -CA19 and Cu(tfa) ₂ -CA19 in scCO ₂	65
4.2.2. Decomposition of metal precursors	67
4.2.2.1. Decomposition of Pt(cod)me ₂	67
4.2.2.2. Decomposition of Cu(tfa) ₂	67
4.2.3. Preliminary Simultaneous and Sequential Deposition Experiments for the Preparation of Pt-Cu/CA19 Composites	71

4.2.4. Pt-Cu/CA19 Composites Prepared via Sequential Deposition Having Pt:Cu Mole Ratios of 1:1	87
4.2.5. Pt-Cu/CA19 Composites Prepared via Sequential Deposition Having Pt:Cu Mole Ratios of 1:3	112
4.2.6. Pt-Cu/CA19 and Pt-Cu/Carbon Black Composites Prepared via Sequential <i>In-situ</i> SCD Followed by <i>Ex-situ</i> Annealing and Having Pt:Cu Mole Ratios of 1:3	134
Chapter 5: Conclusion and Future Work	148
Bibliography	153
Appendix	169

LIST OF TABLES

Table 3.1: Reactants ratios used during the synthesis of RFAs with different pore sizes.	32
Table 4.1: Pore properties of synthesized CAs.	42
Table 4.2: Raman parameters of CA samples obtained from curve fitting.	44
Table 4.3: Area ratios of CA samples obtained from curve fitting of the Raman spectra.	45
Table 4.4: Overall Pt loadings of the prepared samples.	45
Table 4.5: Particle sizes of Pt/CA samples obtained from XRD spectrum and TEM images.	56
Table 4.6: Electrocatalytic properties of Pt/CA samples treated at 400 °C.	62
Table 4.7: Electrocatalytic properties of Pt/CA19 samples.	63
Table 4.8: Langmuir model parameters of Pt(cod)me ₂ -CA19 and Cu(tfa) ₂ -CA19 systems.	66
Table 4.9: Preliminary Pt-Cu/CA19 samples and explanation of deposition approaches.	71
Table 4.10: Pt and Cu weight percentages of the preliminary Pt-Cu/CA19 samples.	72
Table 4.11: Pt:Cu mole ratios of the preliminary Pt-Cu/CA19 samples obtained from XRD and XRF.	74
Table 4.12: The average Pt-Cu particle sizes of preliminary Pt-Cu/CA19 samples.	81
Table 4.13: Annealed Pt-Cu/CA19 samples prepared by sequential SCD and explanation of deposition order.	82
Table 4.14: Pt and Cu weight percentages of the annealed Pt-Cu/CA19 samples.	82
Table 4.15: Pt:Cu mole ratios of Pt-Cu/CA19 samples annealed at 600 °C.	84
Table 4.16: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 samples annealed at 600 °C.	86
Table 4.17: Pt-Cu/CA19 samples prepared by sequential SCD with Pt:Cu mole ratio of 1:1 and the explanation of deposition order.	87
Table 4.18: Pt and Cu weight percentages of the Pt-Cu/CA19 samples before annealing.	87
Table 4.19: Pt:Cu mole ratios of Pt-Cu/CA19 samples obtained from XRF and XRD.	90

Table 4.20: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:1 and annealed at different temperatures.	103
Table 4.21: Electrocatalytic properties of Pt-Cu/CA19 Trial 7 and Trial 8 annealed at different temperatures.	110
Table 4.22: Pt-Cu/CA19 samples prepared by sequential SCD with Pt:Cu mole ratio of 1:3 and the explanation of deposition order.	112
Table 4.23: Pt and Cu weight percentages of the Pt-Cu/CA19 samples before annealing.	112
Table 4.24: Pt:Cu mole ratios of Pt-Cu/CA19 samples obtained from XRF and XRD.	115
Table 4.25: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:3 and annealed at different temperatures.	127
Table 4.26: Electrocatalytic properties of Pt-Cu/CA19 Trial 9 and Trial 10 annealed at different temperatures.	133
Table 4.27: Pt-Cu/CA and Pt-Cu/Vulcan samples prepared by sequential <i>in-situ</i> SCD followed by <i>ex-situ</i> annealing with Pt:Cu mole ratio of 1:3 and the explanation of deposition order.	135
Table 4.28: Pt and Cu weight percentages of the Pt-Cu/CA <i>in-situ</i> and Pt-Cu/Vulcan <i>in-situ</i> samples before annealing.	135
Table 4.29: Pt:Cu mole ratios of Pt-Cu/CA19 <i>in-situ</i> and Pt-Cu/Vulcan <i>in-situ</i> samples obtained from XRF and XRD.	137
Table 4.30: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 <i>in-situ</i> and Pt-Cu/C <i>in-situ</i> samples having Pt:Cu mole ratios of 1:3 and annealed at different temperatures.	142
Table 4.31: Electrocatalytic properties of Pt-Cu/CA19 and Pt-Cu/Vulcan annealed at 800 °C.	146

LIST OF FIGURES

Figure 2.1: The representative pressure-temperature diagram of pure CO ₂ .	9
Figure 2.2: Transmission electron microscope (TEM) images of (a) carbon supported Pt catalyst prepared by SCD [37] and (b) commercial carbon supported Pt catalyst (ETEK) [71].	11
Figure 2.3: Schematic representation of two SCD approaches for the preparation of supported bimetallic alloys; (a) simultaneous SCD and (b) sequential SCD.	12
Figure 2.4: Potential free energy diagram for the ORR pathway on platinum catalyst [85].	17
Figure 2.5: The dependence of Gibbs free energy, ΔG_0 on the adsorption energy of O ₂ on catalyst, ΔE_0 [85].	18
Figure 2.6: Schematic representation of cyclic voltammetry device.	20
Figure 2.7: CV of polycrystalline Pt electrode in N ₂ saturated 0.5 M H ₂ SO ₄ with a scan rate of 50 mV/s [90].	21
Figure 2.8: ORR curves of carbon black supported Pt electrocatalyst taken in O ₂ 0.1 M HClO ₄ at different rotation speeds with a scan rate of 10 mV/s and the inset figure is the Koutecky-Levich plot of the same electrocatalyst [37].	22
Figure 2.9: Pt particle size dependence of mass and specific activity [26].	27
Figure 2.10: Bulk phase diagram of Pt-Cu alloy system [127].	28
Figure 2.11: Representative formation of Pt enriched surface over Pt-Cu alloy core [135].	30
Figure 3.1: Photographs of prepared RFAs (a) and CAs (b); the ones on the left are the monolithic forms and the ones on the right are the crushed forms.	33
Figure 3.2: Experimental setup for metal complex adsorption measurements.	34
Figure 3.3: Experimental setup used for electrochemical characterizations (a) cyclic voltammetry equipment (b) electrochemical cell used.	40

Figure 4.1: Pore size distributions of CA6, CA8, CA19.	43
Figure 4.2: Raman spectra of CA6, CA8 and CA19.	44
Figure 4.3: XRD patterns of (a) Pt/CA6 (b) Pt/CA8 (c) Pt/CA19 which were produced using different precursor conversion temperatures.	47
Figure 4.4: Variation of Pt particle size with precursor conversion temperature.	48
Figure 4.5: TEM images and particle size distributions of Pt/CA6 samples (a) 200 °C, (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 1000 °C	50
Figure 4.6: TEM images and particle size distributions of Pt/CA8 samples (a) 200 °C, (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 1000 °C	52
Figure 4.7: TEM images and particle size distributions of Pt/CA19 samples (a) 200 °C, (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 1000 °C	54
Figure 4.8: Variation of σ/d_m with mean particle size.	57
Figure 4.9: Cyclic voltammograms of Pt/CA6 400 °C, Pt/CA8 400 °C and Pt/CA19 400 °C taken in N ₂ saturated HClO ₄ electrolyte (10 th cycles).	58
Figure 4.10: Cyclic voltammograms of Pt/CA6 400 °C, Pt/CA8 400 °C and Pt/CA19 400 °C taken in N ₂ saturated HClO ₄ electrolyte (200 th cycles).	58
Figure 4.11: ORR curves of Pt/CA6 400 °C after 10 cycles, recorded with a scan rate of 10 mV/s.	60
Figure 4.12: ORR curves of Pt/CA8 400 °C after 10 cycles, recorded with a scan rate of 10 mV/s.	61
Figure 4.13: ORR curves of Pt/CA19 400 °C after 10 cycles, recorded with a scan rate of 10 mV/s.	61
Figure 4.14: Change in mass and specific activity of Pt/CA19 samples with particle sizes.	65
Figure 4.15: Single adsorption isotherms of Pt(cod)me ₂ -CA19 [35] and Cu(tfa) ₂ -CA19 measured at 35 °C and 10.7 MPa in scCO ₂ .	66

Figure 4.16: TGA of pure Cu(tfa) ₂ and Cu(tfa) ₂ adsorbed on CA19 in N ₂ flow; TGA curve of Cu(tfa) ₂ adsorbed on CA19 was plotted by subtracting the CA19 weight of the sample.	68
Figure 4.17: FTIR-spectra of pure Cu(tfa) ₂ , Cu(tfa) ₂ adsorbed on CA19 and Cu/CA19 composites treated at 150 °C and 200 °C under flowing H ₂ .	69
Figure 4.18: XRD of Cu/CA composites treated at 150 °C and 200 °C under flowing H ₂ .	70
Figure 4.19: XRD of preliminary Pt-Cu/CA19 samples prepared via simultaneous and sequential SCD.	73
Figure 4.20: TEM images of (a) Pt-Cu/CA19 Trial 1 (simultaneous) (b) Pt-Cu/CA19 Trial 2 (sequential) (c) Pt-Cu/CA19 Trial 3 (sequential) (d) Pt-Cu/CA19 Trial 4.	76
Figure 4.21: HAADF and EDX mapping images of preliminary Pt-Cu/CA19 samples (a) Trial 1 (simultaneous) (b) Trial 2 (sequential) (c) Trial 3 (sequential) (d) Trial 4 (simultaneous).	79
Figure 4.22: Cu-rich and Pt-rich nanoparticles in Pt-Cu/CA19 Trial 4 (simultaneous).	80
Figure 4.23: XRD of Pt-Cu/CA19 prepared via sequential SCD and annealed at 600 °C.	83
Figure 4.24: TEM and particle size distribution of Pt-Cu/CA19 Trial 5 annealed at 600 °C.	84
Figure 4.25: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 5 annealed at 600 °C.	85
Figure 4.26: XRD of (a) Pt-Cu/CA19 Trial 7 and (b) Pt-Cu/CA19 Trial 8 with Pt:Cu mole ratios of 1:1 prepared via sequential SCD.	89
Figure 4.27: SEM images of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.	92
Figure 4.28: SEM images of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.	93
Figure 4.29: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.	96

Figure 4.30: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.	98
Figure 4.31: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C , (b) 800 °C , and (c) 950 °C.	100
Figure 4.32: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, (c) and 950 °C.	102
Figure 4.33: Cyclic voltammograms of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N ₂ saturated HClO ₄ electrolyte (1 st and 300 th cycles) with a scan rate of 50 mV/s.	105
Figure 4.34: Cyclic voltammograms of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N ₂ saturated HClO ₄ electrolyte (1 st and 300 th cycles).	106
Figure 4.35: ORR curves of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.	108
Figure 4.36: ORR curves of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.	109
Figure 4.37: XRD of (a) Pt-Cu/CA19 Trial 9 and (b) Pt-Cu/CA19 Trial 10 with Pt:Cu mole ratios of 1:3 prepared via sequential SCD.	114
Figure 4.38: SEM images of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.	116
Figure 4.39: SEM images of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.	117
Figure 4.40: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.	119
Figure 4.41: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.	121

Figure 4.42: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.	124
Figure 4.43: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.	126
Figure 4.44: Cyclic voltammograms of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N ₂ saturated HClO ₄ electrolyte (1 st and 300 th cycles).	129
Figure 4.45: Cyclic voltammograms of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N ₂ saturated HClO ₄ electrolyte (1 st and 300 th cycles).	130
Figure 4.46: ORR curves of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.	131
Figure 4.47: ORR curves of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.	132
Figure 4.48: XRD of Pt-Cu/CA19 and Pt-Cu/Vulcan prepared using sequential <i>in-situ</i> SCD with Pt:Cu mole ratios of 1:3 followed by annealing at 800 °C.	136
Figure 4.49: HRTEM images and particle size distributions of Pt-Cu/CA19 <i>in-situ</i> annealed at 800 °C.	138
Figure 4.50: HRTEM images and particle size distributions of Pt-Cu/Vulcan <i>in-situ</i> annealed at 800 °C.	138
Figure 4.51: HAADF and EDX mapping images of Pt-Cu/CA19 <i>in-situ</i> annealed at 800 °C.	140
Figure 4.52: HAADF and EDX mapping images of oxide rich nanoparticles in Pt-Cu/CA19 <i>in-situ</i> annealed at 800 °C.	140
Figure 4.53: HAADF and EDX mapping images of Pt-Cu/Vulcan <i>in-situ</i> annealed at 800 °C.	141

Figure 4.54: Cyclic voltammograms of (a) Pt-Cu/CA19 and (b) Pt-Cu/Vulcan annealed at 800 °C taken in N₂ saturated HClO₄ electrolyte (1st and 300th cycles). 143

Figure 4.55: ORR curves of (a) Pt-Cu/CA19 and (b) Pt-Cu/Vulcan annealed at 800 °C after 300 cycles, recorded with a scan rate of 10 mV/s. 145



NOMENCLATURE

a_i	Lattice parameter of species i
AFC	Alkaline fuel cell
ATR	Attenuated total reflectance
B	Koutecky-Levich constant
C	Precursor equilibrium concentration in scCO ₂ (mol/m ³ scCO ₂)
CA	Carbon aerogel
CE	Counter electrode
Cu(tfa) ₂	Copper(II) trifluoroacetylacetonate
CV	Cyclic voltammetry
d	Average particle size
d_{hkl}	Interplanar distance
d_m	Mean particle size
DMFC	Direct methanol fuel cell
E	Interaction potential between adsorbate and adsorbent
ΔE_0	Adsorption energy of O ₂ onto the catalyst surface
EDX	Energy-dispersive X-ray
ESA	Electrochemical surface area (m ² /g)
FTIR	Fourier Transform Infrared

ΔG_0	Gibbs free energy
HAADF-STEM	High-angle annular dark field scanning transmission electron microscopy
HOR	Hydrogen oxidation reaction
HRTEM	High resolution Transmission Electron Microscopy
j	Current density (A/cm^2)
j_k	Kinetic current density (A/cm^2)
K_0	Adsorption equilibrium constant ($m^3 \text{ scCO}_2/\text{mol}$)
K	Charge density of bulk Pt ($210 \mu C/cm^2$)
L_{Pt}	Platinum loading on electrode ($\mu g/cm^2$)
MA_c	Mass activity (A/mg_{Pt})
MEA	Membrane-electrode assembly
MCFC	Molten carbonate fuel cell
MSI	Metal-support interaction
n	Experimentally determined Freundlich isotherm constant
NHE	Normal hydrogen electrode
ORR	Oxygen reduction reaction
$1/p$	Heterogeneity factor
P	Pressure

P_c	Critical pressure
P_r	Reduced pressure
PAFC	Phosphoric acid fuel cell
PEMFC	Polymer electrolyte membrane fuel cell
$Pt(cod)me_2$	Dimethyl(1,5-cyclooctadene)platinum(II)
q	Uptake
Q_0	Adsorption capacity
RE	Reference electrode
RFA	Resorcinol-formaldehyde aerogel
SA	Surface area (m^2/g)
SA_c	Specific activity (mA/cm^2)
$scCO_2$	Supercritical carbon dioxide
SCD	Supercritical deposition
SCF	Supercritical fluid
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
T	Temperature
T_c	Critical temperature
T_r	Reduced temperature
TEM	Transmission electron microscopy

TGA	Thermogravimetric analysis
WE	Working electrode
XRD	X-ray diffraction
XRF	X-ray fluorescence
x_i	Mole fraction of species i

Greek Letters

ρ	Density of bulk Pt (21.4 g/cm ³)
σ	Standard deviation
θ	Bragg angle
λ	Wavelength of the x-ray
ω	Rotation speed (rpm)

Chapter 1: Introduction

A fuel cell is a device that directly converts chemical energy to electricity, in other words, they are electrochemical reactors. The fuel cell eliminates the energy conversion steps that usually occur in a conventional energy generator and this makes fuel cells thermodynamically more efficient than internal combustion engines [1]. Fuel cells have attracted great attention due to their high performance characteristics. There are several types of fuel cells such as, solid oxide fuel cells (SOFCs), phosphoric acid fuel cells (PAFCs), alkaline fuel cells (AFCs), molten carbonate fuel cells (MCFCs), direct methanol fuel cells (DMFCs) and polymer electrolyte membrane fuel cells (PEMFCs).

PEMFCs have a growing popularity as a newer type of fuel cell. There are several advantages of PEMFCs, it employs a solid polymer membrane as electrolyte which reduces corrosion and avoids electrolyte leakage [1]. Furthermore, PEMFCs operate at relatively low temperatures (60-80 °C) which allows quick start-up. The device is a quite compact system which makes them especially suitable for smaller scale applications such as car engines, home-based power distributions or portable power applications [2]. They have high power densities and most importantly it is a clean energy system since the only products of the process are electricity, water and some heat due to exothermic nature of the reactions [3].

PEMFCs have a sandwich-like structure where the heart of the fuel cell is membrane electrode assembly (MEA) which consists solid membrane with catalyst layer and porous gas diffusion layers on both sides. The MEA is coupled by graphite flow channels, current collectors and bipolar plates at both sides forming a single cell.

H₂ is fed to the anode side of the PEMFC where it is oxidized to form H⁺ cations and electrons. H⁺ cations goes through the perflourinated membrane to the cathode side, whereas,

electrons flow through an external circuit creating electric current. O_2 is fed to the cathode side where it is reduced by combining with H^+ cations and electrons to form H_2O .

PEMFCs are promising applications for the energy production since excessive usage of fossil fuels raises environmental issues such as global warming. However, the high cost of the equipment is a major drawback towards the commercialization of the device. According to the U.S. Department of Energy's 2016 report, approximately half of the cost of PEMFCs arises from the cost of the MEA. Also, all the reactions take place at the interface of gas diffusion layer, catalyst and electrolyte which is called three-phase interface. Therefore, optimization of these layers are extremely important in order to meet U.S. Department of Energy's targets for the technical application of PEMFCs [4].

Carbon-supported Pt nanoparticles are generally used as electrocatalysts in PEMFCs due to the excellent activity of Pt towards the oxygen reduction reaction (ORR) [5-7]. The slow kinetics of the ORR are well known [8], and so catalyst layers with very high Pt loadings are required to achieve the desired PEMFC performance and since Pt is a noble and expensive metal (29\$/g), this results in highly expensive catalyst layers.

Research efforts are directed to reduce the Pt content in the catalyst layers while enhancing the activity. There are several strategies that can be applied for this purpose;

- Employing a better catalyst support [9, 10]
- Using combination of Pt with other non-noble transition metals such as Fe, Ni, Cu, Co [11-18]
- Employing a non-Pt based catalyst

Since non-Pt based catalyst have shown to have electrocatalytic activities lower than Pt based catalyst [9, 19, 20], research efforts have been mostly directed to the other two strategies mentioned above.

Employing a better catalyst support is quite important since the support properties governs the parameters that are directly related to activity (particle size, particle morphology and etc.) [21]. Carbon aerogels (CAs) are getting increasing attention as relatively new carbon material. They are usually obtained by the pyrolysis of organic aerogels under an inert atmosphere [22]. Their controllable properties, high surface areas, high pore volumes and high electrical conductivities make them suitable as electrocatalyst supports. In particular CAs with pore sizes above 20 nm are very suitable as PEMFC catalyst supports because it enables the interaction between catalyst and the Nafion[®] binder which is used in electrode preparation and consisting of ionomers that cannot penetrate into the pores smaller than 20 nm [21]. CA supported Pt nanoparticles as electrocatalysts have been investigated and found to have shown promising activities [23, 24]. Furthermore, it has been demonstrated previously that there is a strong relationship between the Pt particle size and the electrocatalytic activity where the mass activity of the Pt electrocatalyst increases rapidly with increasing particle size up to a certain point (between 1.3 nm and 4 nm) beyond which activity declines rapidly with increasing size [25, 26].

Supported bimetallic nanoparticles have proven to be a good way to decrease the Pt amount while enhancing the activity. Due to the changes in the electronic structure of alloyed Pt as compared to pure Pt, supported bimetallic nanoparticles have shown enhanced electrocatalytic activities towards ORR. Supported Pt-Cu alloy nanoparticles have been widely investigated since they are precursors for highly active Pt-Cu core – Pt shell electrocatalysts for the ORR [27-29]. In the case of supported bimetallic nanoparticles, the control of the metal loading and nanoparticle morphology (core-shell, disordered alloy, segregated etc.) are extremely important since these parameters are directly related to the activity. Hence, the preparation method used should allow one to control these parameters.

Supported mono or bimetallic nanoparticles can be synthesized using different routes such as impregnation, sol-gel route, ion-exchange or chemical vapor deposition. Although, these techniques have been widely used and investigated, there are some drawbacks such as difficulty in controlling particle size, metal loading and etc., usage of toxic solvents and additional steps that are required to remove the solvent. Supercritical deposition (SCD) on the other hand is an alternative way to prepare supported nanoparticles.

SCD involves three main steps;

1. Dissolution of a metal precursor in a supercritical fluid
2. Exposure of a porous substrate to the mixture to allow for metal precursor adsorption onto the substrate
3. Conversion of the precursor to its metal form using various routes [30-32]

The supported nanoparticles prepared via SCD have shown a very homogenous distribution of metal nanoparticles in support with very narrow particle size distributions with excellent control of metal loading [33-35]. Furthermore carbon supported Pt electrocatalyst prepared by SCD have exhibited good electrocatalytic activities when compared to the commercially available Pt/carbon electrocatalysts [36, 37].

There are no studies in the literature on the effect of Pt particle size on electrocatalytic activity for CA supports. However, considering the previous studies in the literature using other carbonaceous supports, such an effect may also exist for CA-supported Pt nanoparticles. Furthermore, Bozbağ *et. al.*, has previously investigated the controlled preparation of CA supported Pt-Cu bimetallic nanoparticles via simultaneous SCD, however, the electrocatalytic activities of these samples were not analyzed [35].

In this study, we demonstrate a way to control the average size of Pt nanoparticles on CAs using SCD, and we show that the technique is effective for CAs with different average pore sizes. The effects of the CA pore size on the electrocatalytic activity of the Pt/CA

composites, and the effects of the Pt particle size on the ORR activity, were also investigated. Furthermore, we have shown that SCD technology can be extended to the preparation of CA and carbon black supported Pt-Cu bimetallic alloy nanoparticles. For this purpose a new and commercially available Cu precursor (Copper(II)trifluoroacetylacetonate) was also introduced. Single component adsorption isotherms of Copper(II)trifluoroacetylacetonate-CA was measured in scCO₂ and modeled using Langmuir equation. CA supported Pt-Cu nanoparticles with varying compositions were prepared by using the single component adsorption isotherms. The conversion of the precursors to their metal forms were carried out using thermal decomposition at ambient pressure, thermal decomposition in scCO₂ and chemical decomposition in scCO₂. Also, we investigated the effect of annealing temperature and metal composition on the alloying, particle size, particle morphology and electrocatalytic activity of the Pt-Cu nanoparticles. We also demonstrated the effect of different supports (CA and carbon black) on the electrocatalytic activity, particle size and particle morphologies of Pt-Cu bimetallic alloy nanoparticles. The samples were characterized using of N₂ physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), Raman spectroscopy, X-ray fluorescence (XRF), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and cyclic voltammetry (CV) techniques.

The properties of CAs, Pt and Pt-Cu nanoparticles on carbonaceous supports along with the description of the SCD technique used are reviewed in Chapter 2. The kinetics of the reactions involved in PEMFCs were also briefly outlined.

The experimental methods and characterization techniques used are presented in Chapter 3. The preparation of CAs, CA supported Pt and Pt-Cu nanoparticles, carbon black supported Pt-Cu nanoparticle, the precursor conversion techniques used were also given in Chapter 3.

The experimental results of this study is given in Chapter 4. This chapter includes the properties of CAs, measurement and modeling of adsorption isotherm of Copper(II)trifluoro - acetylacetonate-CA-scCO₂ system, physical and electrochemical properties of the prepared Pt/CAs, Pt-Cu/CAs and Pt-Cu/carbon black samples.

The conclusions drawn from this study and the recommendations for the future work is given in Chapter 5.



Chapter 2: Literature Review

2.1. Carbon Aerogels

Carbon aerogels are a relatively new class of materials developed first by Pekala at 1989 [22]. Carbon aerogels (CAs) are composed of small carbon particles covalently bonded together. They are micro and/or mesoporous carbon materials with very high surface areas (400-1500 m²/g), low mass densities, low thermal conductivities and sharp pore size distributions [38]. Unlike any other aerogel types carbon aerogels are electrically conductive. In fact, they have higher electrical conductivities than most carbonaceous materials [39]. CAs are usually obtained by pyrolysis of organic aerogels obtained from a condensation polymerization reaction of formaldehyde and an alcohol such as resorcinol in an aqueous solution with a catalyst upon supercritical drying at elevated temperatures (500 °C-2500 °C) [40]. They can be produced as monoliths, powders, thin films or microspheres. The microstructural properties of CAs can be tuned by changing the conditions in the sol-gel polymerization, curing and pyrolysis steps [22]. For example, a low resorcinol/catalyst ratio gave rise to polymeric gels consisting of small carbon particles in a well-connected configuration, a high resorcinol/catalyst ratio on the other hand results in colloidal aerogels with well-defined spherical carbon particles connected by narrow necks [41]. Because of these favorable properties, CAs are attracting increased attention for use in many different applications such as energy storage [42, 43], thermal insulation [23, 44] and control of harmful emissions by adsorption [45], broadband non-reflective materials [46] and catalyst supports [23, 47-50]. Organic aerogels, which are the precursors for CAs, are generally produced by combining resorcinol and formaldehyde at an appropriate molar ratio in an aqueous environment in the presence of an alkaline catalyst [22, 40]. Resorcinol and formaldehyde undergo a series of reactions, first of which the addition reactions to form hydroxymethyl

resorcinol derivatives, then condensation reactions of these derivatives occur to form methylene and methyl ether-bridged compounds resulting crosslinked clusters of the polymer [51, 52]. The resulting material is called a hydrogel, which consists of the polymer and water that fills the pores of the polymer. Since water is not soluble in scCO_2 , it should be replaced by another solvent that is soluble in scCO_2 such as acetone or ethanol. Then the solvent is removed from the pores by supercritical drying with scCO_2 resulting highly porous organic aerogels called resorcinol formaldehyde aerogels (RFAs). Supercritical drying is essential to protect the structure of the aerogel. Ambient drying causes collapse of the pores of the polymer due to the changes in the surface tension upon the formation of vapor-liquid interface, resulting a denser and less porous structure which is called a xerogel, whereas, if freeze-drying is applied the resulting gel is called a cryogel [41]. At the final step RFAs are heated to elevated temperatures under an inert gas flow such as N_2 or Ar and kept at these conditions for several hours. As a result CAs are obtained.

Due to their high electrical conductivity CAs are very suitable for energy related applications. Especially as electrocatalyst supports for fuel cells since the ideal support should have high accessible surface area, suitable pore size and pore volume for efficient ion transport and high electrical conductivity, CAs could therefore be promising candidates as electrocatalyst support [21, 23, 53, 54].

2.2. Supercritical Fluids

A supercritical fluid is a state of the matter which occurs above the critical pressure and temperature of that particular matter. Supercritical fluid region can be demonstrated with the pressure-temperature (P-T) of a pure matter. An example of the P-T diagram is given in Figure 2.1.

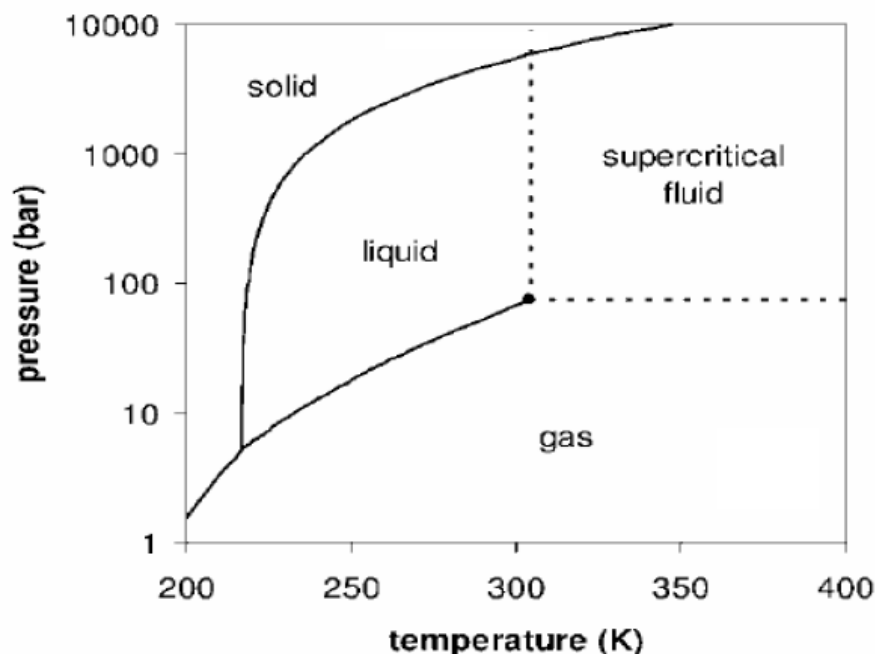


Figure 2.1: The representative pressure-temperature diagram of pure CO₂.

The solid lines in the P-T diagram indicate the phase boundaries between the three common states of matter; solid, liquid and gas. On the phase boundaries the two states of the matter coexist. The liquid-gas phase boundary is also called the vapor pressure curve and this curve ends at the critical pressure (P_c) and critical temperature (T_c). Above which no phase boundaries exist; hence only one homogeneous phase occurs. Generally, a substance should be in the supercritical region if its reduced temperature ($T_r = T/T_c$) and reduced pressure ($P_r = P/P_c$) are in the range of 0.95-1.01 and 1.01, respectively. SCFs exhibit the combination of liquid and gas solvent properties and since their density and viscosity are strong functions of temperature and pressure, the properties of SCFs can easily be adjusted by changing the process parameters. Furthermore, SCFs have very low surface tension which enables better penetration and wetting of the substrates without compromising the structure of the substrate and mass transfer rates in SCFs are significantly faster than that of the liquid solvents [55]. scCO₂ is the most commonly used and preferred SCF because it is abundant, non-toxic, non-flammable, cheap and has easily reachable T_c (31.1 °C) and P_c (7.38 MPa). Also most of the organic solvents used in the industry

are toxic or hazardous raising environmental issues, therefore, they are being replaced by more environmentally friendly and benign solvent and superior and controllable solvent properties of scCO_2 increases its usage in the industry. Furthermore, for the preparation of nanostructured materials additional steps are required to remove the solvent when an organic solvent is used, however CO_2 does not leave a trace on the treated material since it is in gaseous form under ambient conditions. Additionally, scCO_2 can be adsorbed into many types of polymers causing them to swell, a process generally known as foaming, making them suitable for impregnation of metal complexes [32].

2.3. Supercritical Deposition

Supported metal nanoparticles have been widely utilized in industry, especially in catalysis. They are most commonly prepared as dispersion of metal and/or metal oxide atoms or nanoparticles on a support material. As previously mentioned supported metal nanoparticles can be prepared using various different techniques such as ion-exchange, wet impregnation, sol-gel, and chemical vapor deposition [56-62]. These conventional techniques are used widely, however it is quite challenging to control the metal nanoparticle distribution, nanoparticle size, size distribution, metal loading, and nanocrystal orientation with these techniques [63]. The supercritical deposition (SCD) technique is an emerging approach for the preparation of supported nanoparticles that has several advantages over its counterparts [33, 34, 64-70]. SCD is especially suitable for processing of CAs since the low capillary stresses in the supercritical fluid prevent the collapse of the pores of CAs during the adsorption and solvent removal stages. Furthermore, a very homogenous distribution of metal nanoparticles can be achieved with SCD, whereas, agglomeration of nanoparticles usually occurs in other preparation techniques such as wet impregnation and chemical vapor deposition [36, 37, 53]. The TEM images of the carbon supported platinum nanoparticles prepared by SCD and commercially available carbon black supported platinum (EOTEK) are given in Figure 2.2. Figure 2.2 clearly shows that SCD results

in smaller average metal particle size and narrow particle size distributions without any significant agglomeration.

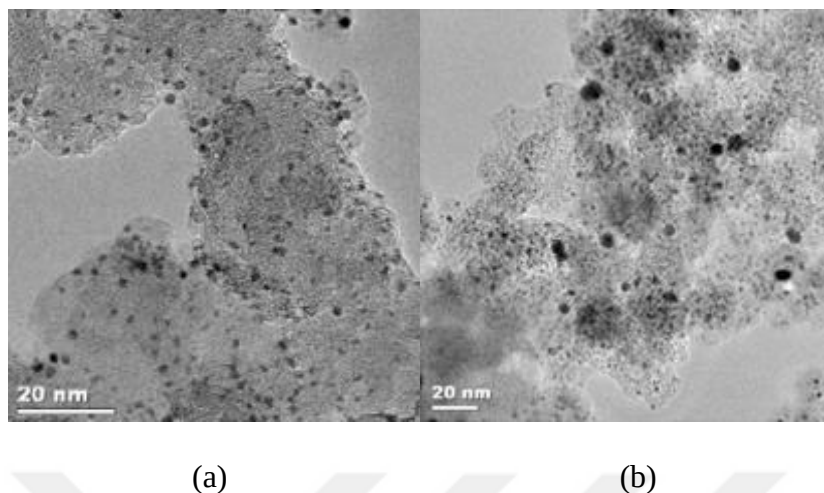


Figure 2.2: Transmission electron microscope (TEM) images of (a) carbon supported Pt catalyst prepared by SCD [37] and (b) commercial carbon supported Pt catalyst (Etek) [71].

Another benefit of SCD is that the metal loading can be controlled by using the adsorption isotherm data alone. The SCD technique involves three steps, the first of which is the dissolution of metal complexes in the supercritical fluid and exposure of a substrate into this mixture followed by the adsorption of the metal complexes from fluid phase onto the substrate and the final step involves the conversion of the metal complexes adsorbed on the substrate into their metal or metal oxide forms using various techniques [72].

SCD has been used to prepare supported monometallic particles previously [33, 73-75], and recently there were some attempts to extend SCD technique for the preparation of supported bimetallic alloy nanoparticles [35, 76]. For this purpose two SCD approaches can be used; simultaneous SCD and sequential SCD. In simultaneous SCD, both metal complexes are adsorbed onto substrate and are converted to their metal or metal oxides forms at the same time. In sequential SCD, on the other hand, one metal complex is adsorbed onto the substrate followed by its conversion and then the second metal complex is adsorbed onto this metal-substrate nanocomposite. At the final step second metal complex is converted to its metal form.

The schematic representation of simultaneous and sequential deposition approaches are given in Figure 2.3.

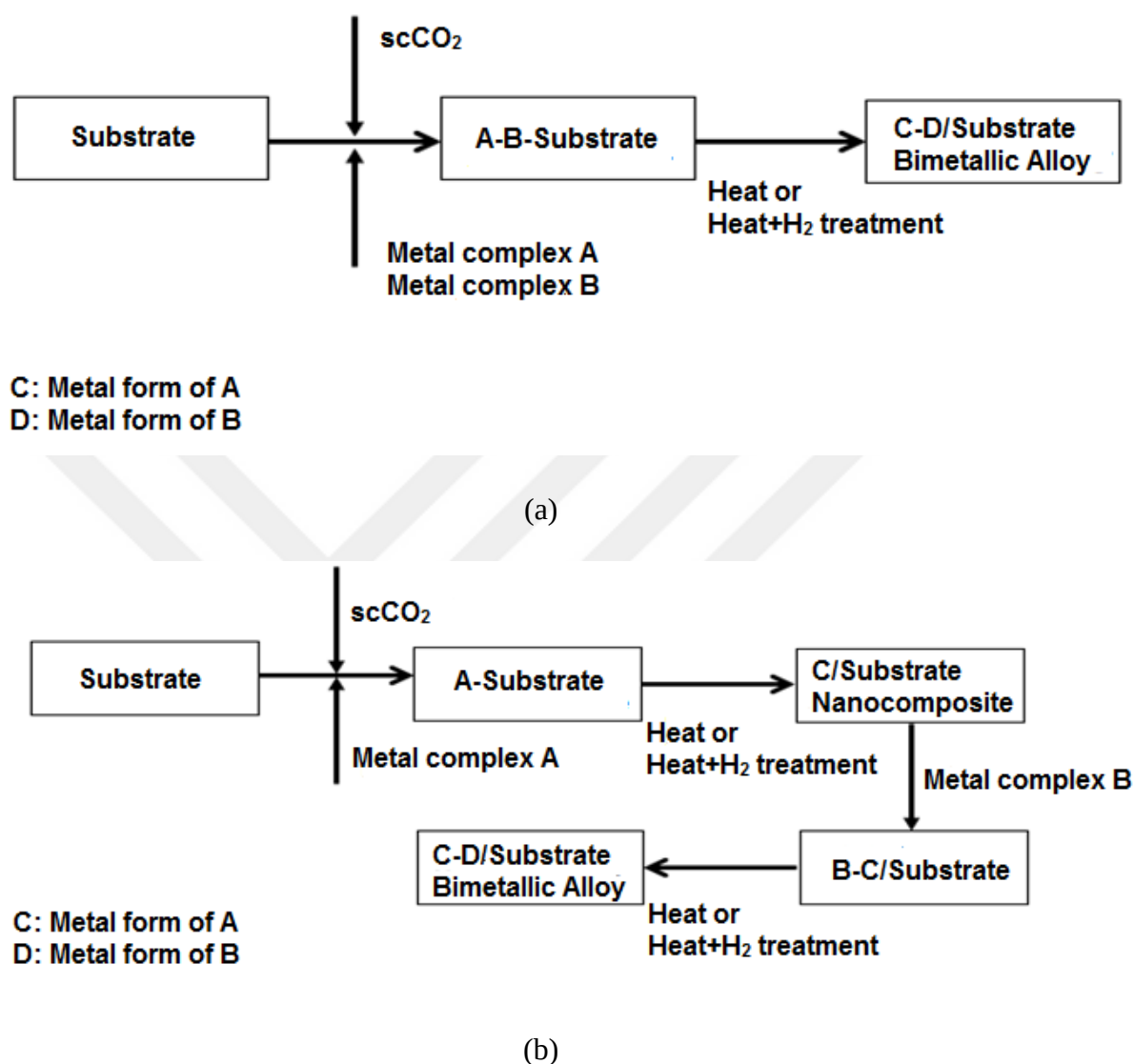


Figure 2.3: Schematic representation of two SCD approaches for the preparation of supported bimetallic alloys; (a) simultaneous SCD and (b) sequential SCD.

2.3.1. Adsorption Isotherms

Adsorption is the selective mass transfer of fluids or solutes of fluid mixture to the surface of an insoluble solid substrate. In this process, the adsorbed components are called adsorbates and the solid substrate is called an adsorbent. When an adsorbent is brought into contact with a fluid phase containing the adsorbate, adsorbate molecules diffuse to the adsorbent's surface

and/or pores and they either chemically bonded to the solid substrate or are held there by weak van der Waals intermolecular forces [77]. When adsorption occurs due to van der Waals forces, the process is called physical adsorption or physisorption. On the other hand, if adsorption occurs due to chemical bonding, it is called chemical adsorption or chemisorption.

The amount of adsorbate per unit adsorbate can be expressed as a function temperature, pressure and the interaction potential between the adsorbate and adsorbent in equilibrium as follows;

$$n = N(T, P, E) \quad (2.1)$$

where, n is the adsorbate amount per unit adsorbate, T is the temperature, P is the pressure and E is the interaction potential. When adsorption process is carried out at constant temperature this expression reduces to;

$$n = N(P, E) \quad (2.2)$$

When adsorption of solutes occurs in the presence of liquids or SCFs, the concentration of the solute in the fluid phase is used instead of pressure. In this case, the adsorbate amount per unit adsorbate is referred to as metal uptake and there are several adsorption isotherm models to express uptake amount in terms of equilibrium fluid phase concentration. We present the most commonly used single component models used for SCD systems; Langmuir model, Sips model and Freundlich model.

Langmuir Model

Langmuir model assumes that all adsorption sites are energetically identical and each site can adsorb only one adsorbate molecule. Also it assumes there are fixed number of adsorption sites and there is no interaction between adsorbed molecules on the adjacent sites [78]. The Langmuir adsorption isotherm is expressed as follows;

$$q = \frac{K_0 Q_0 C}{1 + K_0 C} \quad (2.3)$$

where, q is the uptake amount of adsorbate on adsorbent expressed in mol adsorbate/kg adsorbent, K_0 is the adsorption equilibrium constant expressed in $\text{m}^3 \text{ SCF/mol adsorbate}$, Q_0 is the uptake capacity expressed in mol adsorbate/kg adsorbent and C is the equilibrium concentration in the fluid phase expressed in mol adsorbate/ $\text{m}^3 \text{ SCF}$. Moreover, the term KQ_0 denotes the relative affinity of adsorbate towards the adsorbent.

Sips Model

Sips model, unlike Langmuir model, considers the surface heterogeneity and therefore it is widely used to interpreting the adsorption process [79]. The Sips model is expressed as follows;

$$q = \frac{Q_s(\alpha C)^{1/p}}{1 + (\alpha C)^{1/p}} \quad (2.4)$$

where, Q_s is the total number of binding sites, α is the median association constant and $1/p$ is the heterogeneity factor. When $1/p$ value is close to zero then adsorbent is heterogeneous, whereas $1/p$ value is closer to 1 then the adsorbent surface is said to be homogenous. Also when $1/p$ value is equal to 1, then the Sips model becomes the Langmuir isotherm equation.

Freundlich Model

The Freundlich adsorption model is an empirical model expressed as follows;

$$q = KC^n \quad (2.5)$$

where, K and n are empirically determined constants. Although, this model did not have a theoretical basis, it is widely used, particularly when the adsorbate is not completely identified [80, 81].

2.3.2. Conversion of Adsorbed Metal Complexes to Metallic Nanoparticles

As previously mentioned, metal complexes can be converted to their metal or metal oxide form upon adsorption using different routes: thermally or chemically in scCO_2 (*in-situ*), thermally or chemically at ambient pressure (*ex-situ*) or by laser irradiation; however, latter one

is not a very common technique [30, 31]. One of the methods in *in-situ* conversion is to inject a reducing agent (H_2 or an alcohol) to $scCO_2$ and metal complex mixture, which is in contact with substrate [30, 82]. Another *in-situ* conversion method is the thermal conversion in $scCO_2$ by increasing the mixture temperature after the adsorption period, resulting in decomposition of metal complex precursor molecules to their metal or metal oxide forms [36, 76]. In *ex-situ* conversion two approach can be used: chemical conversion or thermal conversion. In chemical *ex-situ* conversion a reducing gas, such as H_2 , is used. In thermal *ex-situ* conversion an inert atmosphere is used such as N_2 or Ar. Presence of a reducing agent facilitates conversion at lower temperatures but it also results in bigger particle sizes than thermal *ex-situ* conversion. Saquinq *et. al.* have conducted a study involving both thermal and chemical conversion of Pt precursor on CA and have found that chemical conversion in the presence of H_2 gas results in 2-fold increase in the Pt particle size when compared to thermal *ex-situ* conversion [83]. By *ex-situ* conversion control and predict the metal loading before conversion can be done by following the adsorption isotherm of the metal precursor. On the other hand, in the *in-situ* conversion as the chemical reducing agent is injected or as the temperature is increased metal precursor decomposition occurs creating new vacant sites on substrate and eventually all of the metal precursor in the supercritical phase can be adsorbed and converted into metal nanoparticles [44]. Moreover, *in-situ* conversion yields bigger particle sizes when compared to *ex-situ* conversion since the particle size growth continues until reducing agent is consumed.

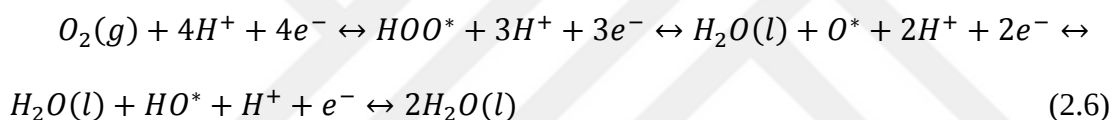
2.4. Oxygen Reduction Reaction

Oxygen reduction reaction (ORR) is the backbone of the PEMFC operations. More energy is required than thermodynamically predicted to drive the ORR in practice, i.e. it has a relatively high overpotential. Therefore, it is not possible to drive the reaction without a catalyst. ORR is also hard to catalyze because catalyst material should be stable enough to endure the acidic condition in a fuel cell, on the other hand it should be chemically active enough to

activate O_2 and sufficiently noble to allow the desorption of H_2O from the surface [84]. Additionally, the mechanism of ORR has not yet been understood completely, however, it has been hypothesized that ORR involves four main steps [85];

1. Adsorption of gaseous O_2 onto the catalyst surface followed by protonation of one O atom
2. Protonation of the same O atom for the second time coupled to the breaking of the O-O bond and desorption of the newly formed water molecule from the surface of the catalyst
3. Protonation of the lone remaining O atom
4. Protonation of the OH^* molecule for the second time and desorption of the resulting water molecule.

The reaction steps of the ORR can be summarized as;



The overall oxygen reduction reaction is expressed as follows;



The rate limiting steps in this reaction are the 1st and 4th step and both of these steps depend heavily upon the adsorption energy of oxygen to catalyst surface. The Gibbs free energy diagram for ORR is given in Figure 2.4.

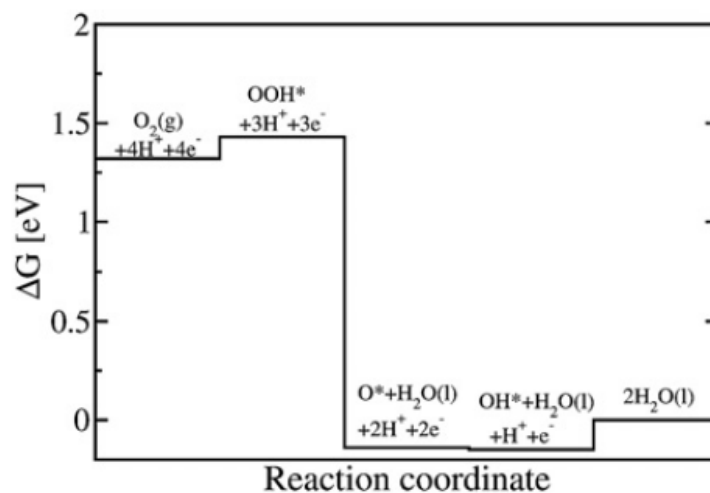


Figure 2.4: Potential free energy diagram for the ORR pathway on platinum catalyst [85].

In order to fully understand the mechanism of ORR, we have to first describe the Volcano plot and d-band theory.

2.4.1. The Volcano Plot

The Volcano plot for the ORR shows the relationship between the Gibbs free energy and calculated O_2 adsorption energy on the catalyst surface. The Volcano plot for the rate limiting steps of ORR is given in Figure 2.5.

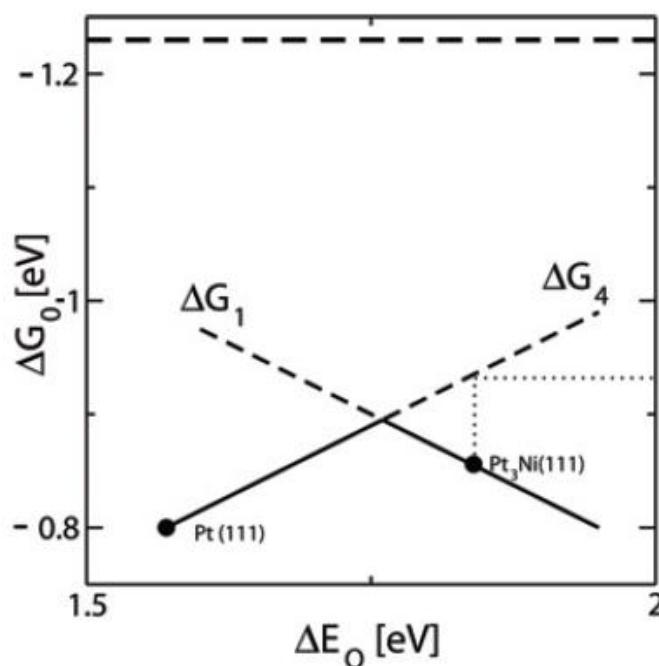


Figure 2.5: The dependence of Gibbs free energy, ΔG_0 on the adsorption energy of O_2 on catalyst, ΔE_0 [85].

In Figure 2.5 the distance between the horizontal dashed line and any point on the Volcano plot represents the overpotential for the ORR, therefore, the ideal catalyst should be at the peak of the Volcano plot so that the overpotential is minimized. The Pt(111) surface is located on the left side of the Volcano plot suggesting that in the case of Pt(111), the rate limiting step is the desorption of the formed H_2O which implies that Pt binds O_2 too strongly whereas in the case of $Pt_3Ni(111)$ the rate limiting step is the adsorption of O_2 to the catalyst surface which means that $Pt_3Ni(111)$ binds O_2 too weakly. The reason for different catalysts have different rate limiting steps on the ORR can be explained through the d-band theory.

2.4.2. The d-band Theory

The d-band theory states that the binding energy of an adsorbate to a metal surface primarily depends on the electronic structure of the surface, in other words, there is a correlation between the catalytic activity of a metal and the state of its d-band center [86-89]. Higher d-band center corresponds to an increase in energy (relative to Fermi level) which results in

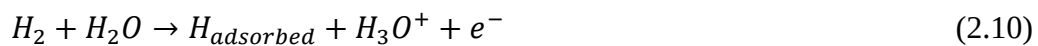
stronger bonding between the metal and adsorbate. Conversely, a lower d-band center shows a decrease in energy (with respect to Fermi level) which results in weaker bonding between the metal and adsorbate. Therefore, it is possible to increase or decrease the catalytic activity can be achieved by shifting the d-band center. As previously mentioned, Norskov *et. al.* found that O and OH species bind to Pt surface to strongly and thus decrease the ORR activity [85, 89]. In order to increase the activity, Pt's d-band center should be lowered with respect to the Fermi level which can be done by alloying with another transition metal.

2.5. Hydrogen Oxidation Reaction

Hydrogen oxidation reaction (HOR) is the other half reaction occurs in the PEMFC. There are two different mechanisms offered for the HOR. These are Tafel-Volmer mechanism and the Heyrovsky-Volmer mechanism [3]. The Tafel-Volmer mechanism is expressed as follows;



The Heyrovsky-Volmer mechanism is expressed as follows;



The mechanism of HOR depends on the employed electrolyte and also on the catalyst but since the HOR is a lot faster than the ORR, the activity enhancement is not necessarily required for the HOR.

2.6. Cyclic Voltammetry

Cyclic voltammetry (CV) is an electrochemical analysis technique which can be used for the simulation of the reactions that take place in a PEMFC. It consist an electrochemical cell connected to a bipotentiostat which is connected to a computer. The electrochemical cell usually contains three electrodes which are working electrode (WE), reference electrode (RE)

and counter electrode (CE). A bipotentiostat is a device that controls the potential between WE and the RE and measures the current between the WE and CE. A schematic representation of the device is given in Figure 2.6.

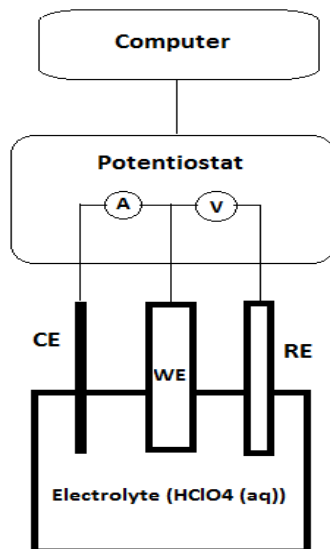


Figure 2.6: Schematic representation of cyclic voltammetry device.

WE is where the desired reactions takes place. Usually a glassy carbon disk is used as WE. RE is used for the determination of the potential of the RE. Ideally, current does not flow through the RE so that the potential of the RE is kept constant during the analysis so that the WE's potential can be accurately determined. Generally silver/silver chloride or saturated calomel electrodes are used as RE. However all the potentials are given normalized according to the normal hydrogen electrode (NHE) since its potential is determined as 0 V. The NHE is not used as a RE commonly because handling H_2 is rather difficult. Normally RE is separated from the electrolyte with the help of a salt bridge and this enables the electroneutrality of the electrolyte. The CE is used to enable the current flow from or to the WE. An inert material with a high surface area such as a Pt wire is used as CE. The CV is used to characterize redox couple reactions and therefore whatever reaction (oxidation or reduction) occurs on WE the reverse reaction takes place on the CE. The electrolyte can be acidic or alkaline depending on the fuel cell environment that is going to be simulated. The acidic electrolytes can be aqueous $HClO_4$

or H_2SO_4 and aqueous KOH solution is generally used as alkaline electrolyte. In the case of PEMFCs acidic electrolytes are preferred since the Nafion[®] which is the commonly used electrolyte in PEMFC is an acidic membrane. A representative CV of platinum in an acidic electrolyte is given in Figure 2.7.

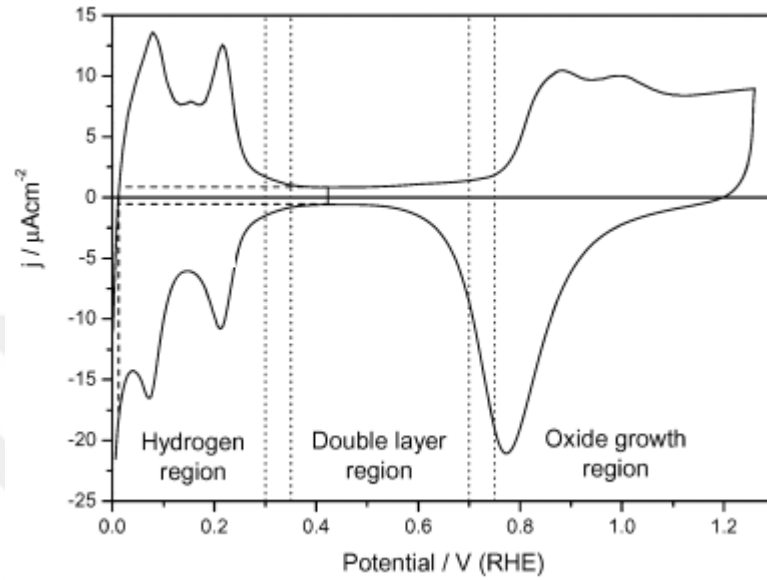


Figure 2.7: CV of polycrystalline Pt electrode in N_2 saturated 0.5 M H_2SO_4 with a scan rate of 50 mV/s [90].

The first region in cyclic voltammogram in the voltage range between 0 V and 0.3 V is associated with the hydrogen adsorption and desorption. The H^+ ions present in the electrolyte adsorbed on or desorbed from the surface of Pt. The reactions take place in this region can be given as follows;



The region between 0.3 V and 0.7 V is called the double layer capacitance region where the current flow in this region is caused by the capacitive properties. After double layer region, between 0.7 V and 1.2 V, the Pt oxidation or reduction region is observed. In this region the following reactions occur;



From the cyclic voltammogram curves the electrochemically active surface area (ESA) of the Pt can be determined by using the area under the hydrogen adsorption region [91]. To simulate the ORR, on the other hand, rotating disk electrode (RDE) analysis is usually applied in an O₂ saturated environment [6, 91]. The WE is rotated in order to accelerate the diffusion of O₂ from the bulk electrolyte to the interface of WE and electrolyte. A representative ORR curve of Pt is given in Figure 2.8.

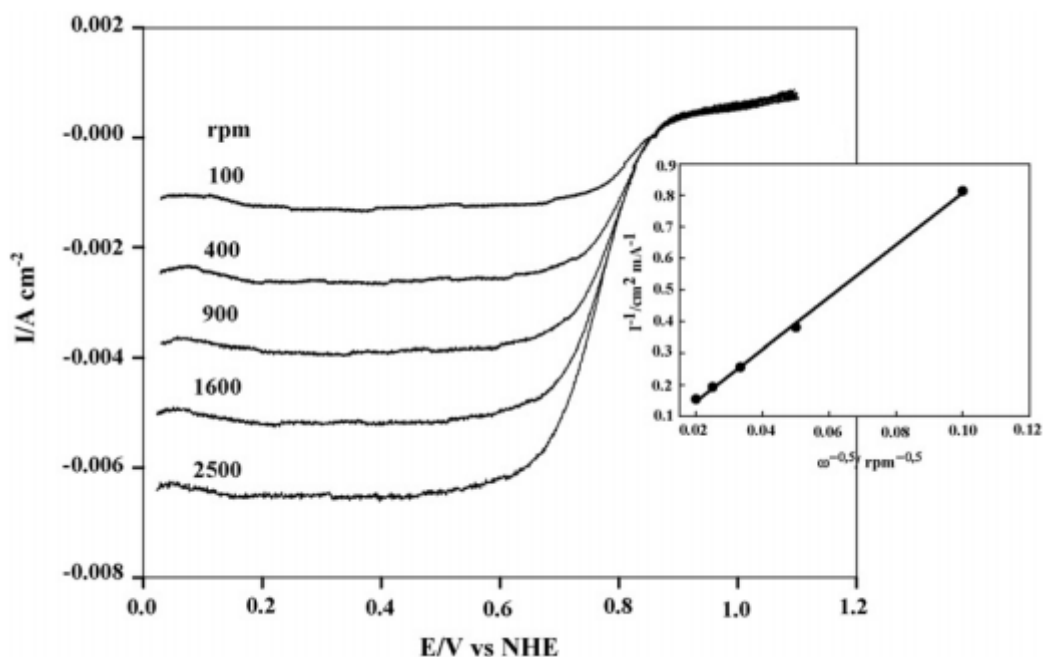


Figure 2.8: ORR curves of carbon black supported Pt electrocatalyst taken in O₂ 0.1 M HClO₄ at different rotation speeds with a scan rate of 10 mV/s and the inset figure is the Koutecky-Levich plot of the same electrocatalyst [37].

The region between 0.05 V and 0.6 V is called the mass transfer controlled region. In this region every O₂ molecule that came into contact with the WE is reduced immediately since this region corresponds to higher overpotentials. The following voltage region between 0.6 V and 0.85 V is the mixed region where the current produced by the combination of diffusional and kinetic currents. Higher potential region, between 0.85 V and 1.1 V, corresponds to the

region where kinetic limitations occur and all ORR curves converged to zero current density when the potential is not sufficient enough to derive the reaction.

Electrocatalytic activity of the catalyst can be determined from the ORR curves since the current density produced corresponds to the rate of the reaction. There are two ways to express the electrocatalytic activity; mass activity and specific activity. Mass activity (MAc) is reported as the rate (current density) normalized to the mass of the electrocatalyst employed whereas specific activity (SAc) is expressed by normalizing the rate to the real surface area of the electrocatalyst. The MAc and SAc are determined by taking the current density value at higher potentials (between 0.85 V and 0.9 V) and at higher rotation speeds (1600 rpm or 2500 rpm) to eliminate the effect of diffusional current. MAc and SAc can be expressed as follows;

$$MAc = \frac{j_k}{L_{catalyst}} \quad (2.13)$$

$$SAc = \frac{j_k}{ESA \times L_{catalyst}} \quad (2.14)$$

where, MAc is the mass activity (A/mg_{catalyst}), j is the kinetic current density at a given potential (A/cm²), $L_{catalyst}$ is the catalyst loading on WE (μg/cm²) and ESA is the electrochemical surface area (m²/g).

Although, at high potentials the current density produced is said to be the kinetic current density, there still may be contribution of diffusional current density. Koutecky-Levich equation is used to determine the real value of kinetic current density at a specific potential value [92]. The Koutecky-Levich equation is given as;

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^2} \quad (2.15)$$

where, j is the total current density (A/cm²), j_k is the kinetic current density (A/cm²), B is the Koutecky-Levich constant and ω is the rotation speed (rpm).

2.5. Platinum Nanoparticles on Carbonaceous Supports as Electrocatalysts

As previously mentioned, carbon supported Pt electrocatalysts are generally used in PEMFCs due to high activity of Pt towards ORR and HOR. The activity of the carbon supported Pt electrocatalyst depends on several factors, such as support properties, Pt content and dispersion, Pt nanoparticle size and etc. These factors should be understood clearly in order to improve the catalytic activity.

2.5.1. Effect of Support Properties on Electrocatalytic Activity

The metal-support interaction (MSI) is quite important in the sense that it unambiguously affects the morphology of the formed nanoparticle [93-95]. The interaction effect can be divided into two categories; electronic effect and geometric effect. The electronic effect can change the electronic structure of the catalyst and therefore, the reaction characteristics of the active sites on the catalyst surface [21]. The geometric effect is related to the shape of the metal nanoparticles formed on the surface of the support, it can alter the number of active catalytic sites and also it can change the activity of the catalytic sites [96]. Furthermore, high surface area that is required for the dispersion metal nanoparticles, can be obtained through porosity and the carbon support employed should have average pore sizes in the region of 20-40 nm to increase the diffusion of the chemical species [21]. Thus, many carbonaceous materials have been investigated as electrocatalyst materials such as activated carbon, carbon black, carbon nanotubes, and graphene and carbon aerogels.

Carbon blacks and their activated derivatives are generally used as electrocatalyst supports in PEMFCs due to their high availability and low cost. However, these materials have a microporous structure rather than a mesoporous one, resulting in inefficient transport of ions or reactant gases [97-101].

Carbon nanotubes are also investigated as electrocatalyst support. Their high crystallinity provides a high electrical conductivity, high surface area and high mesopore

volume enables good metal dispersion and enhanced reactant diffusion in tubular structure. In addition, carbon nanotube supported Pt nanoparticles showed higher electrocatalytic activity and stability than carbon blacks and their activated derivatives [101-104]. One drawback related to carbon nanotubes is the high cost when compared to carbon blacks making their commercial availability harder.

Graphene is a recently developed class of carbon material consists of atomically sheet of hexagonally arranged carbon atoms [105]. Graphene can offer a fast electron transfer mechanism which facilitates ORR in PEMFCs [106]. Especially nitrogen doped graphene showed good activity towards ORR since the defects and disorders introduced by nitrogen doping serves as anchoring sites for metal nanoparticles and introduction of nitrogen in the C-backbone increases the conductivity [107].

As previously mentioned, CAs are very promising candidates as electrocatalyst supports due to their desirable properties [21, 23, 36, 54]. CAs with different pore properties have been investigated previously as electrocatalyst supports. Dawidzuik *et. al.* investigated the effect of CAs porosity on Pt dispersion and found that better dispersion was achieved with the CA having an average pore size of 33 nm [62]. Du *et. al.* conducted a study in which CAs with different mesoporous structures were loaded with Pt using the ethylene glycol reduction method, and the resulting composites had ORR activities higher than those of commercial Pt/C electrocatalysts. The ORR activity of the composites correlated well with the average pore size of the CAs, and the highest activity was achieved with the CA with the largest mesopores [24]. Smirnova *et. al.*, also found that increase in the average pore size of CA (16 nm to 20 nm), resulted in an increase in the electrocatalytic activity in PEMFCs [23]. In another study conducted by Marie *et. al.*, two different CAs were loaded using two different Pt precursors (anionic and cationic) via wet impregnation. The authors did not observe any effect of the CA pore size on activity,

however, the samples prepared using the anionic Pt precursor had higher activities than the ones prepared with the cationic precursor [53].

2.5.2. Effect of Pt Particle Size and Shape on Electrocatalytic Activity

The average particle size of Pt nanoparticles are known to have a drastic effect on the electrocatalytic activity which is called crystallite size effect [108]. Pt nanoparticles generally forms a face-centered cubic crystalline structure in which low index surfaces of (100) and (111) crystal planes surrounds the surface resulting a polyhedral shape and each crystal plane has different catalytic activities towards ORR [109]. Studies involving the determination of catalytic activity of different Pt planes show that in an acidic H_2SO_4 electrolyte ORR activities of Pt planes increases in the order of $\text{Pt}(111) < \text{Pt}(100)$ due to strong adsorption of bisulfate or chlorine ions on $\text{Pt}(111)$ plane resulting a deactivation of this plane [6, 110]. However, when HClO_4 is employed as electrolyte $\text{Pt}(111)$ surface becomes more active than $\text{Pt}(100)$ [111]. The catalytic activity of the $\text{Pt}(111)$ surface for ORR have the strongest sensitivity to the adsorbing ions in all three crystalline planes [112]. Furthermore, octahedral or tetrahedral Pt nanoparticles are found to be more active in HClO_4 whereas, cubic Pt nanoparticles are found to be more active in H_2SO_4 for ORR [111].

It has been demonstrated previously that there is a strong relationship between the Pt particle size and the electrocatalytic activity [25, 26]. The relationship between particle size and the activity is given in Figure 2.9.

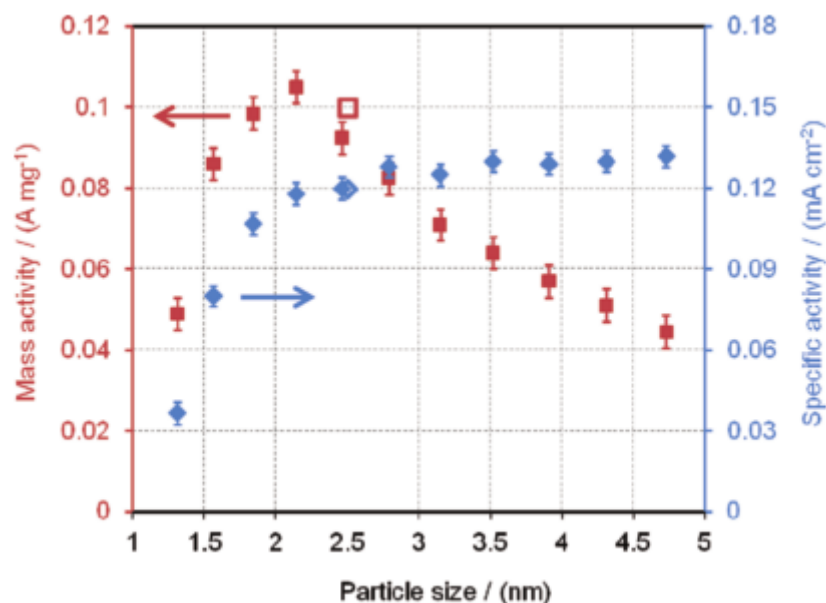


Figure 2.9: Pt particle size dependence of mass and specific activity [26].

Mass activity increases rapidly with increasing particle size up to a certain point (between 1.3 nm and 4 nm) [26, 108, 113], beyond which activity declines with increasing size. Whereas, the specific activity increases with increasing Pt particle size and reaches a plateau at some point (around 3 nm) [26, 114-119]. A recent study conducted by Shao *et al.*, showed both experimentally and theoretically (using Density Functional Theory) that maximum mass activity was obtained for a Pt average particle size of 2.2 nm due to proper oxygen binding energy on Pt(111) facets and the specific activity reached a plateau at around 3 nm [26].

On the other hand, for HOR a negative particle size effect was generally observed; HOR activity increases as particle size decreases due to increased surface area of Pt which leads to higher ESA values [120].

2.6. Pt-Cu Bimetallic Nanoparticles on Carbonaceous Supports as Electrocatalysts

Supported bimetallic alloy nanoparticles have been widely investigated in many areas due to their superior optical, magnetic or catalytic properties over their monometallic forms. In supported alloy nanoparticles, the tunable activity arises from two concepts; the ligand effect

which is caused by the alteration in the electron density of the system with the addition of another metal and the strain effect which is caused by the metal-metal bond length. After the discovery of Pt₃Ni(111) surface by Stamenkovic *et. al.*, which had an exceptional activity towards ORR [15, 121], research efforts are directed to the synthesis and electrochemical investigation of supported bimetallic nanoparticles [14, 27, 84, 122-124]. Among these bimetallic systems, Pt-Cu nanoparticles have shown promising activity values towards ORR [16, 28, 29, 125, 126]. From the bulk phase diagram of Pt-Cu system given in Figure 2.10, it can be seen that Pt-Cu alloys tend to form ordered structures in three different regions Pt₃Cu, PtCu and PtCu₃. Pt₃Cu and PtCu₃ alloys show a L₁₂ structure below 650 °C and 600 °C, respectively. In PtCu₃ L₁₂ structure, Pt atoms take the positions at the eight edges of the cubic unit cell whereas Cu atoms occupy the face centered positions. In the case of Pt₃Cu L₁₂ structure Pt and Cu are reversely occupied. On the other hand PtCu shows a rhombohedral structure [127].

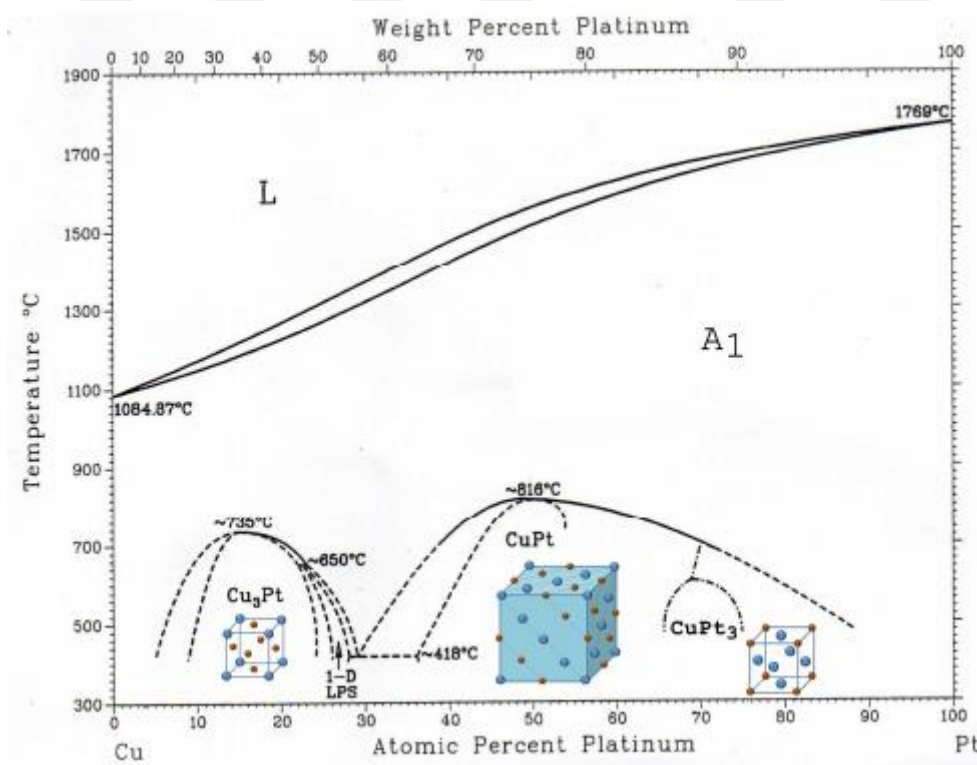


Figure 2.10: Bulk phase diagram of Pt-Cu alloy system [127].

There may be a divergence between the phase diagrams of bulk alloy systems and the supported bimetallic nanoparticles [128, 129], however, supported Pt-Cu bimetallic alloys show similarities with the bulk Pt-Cu phase diagram [130]. Therefore, bulk alloy phase diagrams are useful as they give insights for the supported nanoparticles. The carbon supported Pt-Cu nanoalloys were usually prepared by liquid precursor impregnation-reduction-annealing method [27-29, 125, 126, 130]. Thermal annealing process is necessary to form alloy nanoparticles [131, 132], however, it usually does not result in a single pure alloy phase [133]. Only reduction of the metal precursors without thermal annealing results in only a small alloying between Pt and Cu where most of the unalloyed Cu is in the oxide form due to exposure to ambient air [29, 35]. Oezaslan *et. al.*, conducted a study in which they have prepared high surface area carbon (HSAC) supported Pt-Cu nanoparticles and they have characterized the alloy nanoparticle formation using an in-situ high temperature XRD [130]. They have discovered that the annealing temperature generally determines the resulting Pt-Cu composition of the alloy phase, whereas, extended annealing duration (more than 1.5 h) causes a minor change in the alloy phase concentration but it causes a sustained particle growth and thus determines the resulting Pt-Cu particle size [130]. Moreover, higher annealing temperatures (above 600 °C) promotes alloy formation but at annealing temperatures (above 800 °C), activity may decrease. Therefore, there is an optimum annealing temperature where formed alloy nanoparticles have more uniform structures and high electrocatalytic activities [125, 126]. Upon preparation of Pt-Cu alloy nanoparticles, Cu is preferentially leached from the alloy nanoparticles; a process called dealloying to create a bimetallic nanoparticle with Pt enriched surface (Figure 2.11). Dealloying process can be done either chemically in acidic environment (H₂SO₄ or HNO₃) or electrochemically (continuous potential cycling); however, electrochemical dealloying results in more complete Cu dissolution than chemical acid leaching

and also electrochemically dealloyed Pt-Cu nanoparticles exhibited a higher catalytic activity than chemically dealloyed ones [28, 134].

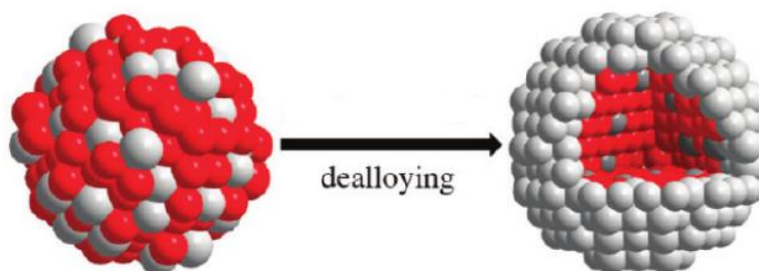


Figure 2.11: Representative formation of Pt enriched surface over Pt-Cu alloy core [135].

Moreover, the dealloyed Pt-Cu electrocatalysts taken on a Pt-shell over Pt-Cu core structure where the difference between the lattice constants in the shell and in the core creates compressive strain on the shell [88]. The Cu rich core below the Pt-shell may impose ligand effects onto the shell which results in a downshift of the Pt's d-band center but the ligand effects are mostly negligible above a Pt-shell thickness of 1 nm [121, 136]. Both of these effects are directly related to activity, as previously mentioned, causing a decrease in the Pt-O bond strength and therefore resulting in higher electrocatalytic activity [137, 138]. Although, the solution phase based impregnation method was used extensively for the preparation, it generally results in broad particle size distributions and also different nanoparticle morphologies where small alloy nanoparticles are in the form of single Pt-shell over a Pt-Cu core, whereas larger nanoparticles (above 10-15 nm) result in Pt-shell over multiple cores [16, 29, 135]. As previously mentioned, the composition of the alloy nanoparticles significantly effects the catalytic activity. Therefore, using the insights provided by the Pt-Cu bulk alloy phase diagram, supported Pt-Cu nanoparticles having compositions of Pt_3Cu , PtCu and PtCu_3 investigated and mass activity towards ORR increase in the order of $\text{Pt}_3\text{Cu} < \text{PtCu} < \text{PtCu}_3$ [27, 126]. In all the cases, dealloyed Pt-Cu nanoparticles exhibited enhanced mass activities (~2 fold to ~4.5 fold) towards ORR when compared to pure Pt [16, 27, 28, 125, 126, 139].

Chapter 3: Experimental Methods and Characterization Techniques

3.1. Materials

Resorcinol ($\geq 99\%$) was purchased from Sigma Aldrich. Formaldehyde (37% stabilized in 10% methanol) was purchased from VWR. Sodium carbonate (99.99%) and perchloric acid (70%) were obtained from Merck. Acetone (technical grade 99.5%) was purchased from Onur Kimya. Dimethyl(1,5-cyclooctadene)platinum(II) ($\text{Pt}(\text{cod})\text{me}_2$, 99%, $\text{MW}=333.33$ g/mol) and Copper(II) trifluoroacetylacetonate ($\text{Cu}(\text{tfa})_2$, $\geq 97\%$, $\text{MW}=369.7$ g/mol) were purchased from STREM Chemicals, Inc. Vulcan XC-72R (hereafter referred as Vulcan) was obtained from Cabot International. Nafion® 117 solution was purchased from Ion Solutions Inc. The chemicals were used as received. The water is distilled and deionized (18.2 M Ω). Carbon dioxide (99.998 %), nitrogen (99.99 %), oxygen (99.99%) and hydrogen (99.99%) were purchased from Air Liquide.

3.2. Synthesis of Resorcinol Formaldehyde Aerogels and Carbon Aerogels

RFAs were synthesized by the reaction of resorcinol (R) with formaldehyde (F) in water (W) with an alkali catalyst (sodium carbonate) (C) as described by Pekala [22]. In order to obtain different pore sizes, three sets of samples were prepared by changing R/C, and R/W molar ratios while keeping R/F molar ratio constant in all three sets. The reactant ratios used and resulting RFAs were given in Table 3.1.

Table 3.1: Reactants ratios used during the synthesis of RFAs with different pore sizes.

Aerogel	R/C	R/W	R/F
RFA6	100	0.08	0.5
RFA10	100	0.04	0.5
RFA17	200	0.02	0.5

A solution was prepared using the desired amounts of resorcinol, water, catalyst and formaldehyde and stirred for 15 min. Then prepared solution was transferred into airtight tubes. The tubes were kept one day at room temperature, one day at 50 °C and three days at 90 °C in order to complete the gelation and the curing process. Afterwards, resulting hydrogels were removed from the tubes and placed in an acetone bath for solvent exchange, in which the water in the pores of the gels were exchanged with acetone, and kept there for three days. Acetone remaining in gel pores was then removed by supercritical extraction using supercritical CO₂ (scCO₂) at 10 MPa and 45 °C using an Applied Separations Spe-ed SFE extraction unit. During supercritical extraction, fresh CO₂ was fed to the system continuously and system was kept at aforementioned conditions for 7 hours once the bulk acetone is removed. Then system was slowly depressurized and as a result, RFAs with different pore sizes were obtained. Resulting RFAs were named according to their average pore sizes. CAs were then obtained by the pyrolysis of RFAs in a tube furnace (Model F1125 Thermolyne Tube Furnace) at 1000 °C for 6 h under flowing N₂ (100 cc/min). Photographs of prepared RFAs and CAs are given in Figure 3.1.

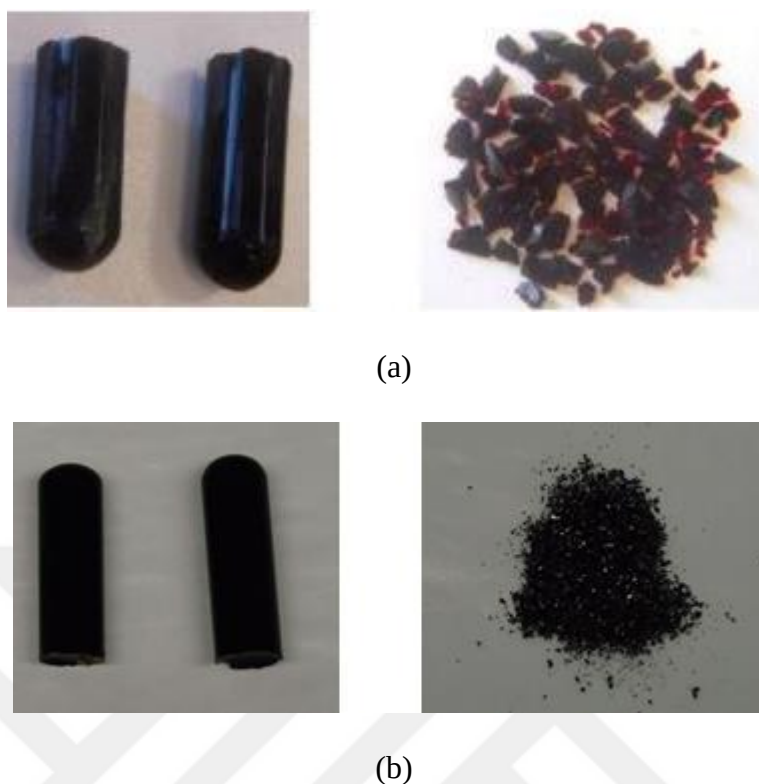


Figure 3.1: Photographs of prepared RFAs (a) and CAs (b); the ones on the left are the monolithic forms and the ones on the right are the crushed forms.

3.4. Metal Complex Adsorption Measurements and Supercritical Deposition Experiments

Supercritical deposition experiments were conducted in a custom-made 57 mL high pressure stainless steel vessel equipped with two sapphire windows 2.5 cm in diameter (Sapphire Engineering, Inc., Pocasset; MA), a pressure transducer (Omega Engineering), a vent line and a rupture disk assembly (Autoclave Engineers). Pressure sealing was ensured with poly (ether ether ketone) O-ring which were placed to the bottom and on to the top of both sapphire windows. Predetermined amounts of CA and $\text{Pt}(\text{cod})\text{me}_2$ or $\text{Cu}(\text{tfa})_2$ were placed along with a magnetic stirrer to ensure mixing of precursor and scCO_2 . A stainless steel screen which was placed in the middle of the vessel enabled the separation of CAs and the magnetic stirrer. A

syringe pump (ISCO Model 260D) was connected to the vessel and was used to pressurize CO₂ to desired level. Temperature was kept constant during all experiments with the help of a circulating heater/cooler (Cole-Parmer, Model 12108-15). After thermodynamic equilibrium was reached, the vessel was slowly depressurized with the rate of 0.7 MPa/min and impregnated CAs were taken out of the vessel. Experimental setup used for the supercritical deposition experiments is given in Figure 3.2.

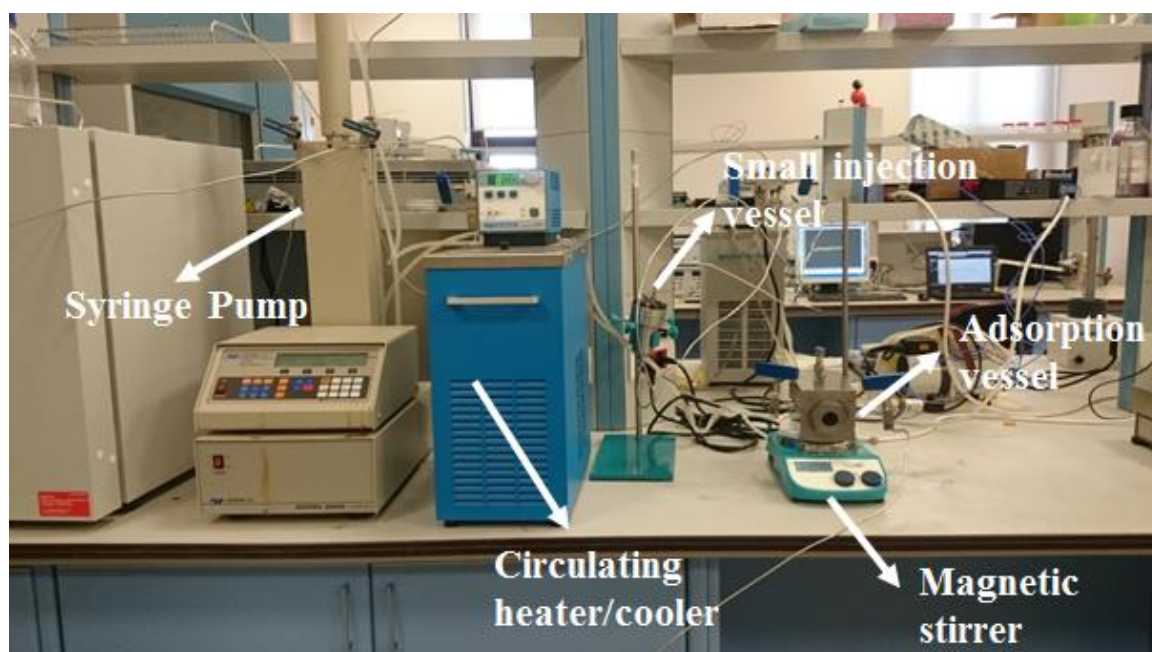


Figure 3.2: Experimental setup for metal complex adsorption measurements.

Pt(cod)me₂/CA6, Pt(cod)me₂/CA8 and Pt(cod)me₂/CA19 composites with high Pt loadings (25-28 wt.%) were prepared at 80 °C and 27.6 MPa in scCO₂. High temperature and pressure value was chosen to increase the concentration of Pt(cod)me₂ in scCO₂ by increasing the solubility which results in higher Pt(cod)me₂ uptake on CAs.

Adsorption isotherm measurements of Cu(tfa)₂-CA19-scCO₂ was carried out at the aforementioned experimental setup at 35 °C and 10.7 MPa. For the adsorption measurements CA19 amounts were kept constant while Cu(tfa)₂ amount was increased at each measurement. The uptake amount of Cu(tfa)₂ on CA19 was determined after depressurization both gravimetrically and using XRF.

3.3. Preparation of Pt-Cu/CA19 composites

For the preparation of Pt-Cu/CA19 composites both simultaneous and sequential SCD methods were used. In simultaneous SCD method certain amount of CA19 was placed into the vessel along with predetermined amounts of $\text{Pt}(\text{cod})\text{me}_2$ and $\text{Cu}(\text{tfa})_2$. Adsorption of metal complexes were allowed to continue until the thermodynamic equilibrium is reached at 35 °C and 10.7 MPa. The vessel was then depressurized and $\text{Pt}(\text{cod})\text{me}_2$ - $\text{Cu}(\text{tfa})_2$ /CA19 composites were taken out of the vessel.

In sequential SCD method either first $\text{Pt}(\text{cod})\text{me}_2$ or $\text{Cu}(\text{tfa})_2$ was adsorbed on CA19 at 35 °C and 10.7 MPa. After conversion of the metal complex ($\text{Pt}(\text{cod})\text{me}_2$ or $\text{Cu}(\text{tfa})_2$) on CA19 was carried out, metal incorporated CA19s were placed in the vessel again and second metal complex ($\text{Pt}(\text{cod})\text{me}_2$ or $\text{Cu}(\text{tfa})_2$) was adsorbed onto the metal incorporated CA19s. In the case of $\text{Pt}(\text{cod})\text{me}_2$, desired Pt loadings on CA19 was achieved at one adsorption step but for $\text{Cu}(\text{tfa})_2$, multiple adsorption/conversion steps were carried out to obtain desired Cu loadings on CA19.

For the *in-situ* SCD experiments, first adsorption of $\text{Pt}(\text{cod})\text{me}_2$ on CA19 or Vulcan was carried out at 80 °C and 17.2 MPa. After *in-situ* conversion of $\text{Pt}(\text{cod})\text{me}_2$ was done, $\text{Cu}(\text{tfa})_2$ was adsorbed on Pt/CA19 or Pt/Vulcan composites at 80 °C and 17.2 MPa. All *in-situ* SCD experiments were carried out in one step for each metal complexes.

3.4. Precursor Conversion and Annealing

The conversion and annealing of impregnated aerogels were conducted by placing incorporated CAs in a custom made quartz tube (220 mm internal diameter, 4 mm wall thickness and 610 mm length) in a tube furnace (Thermolyne model F1125) either under an inert or a reactive gas media (100 mL/min). The conversion of $\text{Pt}(\text{cod})\text{me}_2$ adsorbed on CA6, CA8 and CA19 was carried out at five different temperatures (200 °C, 400 °C, 600 °C, 800 °C and 1000 °C) under an inert gas flow (N_2) at ambient pressure for 4h in order to determine the

effect of temperature on Pt particle size. The conversion of $\text{Cu}(\text{tfa})_2$ on CA19 was investigated at different temperatures at reactive (H_2) gas flow. For Pt-Cu/CA19 samples, precursor conversions were carried out at 200 °C under reactive (H_2) gas flow for 2h at ambient pressure after each sequential supercritical deposition step. After the chemical conversion at atmospheric pressure, Pt-Cu/CA19 samples were then annealed at three different temperatures (600 °C, 800 °C and 950 °C) under flowing N_2 for 4 h to complete the alloying process. All conversion and annealing experiments were conducted in all experiments the system was cooled to room temperature under flowing N_2 . Upon cooling, composites were removed from the quartz tube and total metal loadings were determined from the weight change using an analytical balance (Mettler Toledo Model MS204S accurate to ± 0.1 mg).

In-situ conversion experiments were carried out in the same vessel that adsorption experiments were conducted. After adsorption of metal complex, $\text{Pt}(\text{cod})\text{me}_2$ or $\text{Cu}(\text{tfa})_2$, on CA19/Vulcan, conversion of metal complex was achieved either raising the temperature and pressure of the vessel or injecting a reducing agent (H_2) and scCO_2 mixture in to the adsorption vessel.

In-situ conversion of $\text{Pt}(\text{cod})\text{me}_2$ was achieved thermally in scCO_2 by raising the temperature of the adsorption vessel to 135 °C with the help of an external heater. The final pressure was recorded as 26.7 MPa. The conversion of $\text{Pt}(\text{cod})\text{me}_2$ was allowed to continue at these conditions for 12 hours. After conversion was completed, the vessel was slowly depressurized and converted Pt/CA19 composites were taken out of the vessel.

In-situ conversion of $\text{Cu}(\text{tfa})_2$ on Pt/CA19 or Pt/Vulcan composites was carried out chemically in scCO_2 by injecting H_2 and scCO_2 mixture to the adsorption vessel. For this purpose a smaller high pressure vessel (10 mL internal volume) was placed in between the syringe pump and the adsorption vessel. A three way valve assembly was used to switch from

H₂ to scCO₂. First H₂ at 0.8 MPa was allowed to fill the smaller high pressure vessel, then scCO₂ was pumped to the same vessel at 27.6 MPa using a syringe pump. Then the valve between the smaller high pressure vessel and the adsorption vessel was opened which enabled the flow of H₂ and scCO₂ mixture to the adsorption vessel. When the pressures of the smaller vessel and the adsorption vessel were equalized, the adsorption vessel was disconnected from the small vessel and conversion process was allowed to continue for 2 h. After conversion was completed, the vessel was slowly depressurized and converted Pt-Cu/CA19 or Pt-Cu/Vulcan composites were taken out of the vessel.

3.5. Material Characterization

The pore sizes, pore volumes and the Brunauer, Emmet and Teller (BET) surface areas of the CA samples were determined by N₂ adsorption using Micromeritics ASAP 2020 instrument. N₂ adsorption/desorption isotherms with a relative pressure (P/P_0) ranging from 10^{-7} to 1 were obtained. The pore size distributions of CA samples were determined using the Barret, Joyner and Halenda (BJH) method. Pore sizes were determined using desorption curve due to its thermodynamic stability. Micropore volume and micropore area were obtained using the t-plot method. Raman IR scattering data were acquired from CA samples over the range of 800–2000 cm⁻¹ using a Renishaw Invia Ramascope equipped with a 532 nm argon laser. Thermogravimetric analysis method was used to determine Pt loading of the Pt/CA6, Pt/CA8 and Pt/CA19 composites with higher metal loadings. The decomposition of Pt(cod)me₂, Cu(tfa)₂ and Cu(tfa)₂/CA19 was also investigated using TGA. Furthermore pyrolysis of RFAs were simulated again using TGA. TGA was performed on the samples under flowing N₂ or air using TA Instruments TGA Q500. For the determination of Pt loading on CAs, the samples were heated to 600 °C under flowing air (100 mL/min) with a heating ramp of 10 °C/min. To determine the decomposition temperature of Cu(tfa)₂ was heated to 300 °C under flowing N₂ (100 mL/min) with a heating ramp of 10 °C/min. Decomposition of Cu(tfa)₂ on CA19 was

investigated by heating the composite to 300 °C under flowing N₂ (100 mL/min) with a heating ramp of 10 °C/min. Decomposition of Cu(tfa)₂ on CA19 was investigated by ATR-FTIR spectroscopy using Thermo Scientific Nicolet iS Smart iTR spectrometer. Elemental compositions of the samples was determined using Bruker Tiger S8 XRF device in standardless mode under He atmosphere. Loose powder method was used to prepare samples in a 18 mm sample holder (Chemplex Industries, Inc.) with a thin film support (Prolene film, 4 µm thickness, Chemplex Industries, Inc.). Evaluation of the elemental compositions was done based on ‘‘Best analysis’’ and carbon matrix methods in SpectraPlus Eval2 V2.2.454. XRD measurements were carried out by using Bruker D8 Advance Diffractometer equipped with a Cu Kα source in the 2θ range of 20°-90° with a plate rotating rate of 30 min⁻¹. Particle sizes of prepared samples were determined using XRD data and Scherrer Equation as follows:

$$d = \frac{K\lambda}{B \cos \theta_B} \quad (3.1)$$

where, K is the Scherrer constant (0.9), λ is the wavelength of radiation (λ_{Cu-Kα}=0.154 nm), B is the width at half maximum and θ_B is half of the peak angle 2θ_B in radians. For the particle size determination {220} reflection angle was used. Pt:Cu molar ratios of the prepared Pt-Cu/CA19 and Pt-Cu/Vulcan samples were calculated from {111} reflection angle and using Vegard’s Law with the following equations:

$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a_{Pt-Cu}^2} \quad (3.2)$$

$$2d_{hkl} \sin \theta = \lambda \quad (3.3)$$

$$a_{Pt-Cu} = x_{Pt}a_{Pt} + (1 - x_{Pt})a_{Cu} \quad (3.4)$$

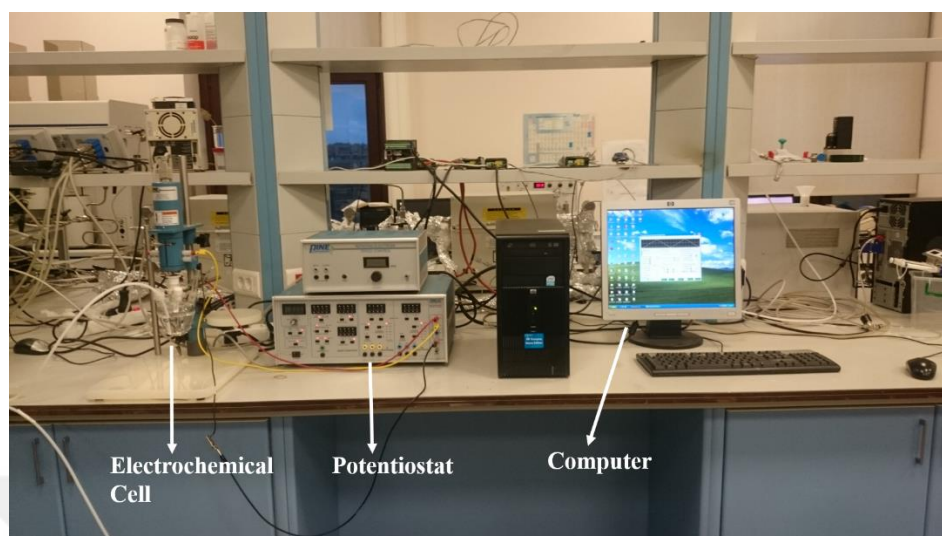
Scanning electron microscopy (SEM) images of the samples were taken using Zeiss Evo LS 15 scanning electron microscope under ultra-high vacuum with an accelerating voltage of 10 kV and a working distance of 6-8.5 nm. Energy-dispersive X-ray spectroscopy (EDX)

experiments were performed using Rontec xflash 1106 EDX detector. The morphologies of the samples were characterized by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). Specimens were prepared by grinding the samples carefully in a mortar and pestle set, and then obtaining a uniform suspension by adding distilled water into the mortar and stirring carefully with the pestle. A Quantifoil 200 mesh copper TEM grid coated with a holey carbon film was then immersed in the suspension, removed with a droplet of suspension on the grid surface, allowed to dry in air, and then kept in a vacuum desiccator overnight to remove any residual moisture. High-resolution phase contrast TEM images and high-angle annular dark-field (HAADF) STEM images were taken using JEOL 2010 FasTEM and FEI Talos F200X S/TEM instruments, operating at 200 kV equipped with a high-resolution objective lens pole piece (spherical aberration coefficient $C_s = 0.5$ mm) which gives a point-to-point resolution of <0.19 nm in phase contrast images. Particle size distributions were obtained from HAADF STEM images by measuring 200 nanoparticles and plotting histograms binned in 0.5 nm increments. STEM X-ray maps were also obtained in the FEI Talos F200X, which is equipped with a Super-X silicon drift detector (SDD) that allows for rapid acquisition of energy-dispersive X-ray spectroscopy (EDXS) data. The Pt and Cu X-ray maps correspond to the integrated EDXS intensities in the Pt L and Cu K peaks, respectively.

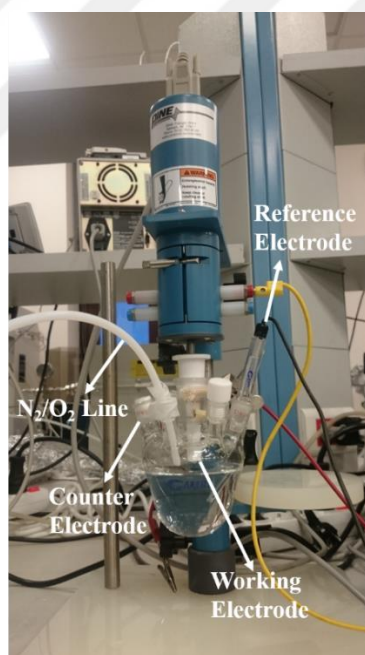
3.6. Electrochemical Characterization

Electrochemical characterization of the samples was carried out using cyclic voltammetry analysis using a conventional three electrode electrochemical cell connected to a potentiostat (Pine Instrument Company Model AFCBP1). A glassy carbon disk (internal diameter 0.196 cm^2) was used as working electrode (Pine Instruments), Ag/AgCl filled with saturated KCl solution (Gamry Instruments) was used as reference electrode and a Pt wire was

utilized as counter electrode. The electrolyte employed was 0.1 M HClO_4 solution. The setup used for electrochemical characterization is given in Figure 3.3.



(a)



(b)

Figure 3.3: Experimental setup used for electrochemical characterizations (a) cyclic voltammetry equipment (b) electrochemical cell used.

A catalyst ink was prepared using certain amount of catalyst, 1 mL 1,2-propandiol, 1 mL distilled water and 400 μL 5 wt.% Nafion solution (Ion Solutions Inc.). The suspension was

achieved using an ultrasonic water bath (Ultra-Turrax® T25) for 30 min prior to deposition. 5.8 μL of the ink prepared was deposited on glassy carbon disk and left to dry at ambient temperature and pressure overnight. The resulting Pt loading on the electrode was 28 $\mu\text{g}/\text{cm}^2$. Electrolyte was purged for 30 min with N_2 prior to analysis to remove O_2 . Then N_2 supply was removed from solution and placed just above the electrolyte to provide N_2 blanket during analysis. All CV analyses were conducted at room temperature. The CV curves were recorded between 0 and 1.2 V with respect to normal hydrogen electrode (NHE) at scan rate of 50 mV/s. Rotating disk electrode (RDE) experiments were conducted in the same electrochemical cell by saturating the electrolyte solution with O_2 for 30 min prior to analysis. Five different rotation speeds (100-2500 rpm) were employed with a scan rate of 10 mV/s. The ORR curves were recorded between 0.1 and 1 V with respect to NHE.

Chapter 4: Results and Discussion

4.1. CA supported Pt Nanoparticles

4.1.1. Properties of CAs

As explained previously, CA samples with different physical characteristics were prepared by changing the reactant ratios. R/F ratio was kept constant at 0.5. Table 4.1 presents the physical properties of CA samples and the reactant ratios used.

Table 4.1: Pore properties of synthesized CAs.

Aerogel	R/C	R/W	BET SA (m²/g)	Pore Size (nm)	Micropore Volume (cm³/g)	Pore Volume (cm³/g)
CA6	100	0.08	602	6	0.088	0.9
CA8	100	0.04	790	8	0.127	1.6
CA19	200	0.02	750	19	0.151	3.6

Table 4.1 shows that all CA samples have high surface areas which are relatively close to each other. When R/W ratio was increased at constant R/C, the average pore size decreased. Conversely, increasing R/C ratio at constant R/W ratios resulted in an increase in average pore size. Same trend was observed for pore volume as well. However, a correlation between the surface area and the pore volume was not observed.

Figure 4.1 shows the differential pore volumes of CAs, plotted against pore size. Figure 4.1 indicates that all synthesized CAs had sharp pore size distributions where the majority of the pores were in between 1 nm and 20 nm range for all three CAs.

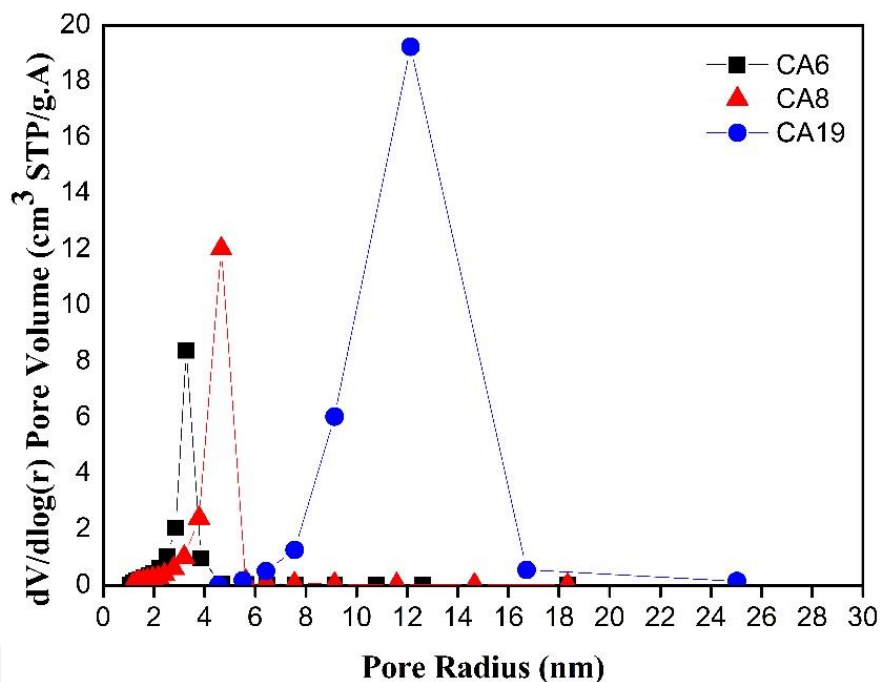


Figure 4.1: Pore size distributions of CA6, CA8, CA19.

Figure 4.2 shows the Raman spectra of the CA6, CA8 and CA19 samples. Two broad peaks were observed; the D-band peak around 1340 cm^{-1} , which is related to disorder-induced scattering that does not appear in perfect graphite crystals, and the G-band peak around 1580 cm^{-1} , which is related to the disorder-broadened Raman-active E_{2g2} mode. The peaks were deconvoluted because the D-band peak consists of four different D-band contributions: D1, D2, D3 and D4 [140]. Tables 4.2 and 4.3 summarize the parameters obtained from curve fitting for the D- and G-bands along with the ratios of the areas of fitted D-band peaks to the area of fitted G-band peak for all three CAs.

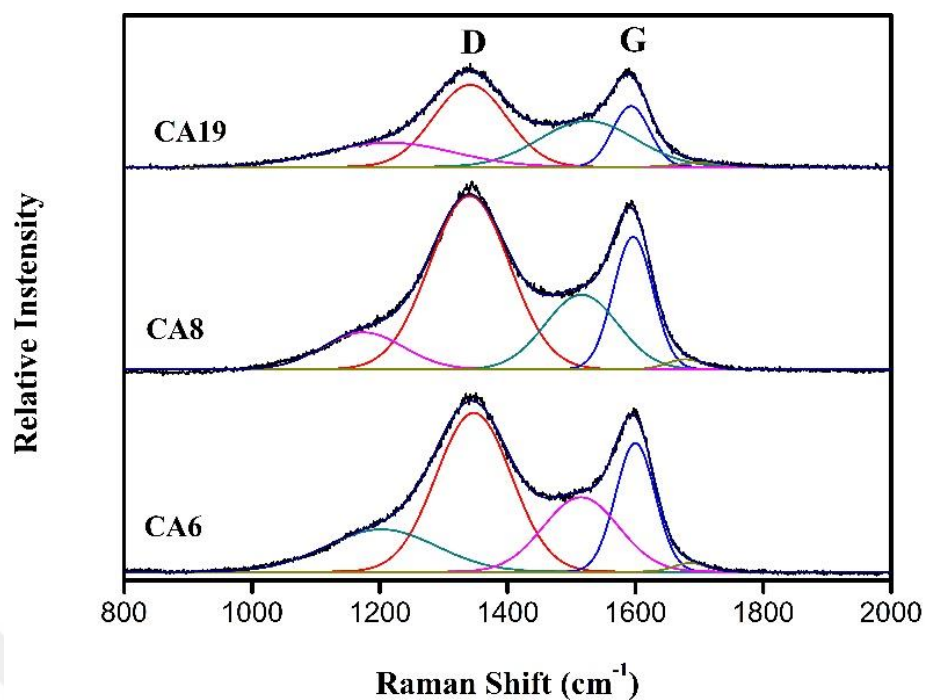


Figure 0.2: Raman spectra of CA6, CA8 and CA19.

Table 4.2: Raman parameters of CA samples obtained from curve fitting.

Band	Raman Shift (cm ⁻¹)			Vibration Mode
	CA6	CA8	CA19	
G	1599	1596	1593	Ideal graphitic lattice
D1	1347	1341	1342	Disordered graphitic lattice- graphene layer edge
D2	1686	1677	1701	Disordered graphitic lattice- surface graphene layer
D3	1515	1516	1525	Amorphous carbon
D4	1203	1174	1214	Polynes, ionic impurities

Table 4.3: Area ratios of CA samples obtained from curve fitting of the Raman spectra.

Area Ratio	CA6	CA8	CA19
$A_{D1/G}$	2.35	2.40	2.67
$A_{D2/G}$	0.06	0.07	0.09
$A_{D3/G}$	1.11	1.04	1.97
$A_{D4/G}$	0.92	0.57	1.39

Table 4.3 clearly shows that the local order in CA6 and CA8 is similar to each other whereas, CA19 showed clear differences, especially the ratios of amorphous carbon and polynes to graphitic lattice are significantly greater in CA19 than in CA6 and CA8.

4.1.2. CA Supported Pt Nanoparticles

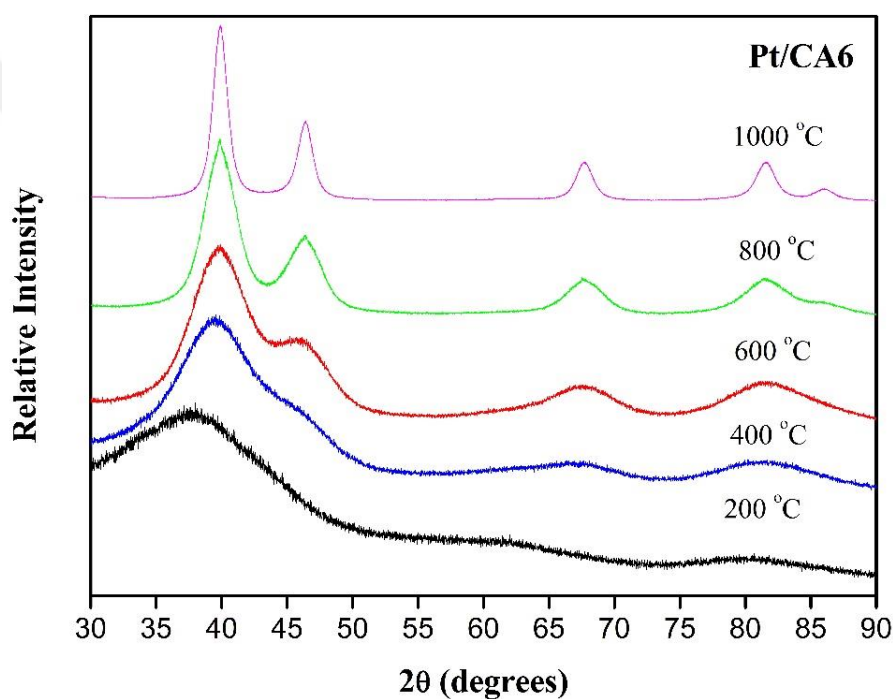
All of the Pt/CA samples were prepared using the Pt(cod)me₂-CA-scCO₂ system isotherms that were measured previously by Saquing *et. al.* at 80 °C and 27.6 MPa [83, 141]. Metal loadings were also determined after deposition by using both gravimetric and TGA methods. Table 4.4 shows the overall Pt loadings of the prepared Pt/CA samples.

Table 4.4: Overall Pt loadings of the prepared samples.

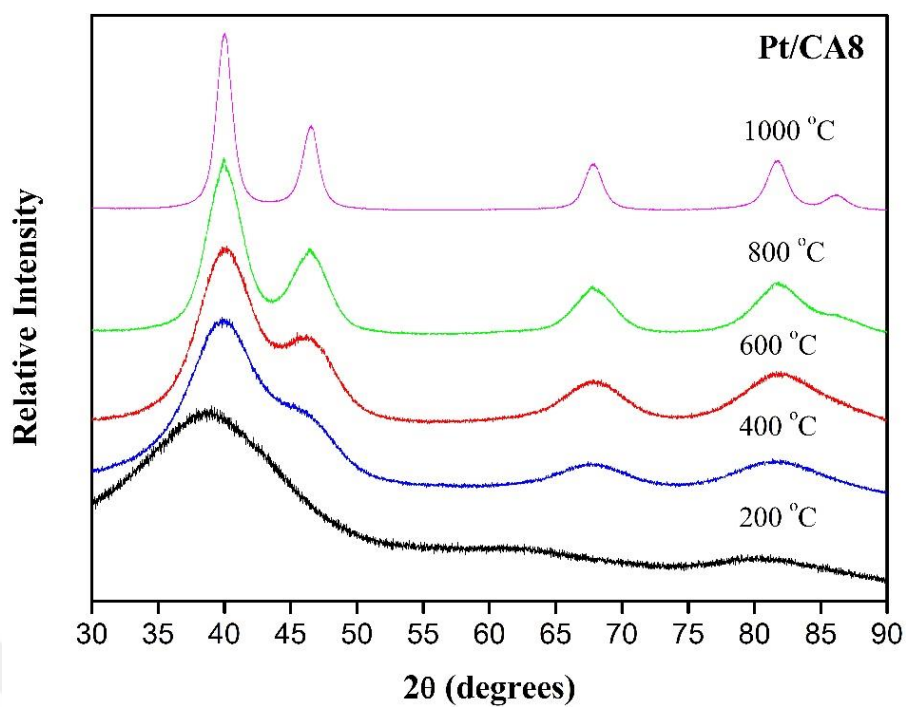
Pt Loading (wt. %)		
Sample	Gravimetric	TGA
Pt/CA6	25.3	23.7
Pt/CA8	29.8	27.4
Pt/CA19	28.7	26.4

In order to determine the effect of precursor conversion temperature on the physical properties of the Pt/CA samples, conversion treatments were performed at five different

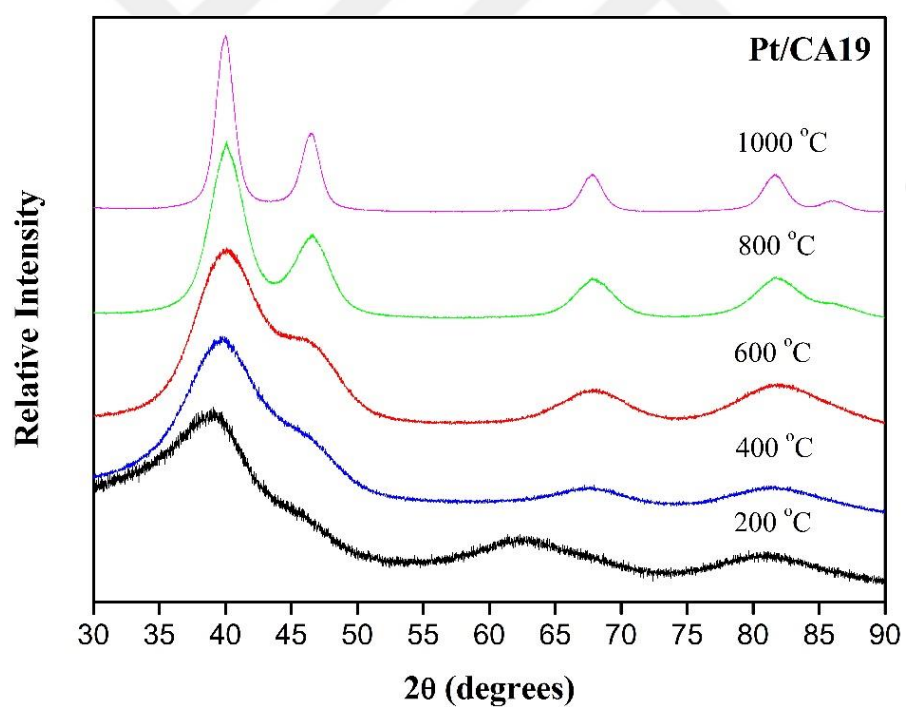
temperatures from 200-1000°C. Figure 4.3 shows the XRD data from the resulting Pt/CA samples. The presence of the four main peaks ($\{111\}$, $\{200\}$, $\{220\}$ and $\{311\}$) for face-centered cubic Pt indicates that Pt is in its metallic form in all of the samples, and thus the conversion of $\text{Pt}(\text{cod})\text{me}_2$ can be achieved at temperatures as low as 200 °C. The peaks are sharper at higher conversion temperatures, indicating that the Pt particle sizes are increasing. Particle sizes were obtained from the $\{220\}$ peak widths using the Scherrer equation, and these are plotted as a function of conversion temperature in Figure 4.4.



(a)



(b)



(c)

Figure 4.3: XRD patterns of (a) Pt/CA6 (b) Pt/CA8 (c) Pt/CA19 which were produced using different precursor conversion temperatures.

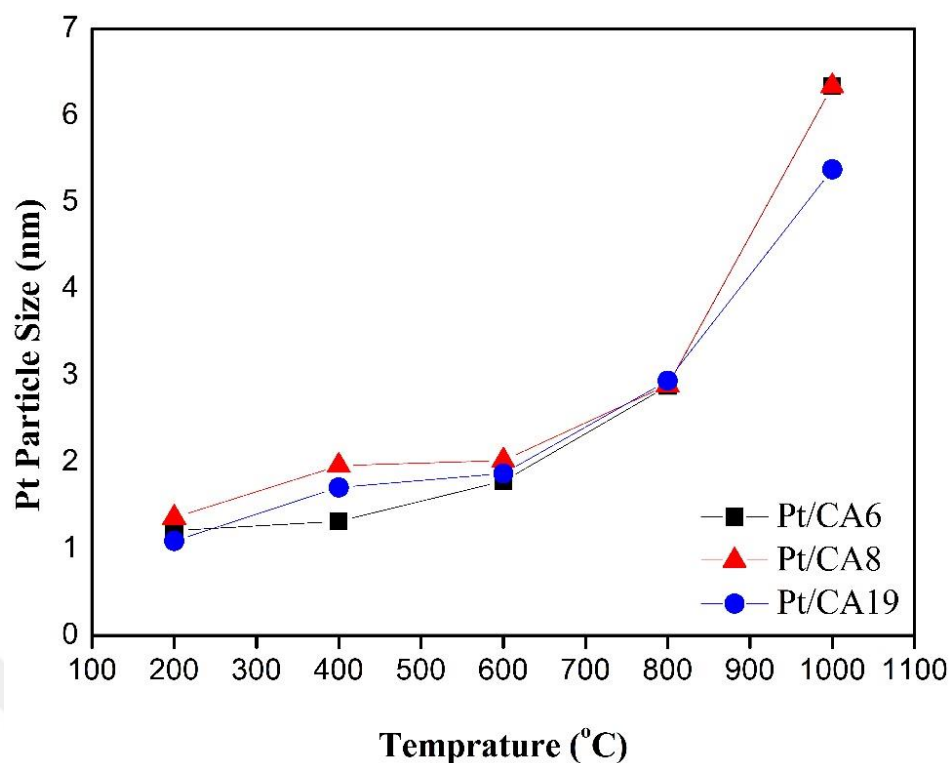
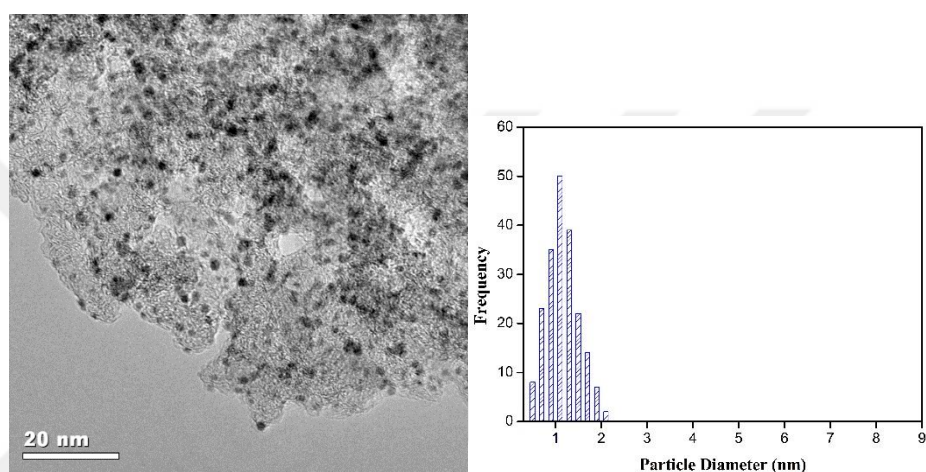


Figure 4.4: Variation of Pt particle size with precursor conversion temperature.

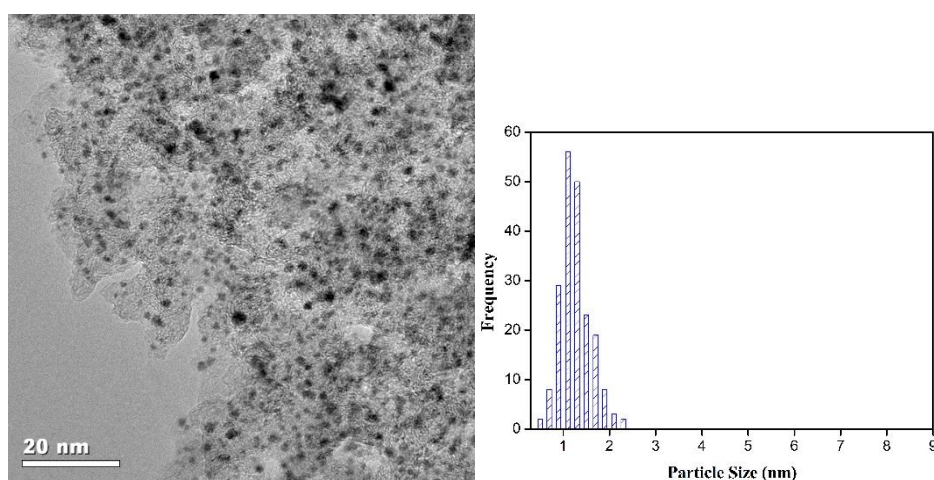
Figure 4.4 shows that the average particle size increases steadily with increasing conversion temperature. The particle sizes obtained were between 1.1 nm and 6.3 nm for all of the Pt/CA samples produced in this study, and this corresponds to the size range where there is a large change in activity with average Pt particle size for fuel cell catalysts. Pt particle sizes increased from 1.2 nm to 6.3 nm for Pt/CA6, 1.4 nm to 6.3 nm for Pt/CA8 and 1.1 nm to 5.4 nm for Pt/CA19. Thus, the pore size of the CA support does not have a significant effect on the Pt particle size. Figure 4.4 clearly shows that up to 600 °C, the Pt particle size increased gradually to around 2 nm; more significant Pt particle growth was observed above this temperature. The particle size increased to around 3 and 6 nm when temperature was increased to 800 and 1000 °C, respectively. The trends in observed in Figure 4.4 cannot be due to differences in Pt loading, because the precursor uptake values are the same for each CA sample with a particular pore size, and are similar for the three groups of samples. Thus, the larger

nanoparticle sizes observed at the higher decomposition temperatures must be related to the higher mobility of the Pt atoms on the CA surface once the precursor has decomposed.

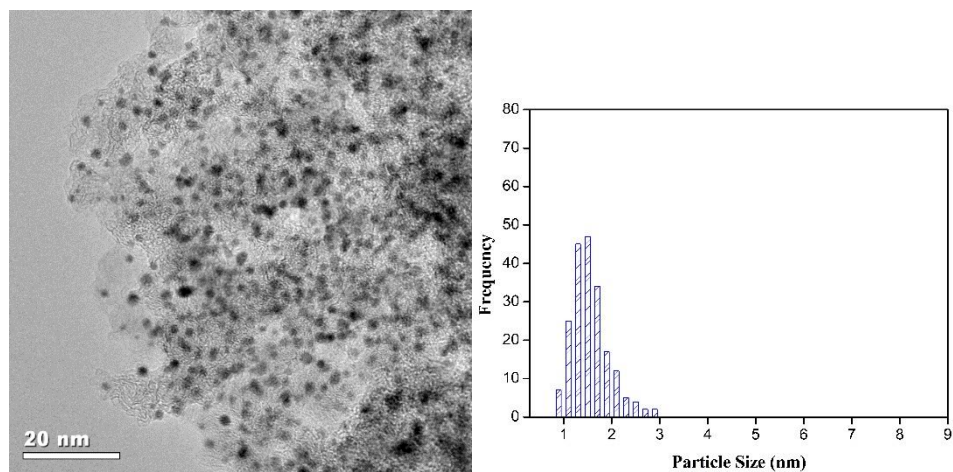
Figures 4.5, 4.6 and 4.7 are examples of representative TEM images from the Pt/CA samples together with Pt particle size distributions. In such TEM images the gray background is the CA framework and the black dots are the Pt nanoparticles. These data show that even though higher decomposition temperatures result in larger particles, this does not affect the homogeneity of the Pt nanoparticle distributions on the CA supports.



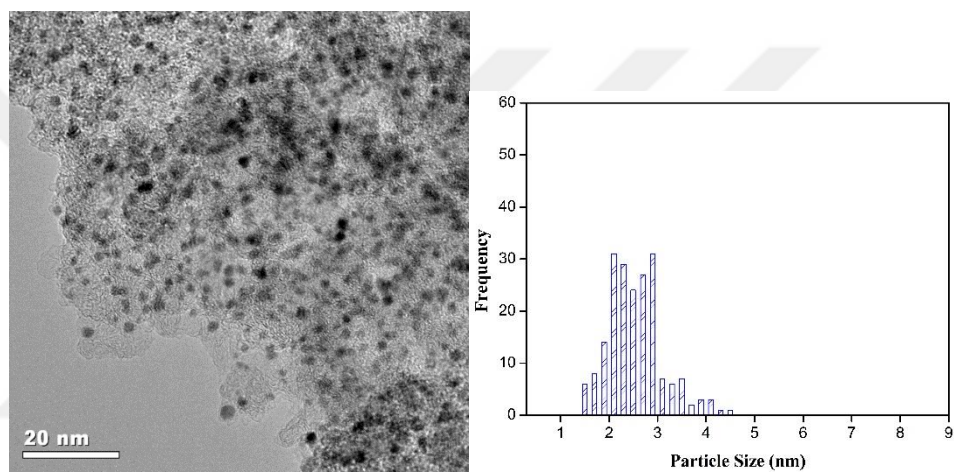
(a)



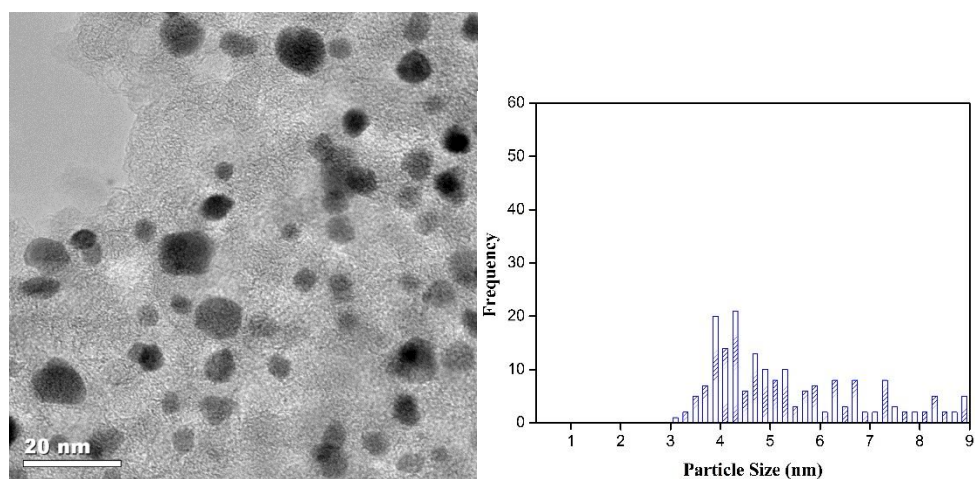
(b)



(c)

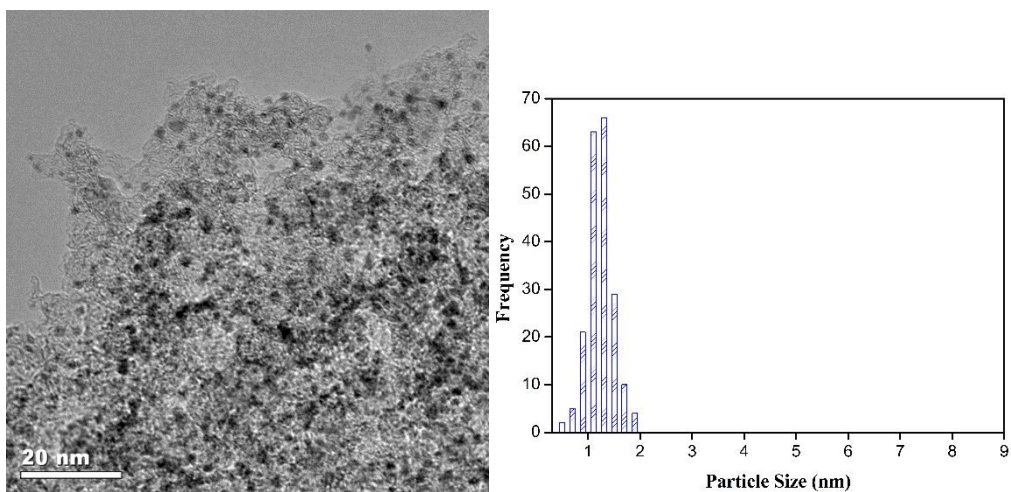


(d)

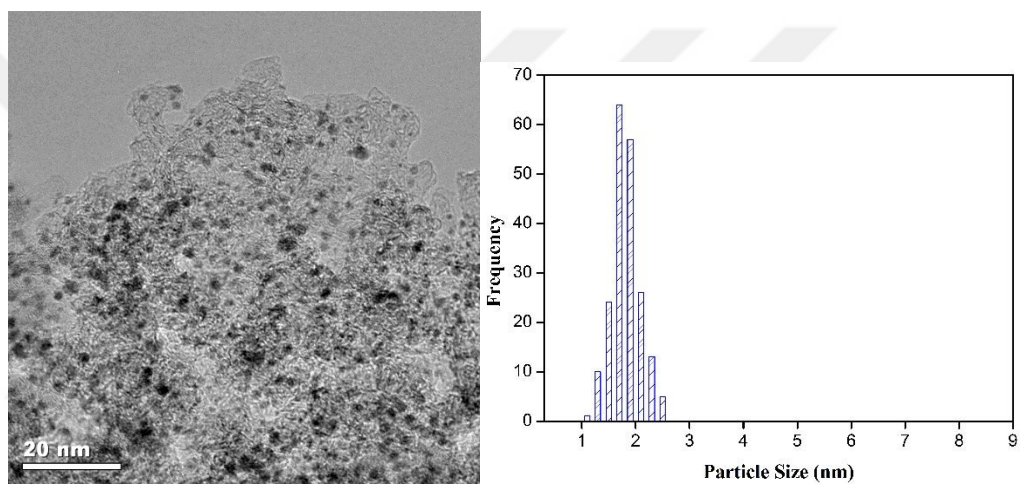


(e)

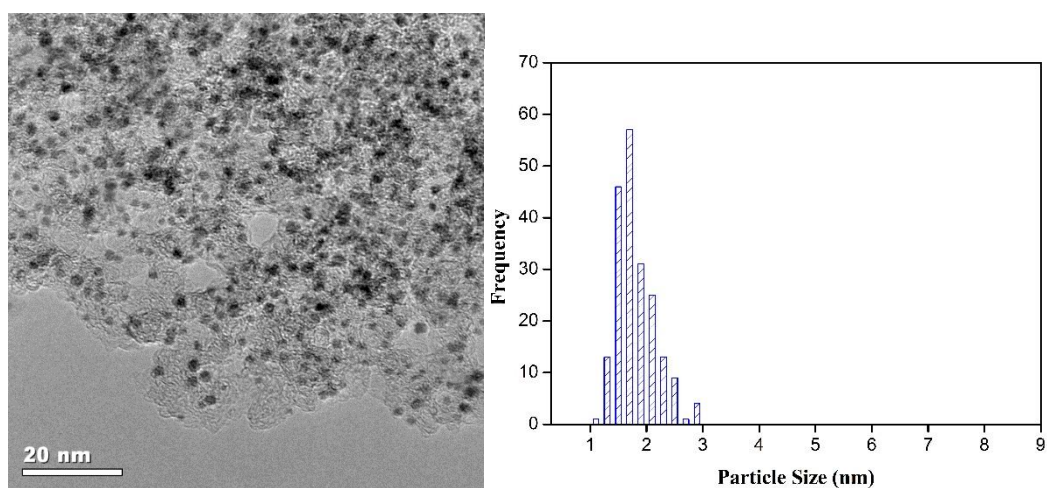
Figure 4.5: TEM images and particle size distributions of Pt/CA6 samples (a) 200 °C, (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 1000 °C



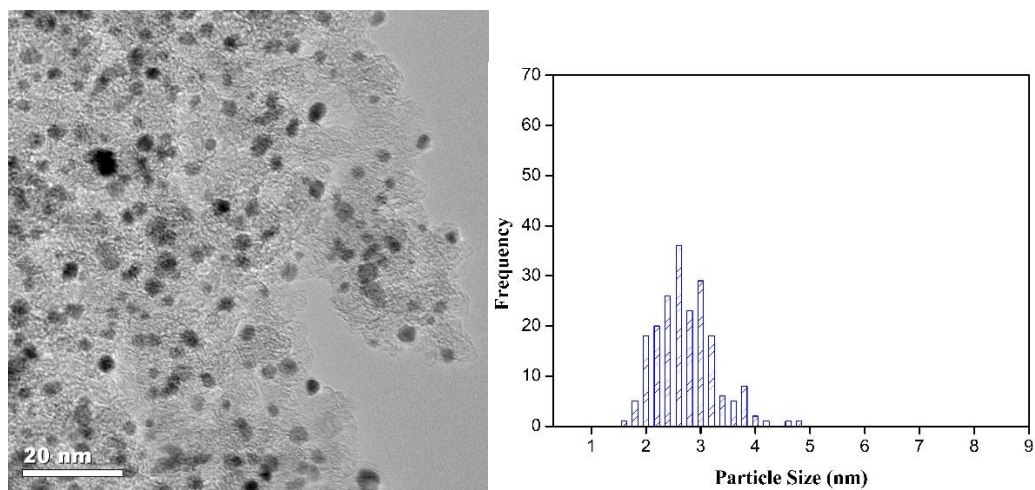
(a)



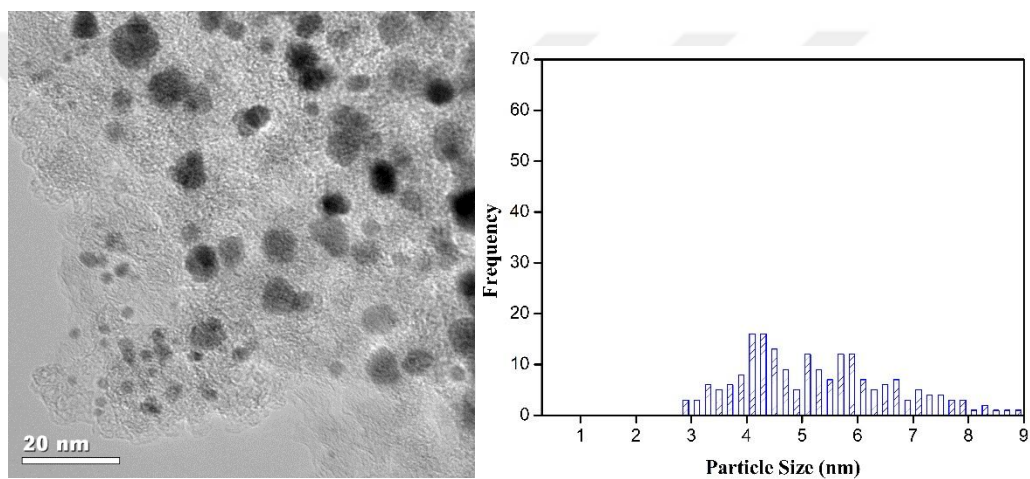
(b)



(c)

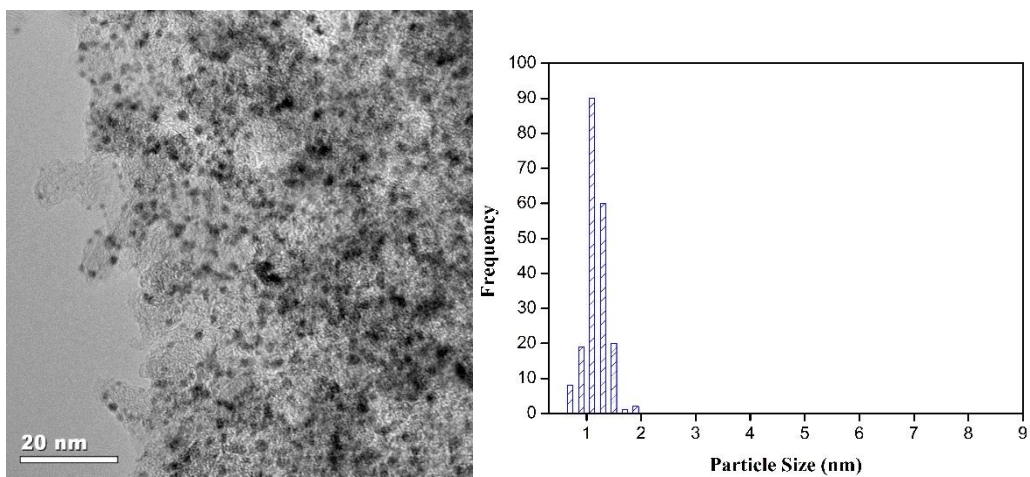


(d)

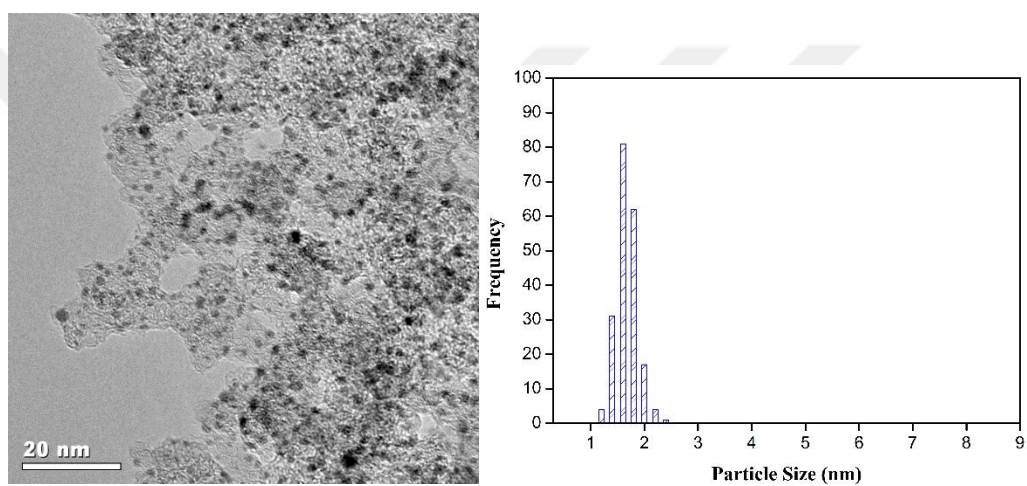


(e)

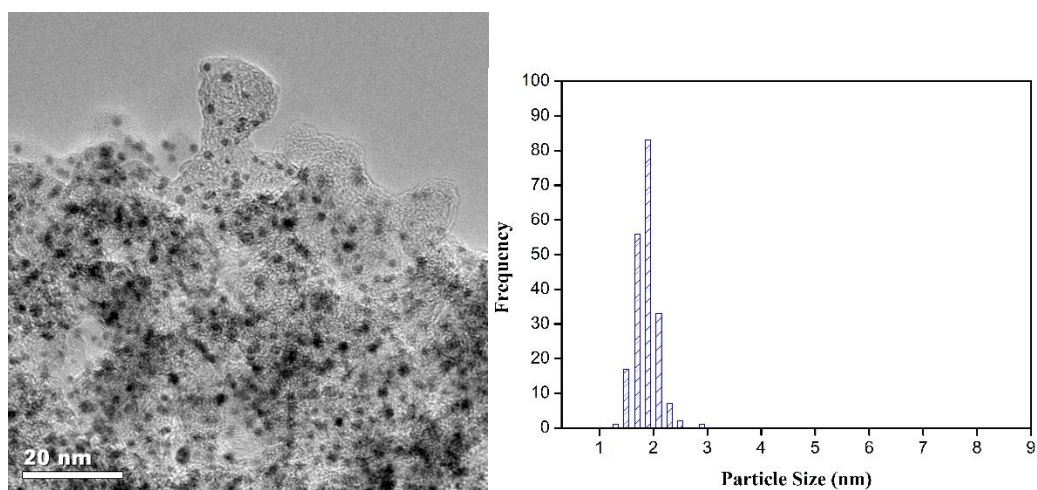
Figure 4.6: TEM images and particle size distributions of Pt/CA8 samples (a) 200 °C, (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 1000 °C



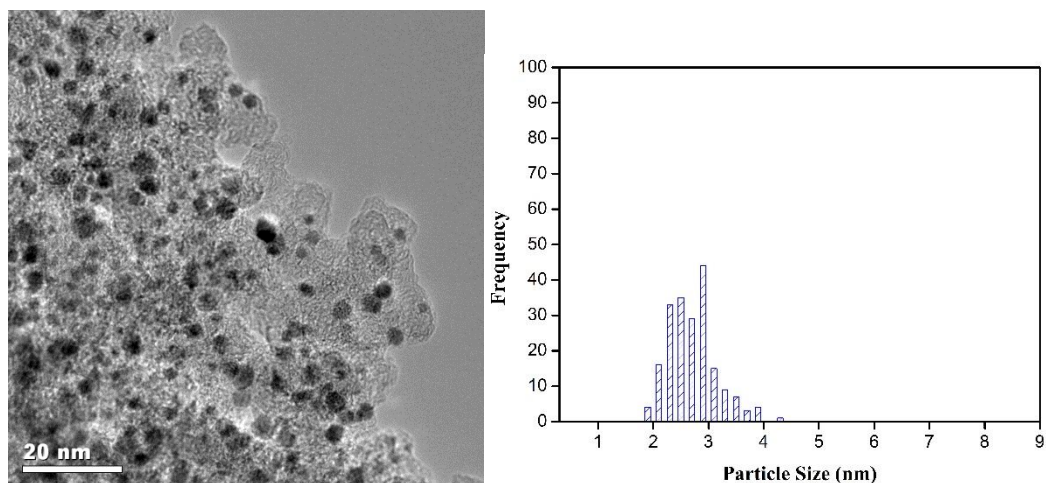
(a)



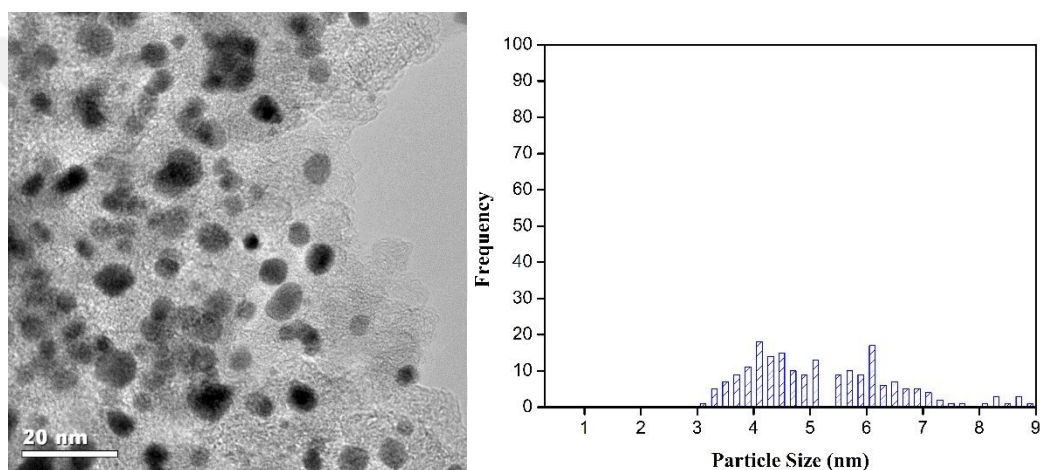
(b)



(c)



(d)



(e)

Figure 4.7: TEM images and particle size distributions of Pt/CA19 samples (a) 200 °C, (b) 400 °C, (c) 600 °C, (d) 800 °C, and (e) 1000 °C

The Pt particle sizes measured from the TEM images are compared with those from the XRD data in Table 4.5. The particle sizes from the TEM images are remarkably uniform with standard deviations from the averages in the range of ± 0.2 -0.6 nm except for the samples with a decomposition temperature of 1000°C. At 1000°C, the deviations from the average particle size increases to ± 1.8 nm for Pt/CA6, ± 1.5 nm for Pt/CA8 and ± 1.4 nm for Pt/CA19. While these particle size distributions are broader than those for samples processed at lower

decomposition temperatures, they are still very narrow when compared with those produced by competing techniques. Therefore, it can be said that all of the samples considered in this study have a homogenous distribution of Pt nanoparticles.



Table 4.5: Particle sizes of Pt/CA samples obtained from XRD spectrum and TEM images.

Particle Size (nm)			Particle Size (nm)			Particle Size (nm)		
Sample	From XRD	From TEM	Sample	From XRD	From TEM	Sample	From XRD	From TEM
Pt/CA6 200 °C	1.2	1.1±0.3	Pt/CA8 200 °C	1.4	1.2±0.2	Pt/CA19 200 °C	1.1	1.2±0.2
Pt/CA6 400 °C	1.3	1.3±0.3	Pt/CA8 400 °C	1.9	1.8±0.3	Pt/CA19 400 °C	1.7	1.7±0.2
Pt/CA6 600 °C	1.8	1.6±0.4	Pt/CA8 600 °C	2.0	1.8±0.3	Pt/CA19 600 °C	1.9	1.9±0.2
Pt/CA6 800 °C	2.9	2.5±0.6	Pt/CA8 800 °C	2.9	2.7±0.5	Pt/CA19 800 °C	2.9	2.7±0.4
Pt/CA6 1000 °C	6.3	5.6±1.8	Pt/CA8 1000 °C	6.3	5.4±1.5	Pt/CA19 1000 °C	5.4	5.3±1.4

Figure 4.8 shows the variation of the ratio of standard deviation, σ , to mean particle size, d_m). Growth mechanism of the nanoparticles can be explained through this variation in systems where there is homogenous nucleation [142]. Until 800 °C, there are not any significant changes in σ/d_m with respect to particle size. At 1000 °C, however; change becomes nearly 2-fold indicative of a less homogenous distribution of Pt particles. This can perhaps be attributed to the weakening interaction between Pt nanoparticles and CA at such high annealing temperatures so that small particles that are close to each other can diffuse towards each other forming larger particles whereas smaller particles that are trapped inside micropores stays immobile resulting a higher standard deviation.

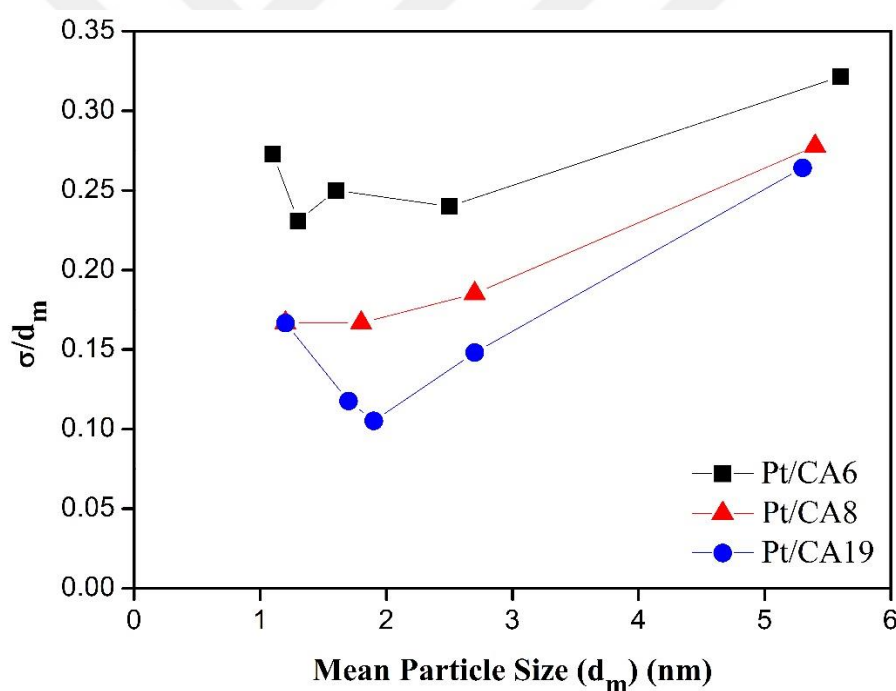


Figure 4.8: Variation of σ/d_m with mean particle size.

4.1.3. Effect of Pore Properties of CA on the Electrocatalytic Properties

The Pt/CA samples processed at a decomposition temperature of 400 °C were chosen to determine the effect of pore properties on electrocatalytic properties due their moderate particle size and homogenous distribution of Pt nanoparticles.

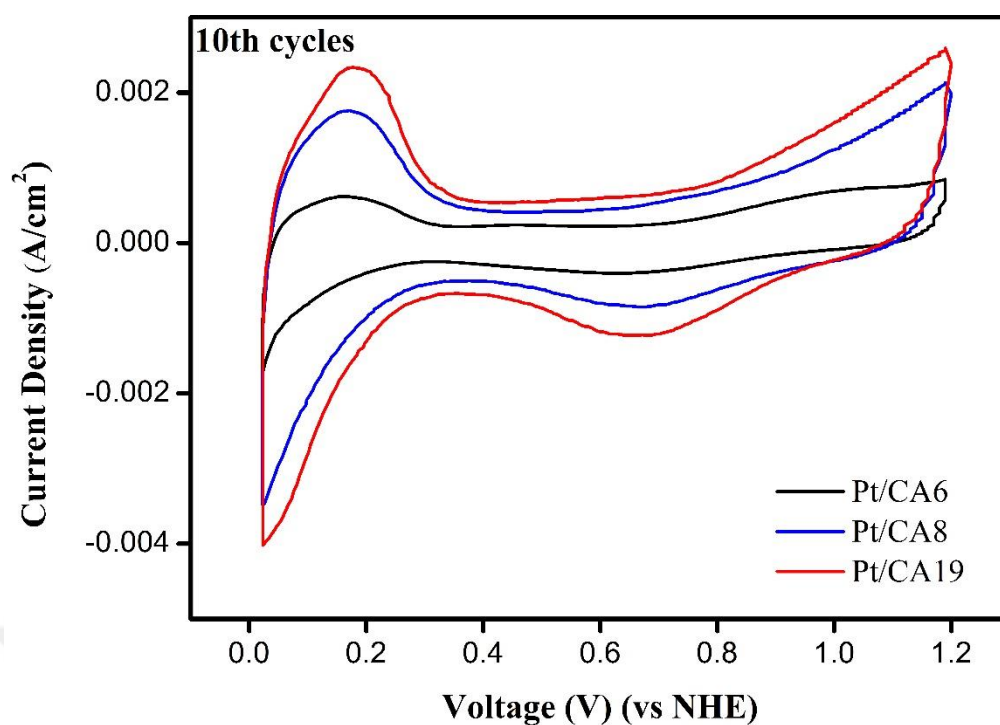


Figure 4.9: Cyclic voltammograms of Pt/CA6 400 °C, Pt/CA8 400 °C and Pt/CA19 400 °C taken in N_2 saturated HClO_4 electrolyte (10th cycles).

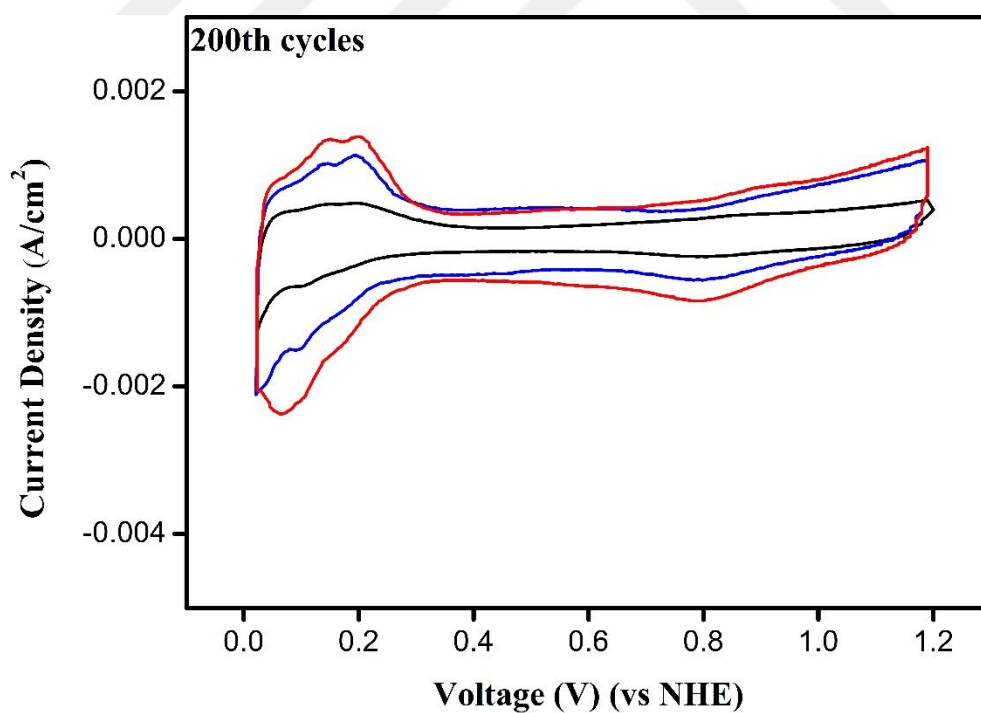


Figure 4.10: Cyclic voltammograms of Pt/CA6 400 °C, Pt/CA8 400 °C and Pt/CA19 400 °C taken in N_2 saturated HClO_4 electrolyte (200th cycles).

The cyclic voltammograms of Pt/CA6 400 °C, Pt/CA8 400 °C and Pt/CA19 400 °C are presented in Figure 4.9 and 4.10. All three catalysts exhibited decreasing hydrogen adsorption and desorption peaks with continuous cycling. This decrease is most significant in the Pt/CA8 400 °C and it least significant in the Pt/CA6 400 °C. Furthermore, the hydrogen adsorption/desorption peaks which are usually observed around 0-0.3 V are present in samples, but the highest intensity was exhibited by Pt/CA19 400 °C.

The ESA values of the prepared samples were determined after the 10th and 200th cycle using the area under the hydrogen adsorption region by eliminating the effect of capacitive current. The ESA was calculated using the following formula:

$$ESA = \frac{A}{K \times L_{Pt} \times S} \quad (4.1)$$

where A is the area under the hydrogen adsorption region, K is the charge density of bulk Pt (210 µC/cm²), L_{Pt} is Pt loading on electrode surface (28 µg/cm²) and S is the scan rate (50 mV/s).

Table 4.6 presents the electrocatalytic properties of the Pt/CA samples. Pt/CA19 400 °C had the highest ESA values for both 10th and 200th cycles which are 126 m²/g and 87 m²/g, respectively. Whereas, Pt/CA6 400 °C exhibited the lowest ESA values, 36 m²/g for 10th cycle and 29 m²/g for 200th cycle; although, it has the smallest particle size (1.3 nm). Nafion may block the pores of CA6 which in turn blocks some of the Pt nanoparticles inside the pores. Pt/CA8 400 °C showed a slightly lower ESA than Pt/CA19 400 °C at 10th cycle as expected since Pt/CA8 400 °C have higher Pt particle size than Pt/CA19 400 °C. The ESAs of all three samples decreases with continuous cycling. Pt/CA8 400 °C had the highest ESA decrease (from 96 m²/g to 56 m²/g, respectively) which corresponds to 42%, whereas the ESA loss of the Pt/CA6 400 °C sample is only 19%. Pt/CA19 400 °C exhibited an ESA loss of 31% at the end of the 200th cycle which can be considered as moderate.

Figure 4.11, 4.12 and 4.13 shows the ORR curves of the Pt/CA6 400 °C, Pt/CA8 400 °C, Pt/CA19 400°C samples after 10 cycles. Rotating disk electrode experiments were conducted in an O₂ saturated environment to simulate the ORR in an acidic electrolyte. Mass activity and specific activity values were calculated by taking the current density value at 0.85 V at 1600 rpm to exclude the mass transport effects. ORR curves from all of the samples exhibit an expected trend, namely that the current densities increase with increasing rotation speed.

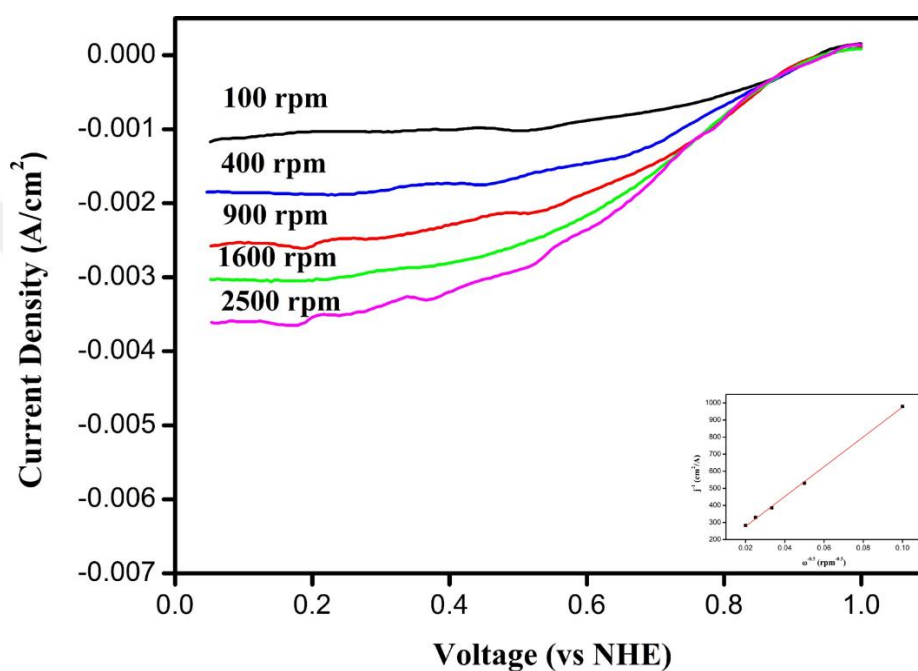


Figure 4.11: ORR curves of Pt/CA6 400 °C after 10 cycles, recorded with a scan rate of 10 mV/s.

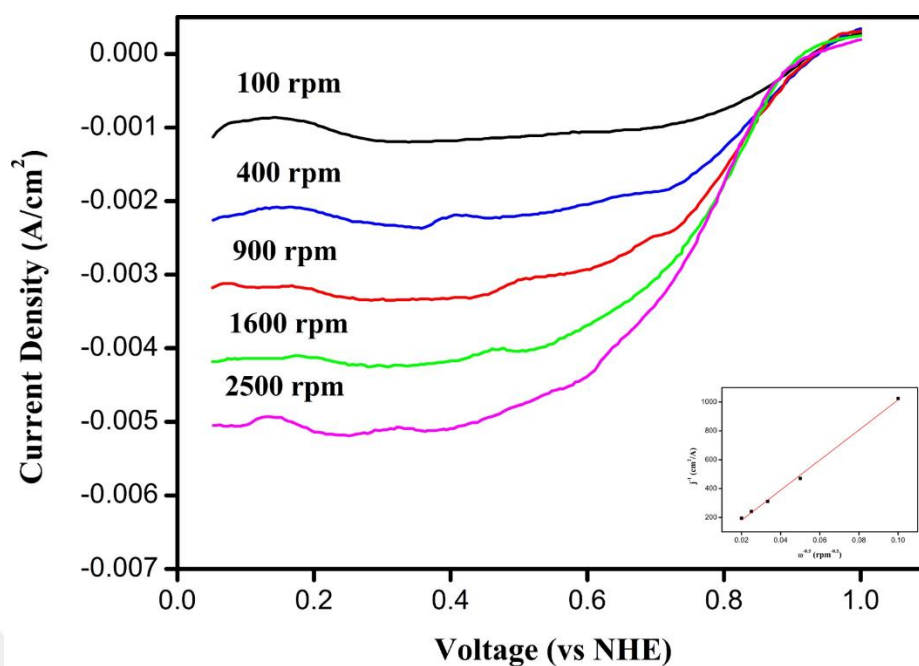


Figure 4.12: ORR curves of Pt/CA8 400 °C after 10 cycles, recorded with a scan rate of 10 mV/s.

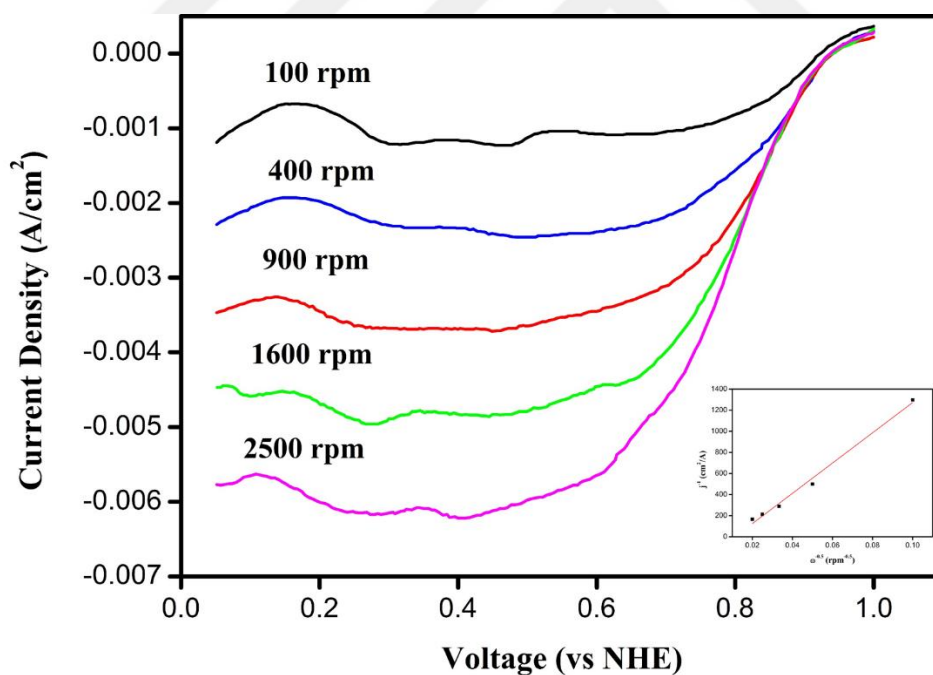


Figure 4.13: ORR curves of Pt/CA19 400 °C after 10 cycles, recorded with a scan rate of 10 mV/s.

Table 4.6: Electrocatalytic properties of Pt/CA samples treated at 400 °C.

Sample	ESA (m ² /g)	Surface Area (m ² /g)	Pt Utilization (%)	Mass Activity (A/mg _{Pt})	Specific Activity (mA/cm ²)
Pt/CA6 400 °C	36 ^a	213	17 ^a	0.02 ^a	0.04 ^a
	29 ^b		14 ^b		
Pt/CA8 400 °C	97 ^a	143	68 ^a	0.03 ^a	0.03 ^a
	56 ^b		39 ^b		
Pt/CA19 400 °C	126 ^a	164	77 ^a	0.05 ^a	0.06 ^a
	87 ^b		53 ^b		

^a10th cycle, ^b200th cycle. Surface Area (SA)= $6 \times 10^3 / \rho_d$, Pt Utilization= (ESA/SA)*100

The Pt/CA6 400 °C and Pt/CA8 400 °C samples had a very low mass activity of 0.02 A/mg_{Pt} and 0.03 m²/g towards ORR when compared to commercial Pt/C catalysts [117]. The different electrochemical behaviors exhibited by the Pt/CA6 400 °C and Pt/CA8 400 °C samples compared to Pt/CA19 400 °C can perhaps be attributed to differences in the CA framework. Raman spectra of CA19 (Table 4.3), shows that CA19 exhibits a different local order than CA6 and CA8. Changing the reactant ratios during synthesis of these aerogels may result in different functional groups on the CA framework, which in turn may affect the interaction between the Pt nanoparticles and the CA support resulting in undesired ESA and activity values.

The Pt/CA19 400 °C sample exhibited good mass and specific activity values which are 0.05 A/mg_{Pt} and 0.06 mA/cm² respectively, indicative of a promising electrocatalyst. The mass activity of Pt/CA19 400 °C (i.e. 0.05 A/mg_{Pt}) was in good agreement with those in the literature for other Pt/carbon catalysts having similar particle sizes [26, 115].

4.1.4. Effect of Pt Particle Size on Electrocatalytic Behavior

The Pt/CA19 samples were chosen to determine the effect of Pt particle size on the electrocatalytic behavior, since these showed better stability and activity with potential cycling in acidic conditions as compared to other CA samples. The particle size effect on activity was investigated after the 10th cycle. Table 4.7 summarizes the electrocatalytic properties of all of the Pt/CA19 samples.

Table 4.7: Electrocatalytic properties of Pt/CA19 samples.

Sample	ESA (m ² /g)	Surface Area (m ² /g)	Pt Utilization (%)	Mass Activity (A/mg _{Pt})	Specific Activity (mA/cm ²)
Pt/CA19 200 °C	74 ^a	257	29 ^a	0.03 ^a	0.04 ^a
	63 ^b		25 ^b		
Pt/CA19 400 °C	126 ^a	164	77 ^a	0.05 ^a	0.06 ^a
	87 ^b		53 ^b		
Pt/CA19 600 °C	44 ^a	150	29 ^a	0.10 ^a	0.24 ^a
	78 ^b		52 ^b		
Pt/CA19 800 °C	52 ^a	95	55 ^a	0.10 ^a	0.18 ^a
	60 ^b		63 ^b		
Pt/CA19 1000 °C	8 ^a	52	15 ^a	0.01 ^a	0.16 ^a
	31 ^b		59 ^b		

^a10th cycle, ^b200th cycle. Surface Area (SA)= $6 \times 10^3 / \rho_d$, Pt Utilization= (ESA/SA)*100

The ESA values decreased as the Pt particle size increased starting from Pt/CA19 400 °C (1.7 nm) to Pt/CA19 1000 °C (5.3 nm) for the 10th cycles, which is in agreement with the data in the literature for other types of carbon supports [114, 117]. However, Pt/CA19 200 °C did not follow this trend. The XRD data from Pt/CA19 200 °C showed a slight shift of the {220}

peak towards lower Bragg angle values indicating that the lattice constant is larger. We infer from this that Pt nanoparticle formation was incomplete at this annealing temperature, resulting in a lower ESA value for Pt/CA19 200 °C than expected. Furthermore starting from Pt/CA19 600°C, ESA values start to increase with continuous cycling. As Pt particle sizes started to increase significantly from 600 °C to 1000 °C, this increase in ESA can be the result of dissolution of some Pt atoms into the acidic electrolyte with continuous cycling creating decreased Pt particle size and therefore increased ESA. Pt/CA19 600°C sample showed the best performance, with a mass activity of 0.1 A/mg_{Pt}, a specific activity of 0.24 mA/cm² and an ESA of 78 m²/g (200th cycle). The Pt/CA19 1000°C sample exhibited the lowest performance with a mass activity of 0.01 A/mg_{Pt}, a specific activity of 0.16 mA/cm² and an ESA of 30 m²/g (200th cycle).

Figure 4.14 shows the variation of the mass and the specific activity values of the Pt/CA19 samples with the average size of Pt particles. The specific activity shows an increasing trend with increasing particle sizes up to 1.9 nm. The specific activity showed a 6-fold increase at 1.9 nm (0.24 mA/cm²) when compared to 1.1 nm which has a specific activity of 0.04 mA/cm². However, at a Pt particle size of 2.7 nm, the specific activity decreases slightly to 0.18 mA/cm² and at 5.3 nm it becomes 0.16 mA/cm² which is nearly the same as 2.7 nm. The number of terrace sites on the surface of the Pt nanoparticles, which are widely accepted as the active sites for the ORR, increases as particle size increases, whereas the surface density of edge sites decreases. A similar behavior is observed on studies with other types of carbon supports [26, 114-119] where the specific activity increases with increasing Pt particle size and reach a plateau at some point. Moreover, the mass activities of the Pt/CA19 samples also increases with increasing particle sizes, and reaches a plateau at 1.9 nm, becoming more than 3-fold of that at 1.1 nm. The Pt/CA19 600°C (1.9 nm) and Pt/CA19 800°C (2.7 nm) samples showed the same mass activity value of 0.1 A/mg_{Pt}, which is the highest among all of the samples studied here.

Moreover, the higher particle size (5.3 nm) gave the lowest mass activity value of 0.01 A/mg_{Pt}, in agreement with literature [26, 116, 117].

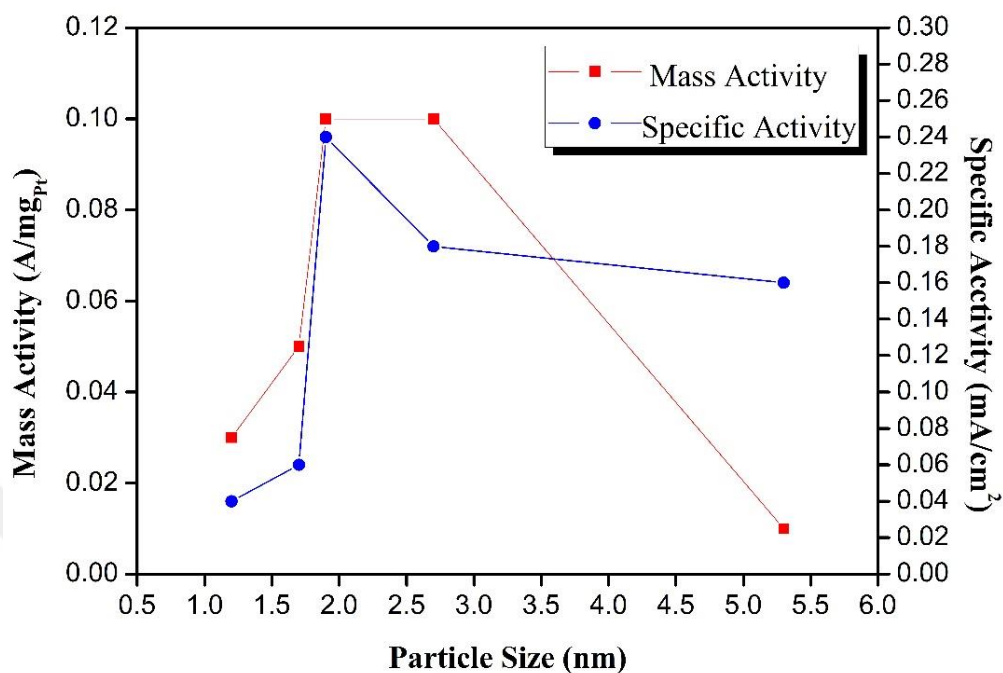


Figure 4.14: Change in mass and specific activity of Pt/CA19 samples with particle sizes.

4.2. CA19 Supported Pt-Cu Bimetallic Alloy Nanoparticles

4.2.1. Single Adsorption Isotherms of Pt(cod)me₂-CA19 and Cu(tfa)₂-CA19 in scCO₂

The single adsorption isotherm of Pt(cod)me₂-CA19-scCO₂ system at 35 °C and 10.7 MPa was previously measured by Bozbağ *et. al.* [35]. However, for Cu(tfa)₂-CA19-scCO₂ system adsorption data was not present in the literature. Therefore, in order to control the metal loadings prior to adsorption experiments, single adsorption isotherm of Cu(tfa)₂-CA19 system was measured scCO₂ at 35 °C and 10.7 MPa. The adsorption isotherms were fitted to Langmuir adsorption model presented below;

$$q = \frac{K_0 Q_0 C}{1 + K_0 C} \quad (4.2)$$

where, q is the uptake amount of metal precursor on CA19 (mol metal precursor/kg CA19), K_0 is the Langmuir adsorption equilibrium constant (m³ scCO₂/mol metal precursor), Q_0 is the

uptake capacity of CA19 (mol metal precursor/kg CA19) and C is the concentration in fluid phase (mol metal precursor/ m^3 scCO₂). Langmuir parameters were obtained using non-linear regression and presented Table 4.8.

Table 4.8: Langmuir model parameters of Pt(cod)me₂-CA19 and Cu(tfa)₂-CA19 systems.

Model Parameters	Pt(cod)me ₂ [35]	Cu(tfa) ₂
Langmuir		
Q₀ (mol/kg)	2.343	0.657
K₀ (m³/mol)	0.480	2.490
R²	0.999	0.999

The single adsorption isotherms of Pt(cod)me₂-CA19 and Cu(tfa)₂-CA19 were given in Figure 4.15. Both isotherms fit perfectly to the Langmuir model.

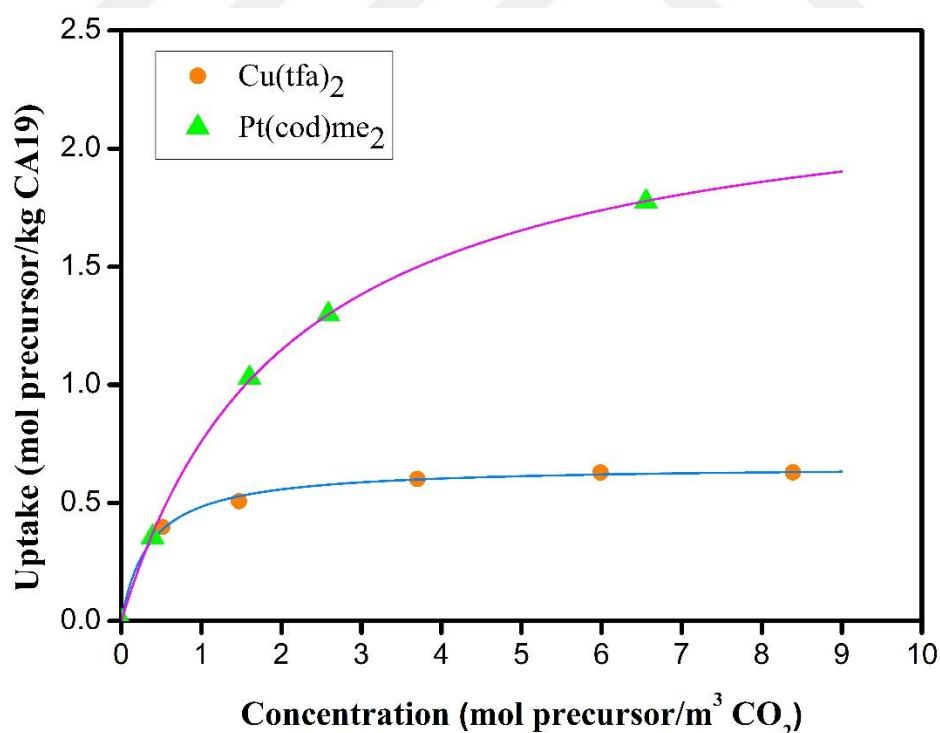


Figure 4.15: Single adsorption isotherms of Pt(cod)me₂-CA19 [35] and Cu(tfa)₂-CA19 measured at 35 °C and 10.7 MPa in scCO₂.

From Figure 4.15, it can be seen that uptake values of both $\text{Pt}(\text{cod})\text{me}_2$ and $\text{Cu}(\text{tfa})_2$ increases nonlinearly with increasing metal complex concentration in the fluid phase. At a certain equilibrium concentration uptake of $\text{Pt}(\text{cod})\text{me}_2$ on CA19 is greater than the uptake of $\text{Cu}(\text{tfa})_2$. Also the uptake capacity of CA19 is greater for $\text{Pt}(\text{cod})\text{me}_2$ than for $\text{Cu}(\text{tfa})_2$.

4.2.2. Decomposition of metal precursors

4.2.2.1. Decomposition of $\text{Pt}(\text{cod})\text{me}_2$

Decomposition of pure $\text{Pt}(\text{cod})\text{me}_2$ and $\text{Pt}(\text{cod})\text{me}_2$ adsorbed on CA19 was previously investigated using TGA under N_2 flow (100 mL/min) with a heating ramp of 20 °C [141]. The significant weight loss was observed between 100 and 200 °C for both $\text{Pt}(\text{cod})\text{me}_2$ and $\text{Pt}(\text{cod})\text{me}_2/\text{CA}$. The expected weight loss was 41% considering all the ligands were removed, however, the weight loss observed in pure $\text{Pt}(\text{cod})\text{me}_2$ was higher suggesting a mixed process of evaporation and thermal decomposition of the precursor had occurred. The weight loss of the $\text{Pt}(\text{cod})\text{me}_2/\text{CA19}$ composite was approximately the same as the theoretical value which proves that the ligands of the Pt precursor adsorbed on CA19 were successfully eliminated during heating process. Furthermore, FTIR analysis of Pt/CA did not showed any of the spectral peaks of ligands associated with the ligand of $\text{Pt}(\text{cod})\text{me}_2$.

4.2.2.2. Decomposition of $\text{Cu}(\text{tfa})_2$

Decomposition of $\text{Cu}(\text{tfa})_2$ was also investigated using TGA where pure $\text{Cu}(\text{tfa})_2$ was heated to 300 °C with a heating ramp of 10 °C/min under flowing N_2 (100 mL/min). The TGA data obtained is given in Figure 4.16.

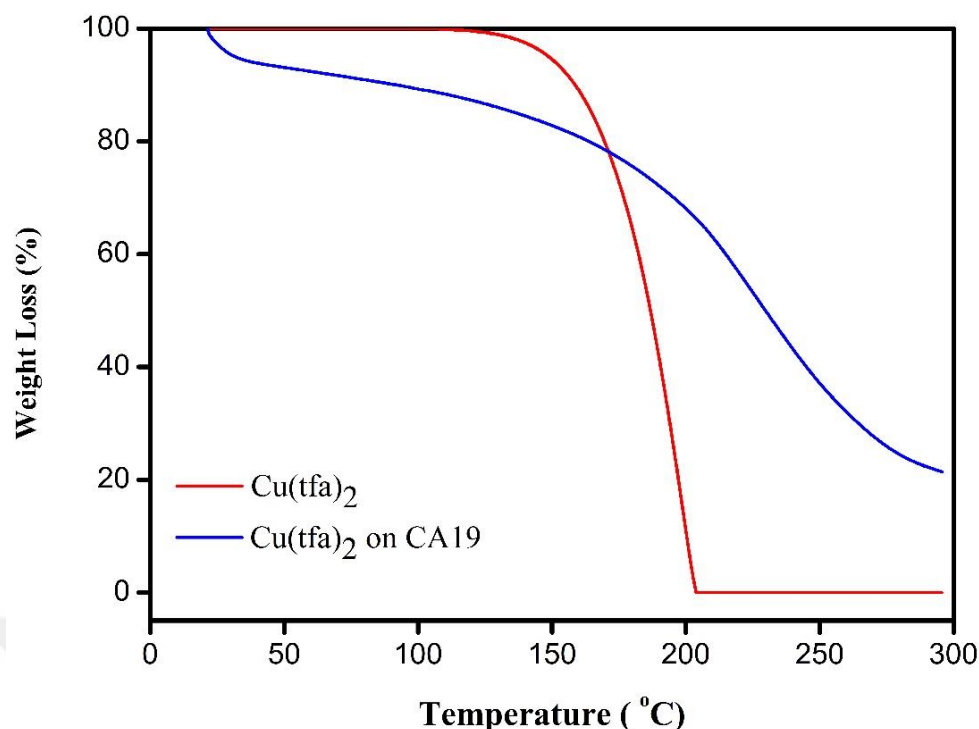


Figure 4.16: TGA of pure Cu(tfa)₂ and Cu(tfa)₂ adsorbed on CA19 in N₂ flow; TGA curve of Cu(tfa)₂ adsorbed on CA19 was plotted by subtracting the CA19 weight of the sample.

Since the weight percentage of ligands in Cu(tfa)₂ is 82.8%, the expected weight loss in the TGA of pure Cu(tfa)₂ should be 82.8% if thermal decomposition of the precursor was complete. The weight loss started around 130 °C and at 200 °C the weight loss was 100% which suggests all of the precursor was evaporated during heating process. The weight loss observed on the TGA of Cu(tfa)₂/CA19 composite at 300 °C was 78.2 % indicating thermal decomposition of Cu(tfa)₂ occurred when it is adsorbed on CA19 even though ligands were not completely removed at 300 °C.

The TGA of Cu(tfa)₂/CA19 composite showed that complete decomposition cannot be achieved under an inert atmosphere unless higher temperatures were applied. Therefore decomposition of Cu(tfa)₂ adsorbed on CA19 was investigated under a reactive gas medium (H₂) in the tube furnace at two different temperatures (150 °C and 200 °C) with a heating ramp of 20 °C/min. The weight loss was determined gravimetrically. Gravimetric results showed that

at 150 °C, the decomposition of $\text{Cu}(\text{tfa})_2$ adsorbed on CA19 was not completed whereas at 200 °C complete decomposition was achieved in the presence of H_2 meaning that after this treatment, the weight of the sample was in very good agreement with the Cu loading expected from the adsorption isotherm and assuming all the ligands were decomposed and desorbed $\text{Cu}(\text{tfa})_2/\text{CA19}$ composite during chemical conversion at atmospheric pressure. FTIR analysis was conducted on the treated samples to further support the gravimetric results. Figure 4.17 shows the FTIR spectra of pure $\text{Cu}(\text{tfa})_2$, $\text{Cu}(\text{tfa})_2$ adsorbed on CA19 and $\text{Cu}/\text{CA19}$ composites treated at 150 °C and 200 °C.

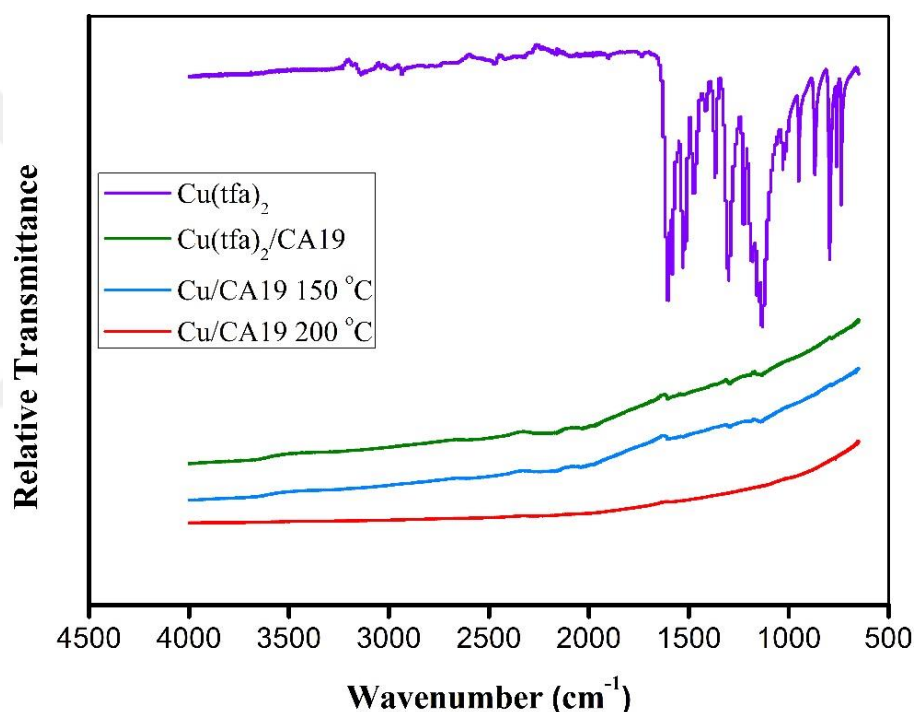


Figure 4.17: FTIR-spectra of pure $\text{Cu}(\text{tfa})_2$, $\text{Cu}(\text{tfa})_2$ adsorbed on CA19 and $\text{Cu}/\text{CA19}$ composites treated at 150 °C and 200 °C under flowing H_2 .

The FTIR-spectra of $\text{Cu}(\text{tfa})_2$ on CA19 showed that $\text{Cu}(\text{tfa})_2$ was adsorbed on CA19. The peaks at the 1130-1300 cm^{-1} range, associated with $\nu(\text{CF}_2\text{-CF}_3)$ on pure $\text{Cu}(\text{tfa})_2$ spectra and the peaks at the 1400-1600 cm^{-1} range associated with $\nu(\text{C-O})$ and $\nu(\text{C=C})$, are also present in the spectra of $\text{Cu}(\text{tfa})_2$ adsorbed on CA19. These features were also present in the spectra of $\text{Cu}/\text{CA19}$ composite treated at 150 °C showing that complete conversion of $\text{Cu}(\text{tfa})_2$ to Cu was

not achieved at this temperature in agreement with the gravimetric results. However, the ligand peaks of $\text{Cu}(\text{tfa})_2$ was not observed in the FTIR-spectra of Cu/CA19 composite treated at 200 °C with H_2 which strongly suggests that the complete conversion was achieved at 200 °C under flowing H_2 . The treated Cu/CA19 composites were further characterized using XRD to determine the crystal structure differences of the samples treated at two different temperatures. XRD of treated Cu/CA19 composites are given in Figure 4.18.

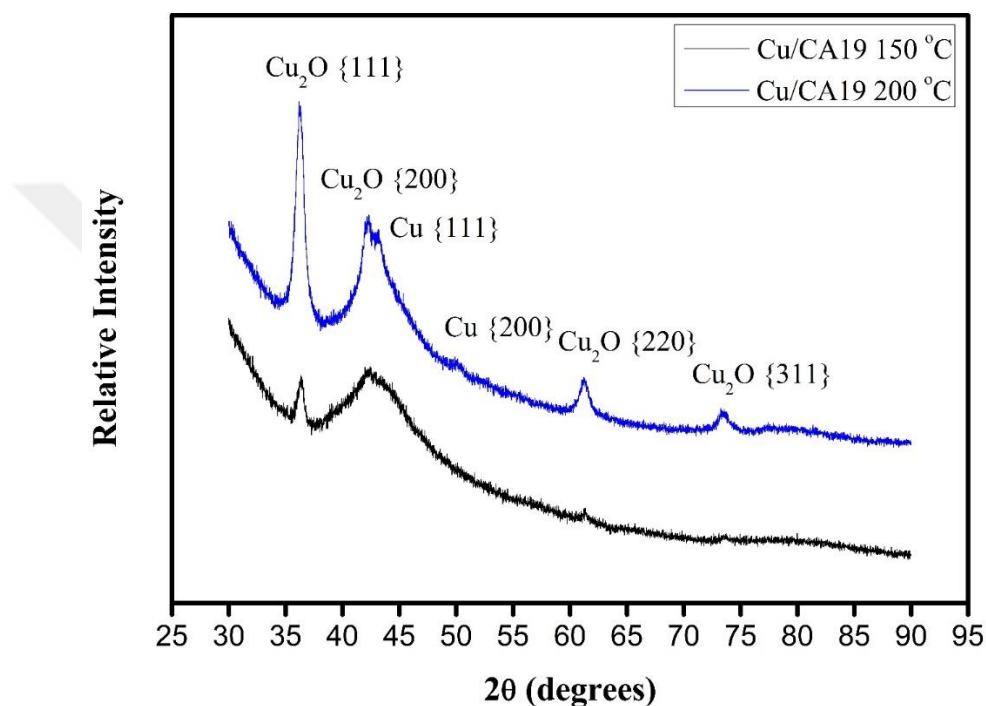


Figure 4.18: XRD of Cu/CA composites treated at 150 °C and 200 °C under flowing H_2 .

Figure 4.18 shows that both Cu/CA19 composites show the cubic cuprous oxide (Cu_2O) peaks at $2\theta=36.58^\circ$ {111}, 42.49° (200), 61.65° {220}, 73.86° {311} and also {111} peak of face-centered cubic Cu at $2\theta=43.32^\circ$. However, Cu {111} of both Cu/CA19 composites overlaps with Cu_2O {111}. The intensities of all cubic Cu_2O are significantly higher in Cu/CA19 treated at 200 °C. Furthermore, Cu/CA19 treated at 200 °C also showed {200} peak of face centered cubic Cu at $2\theta=50.45^\circ$ whereas, Cu/CA19 treated at 150 °C lack of this peak. The Cu on CA19 most likely oxides immediately when samples were exposed to ambient air after conversion which results in cubic Cu_2O peaks observed on XRD. The XRD of two Cu/CA

composites are in good agreement with gravimetric and FTIR results. The complete conversion was achieved at 200 °C.

4.2.3. Preliminary Simultaneous and Sequential Deposition Experiments for the Preparation of Pt-Cu/CA19 Composites

A series of deposition experiments were conducted using both simultaneous and sequential SCD methods to prepare Pt-Cu/CA19 composites having different molar composition. These experiments were carried out to elucidate the effects of the metal deposition order on the structure of supported Pt-Cu nanoparticles. Four sets of samples were prepared, two of which using simultaneous SCD and the other two were prepared using sequential SCD method. In sequential SCD method, deposition order was changed, in one sample first $\text{Cu}(\text{tfa})_2$ was adsorbed on CA19 followed by the precursor conversion then $\text{Pt}(\text{cod})\text{me}_2$ was adsorbed on Cu/CA19 composite and reverse order was used in the other sample. The detailed explanations of the samples are given in Table 4.9.

Table 4.9: Preliminary Pt-Cu/CA19 samples and explanation of deposition approaches.

Sample	Explanation
Pt-Cu/CA19 Trial 1	Simultaneous
Pt-Cu/CA19 Trial 2	First $\text{Cu}(\text{tfa})_2$ (I)* on CA19 then $\text{Pt}(\text{cod})\text{me}_2$ (I) on Cu/CA19
Pt-Cu/CA19 Trial 3	First $\text{Pt}(\text{cod})\text{me}_2$ (I) on CA19 then $\text{Cu}(\text{tfa})_2$ (I) on Pt/CA19
Pt-Cu/CA19 Trial 4	Simultaneous

*The number of deposition steps are given in parenthesis.

For sequential SCD experiments single adsorption isotherms of $\text{Pt}(\text{cod})\text{me}_2$ -CA19 and $\text{Cu}(\text{tfa})_2$ -CA19 were used to control the metal content before the experiments. The metal content of all samples were also determined using XRF. The metal loadings of the prepared samples are given in Table 4.10.

Table 4.10: Pt and Cu weight percentages of the preliminary Pt-Cu/CA19 samples.

Sample	Metal Loadings (wt.%)			
	Gravimetric		XRF	
	Pt	Cu	Pt	Cu
Pt-Cu/CA19 Trial 1	Simultaneous		12.2	1.6
Pt-Cu/CA19 Trial 2	12.7	3.6	8.5	2.9
Pt-Cu/CA19 Trial 3	28.4	2.2	25.8	2.9
Pt-Cu/CA19 Trial 4	Simultaneous		11.8	2.0

Table 4.10 clearly shows that metal content values of the sequentially deposited samples are close to the ones obtained from XRF which shows that the presence of one metal (Pt or Cu) on CA19 did not affect the adsorption of the other precursor ($\text{Pt}(\text{cod})\text{me}_2$ or $\text{Cu}(\text{tfa})_2$) so that single adsorption isotherms can be used to determine metal content before the deposition. When the simultaneous SCD approach was applied, Cu loading on CA19 could not exceed 2 wt.% even though the concentration of $\text{Cu}(\text{tfa})_2$ in scCO_2 was $8.4 \text{ mol Cu}(\text{tfa})_2/\text{m}^3 \text{ scCO}_2$ which corresponds to the solubility of the complex. This results suggest that there is competitive adsorption between $\text{Pt}(\text{cod})\text{me}_2$ and $\text{Cu}(\text{tfa})_2$ where $\text{Pt}(\text{cod})\text{me}_2$ preferentially adsorbed on CA19.

The four preliminary Pt-Cu/CA samples were converted at 200°C under flowing H_2 . In order to determine the difference between the two deposition approaches (simultaneous and sequential SCD) and the deposition order (for sequential SCD) to particle size and to the alloying degree, the prepared samples were subjected to XRD. The XRD of the prepared Pt-Cu/CA19 samples are given in Figure 4.19.

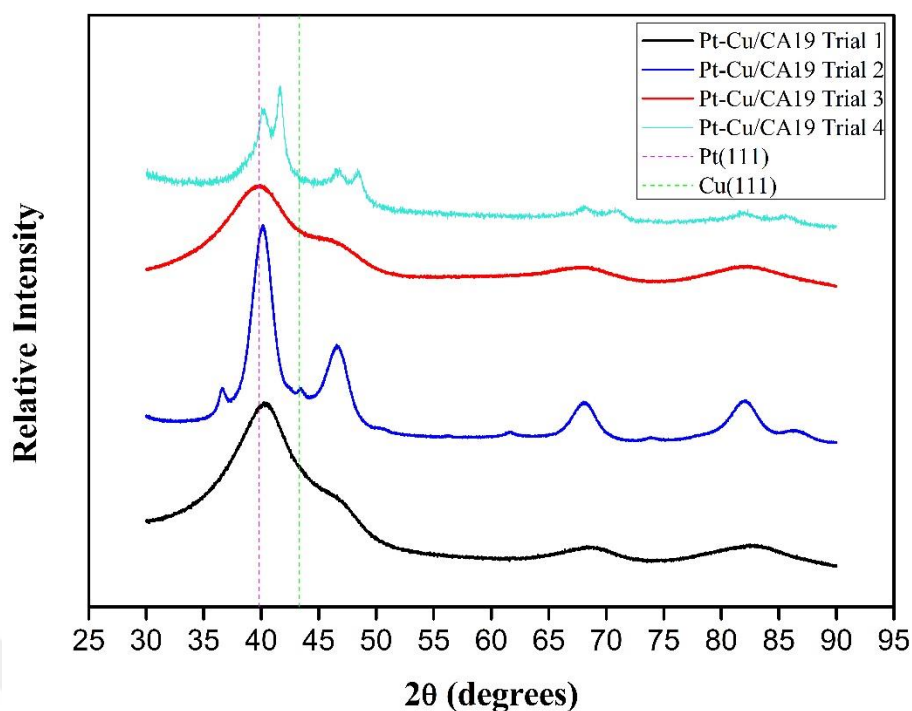


Figure 4.19: XRD of preliminary Pt-Cu/CA19 samples prepared via simultaneous and sequential SCD.

Figure 4.19 shows that all prepared samples have face-centered alloy crystalline structures and a slight shift at all of the reflection angles when compared to pure Pt {111} reflection towards higher Bragg angle values which can be associated with lattice contraction suggesting a degree of alloying in all samples. The XRD of the samples prepared via simultaneous SCD (Trial 1 and 4) showed that at high Pt loadings (Trial 1), Cu or Cu₂O peaks were not observed. When Pt content was decreased (Trial 4), XRD showed two peaks between 39.79° and 43.32° Bragg angles which are the {111} reflections of pure Pt and Cu. Here each reflection indicates the presence of two different types of alloy nanoparticles: a fraction of alloyed Pt-Cu nanoparticles were rich in Pt and the others were rich in Cu. The XRD of Pt-Cu/CA19 samples prepared via sequential SCD approach (Trial 2 and 3) showed that different deposition order (first Pt or Cu) have a significant effect on the crystalline structure of the Pt-Cu nanoparticles. When first Cu was adsorbed on CA19 (Trial , XRD showed Cu and Cu₂O peaks indicating not all of the Cu formed alloy nanoparticle with Pt. Whereas, when first Pt was

adsorbed on CA19, XRD did not showed any individual Cu or Cu₂O peaks suggesting that most of the Cu formed alloy nanoparticles with Pt.

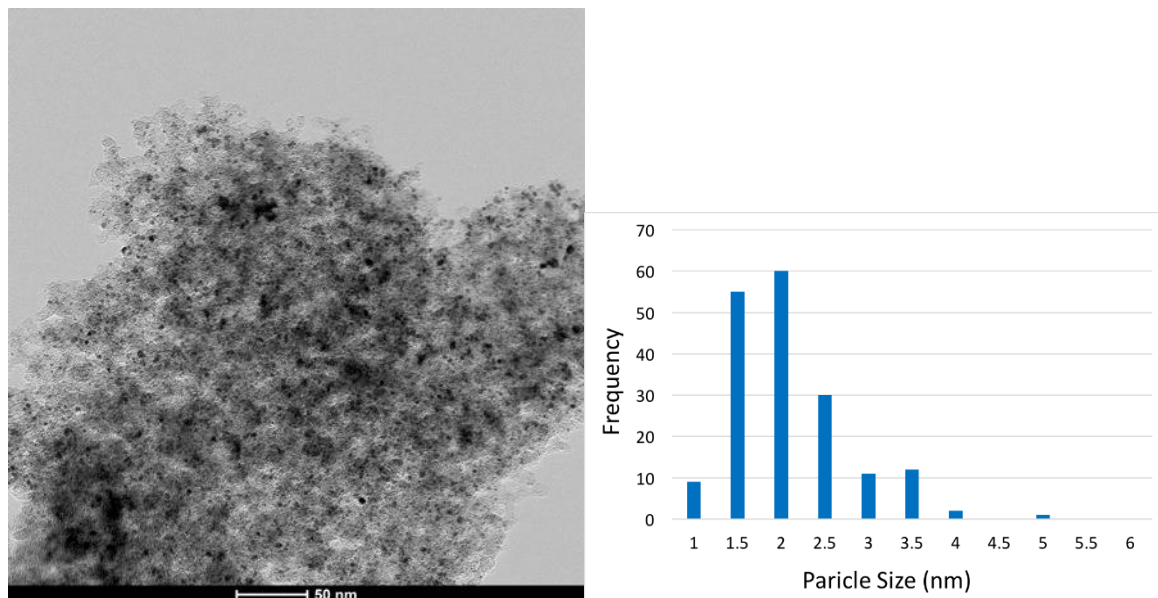
Table 4.11 summarizes the mole ratios obtained from XRD and XRF. Due to presence of multiple crystalline phases in this set evidenced by the XRD, It is not possible to determine the Pt:Cu mole ratios of the Pt-Cu alloy nanoparticles from XRF, on the other hand, XRD and the Vegard's law can be used to determine the mole ratios of the Pt-Cu alloy nanoparticles.

Table 4.11: Pt:Cu mole ratios of the preliminary Pt-Cu/CA19 samples obtained from XRD and XRF.

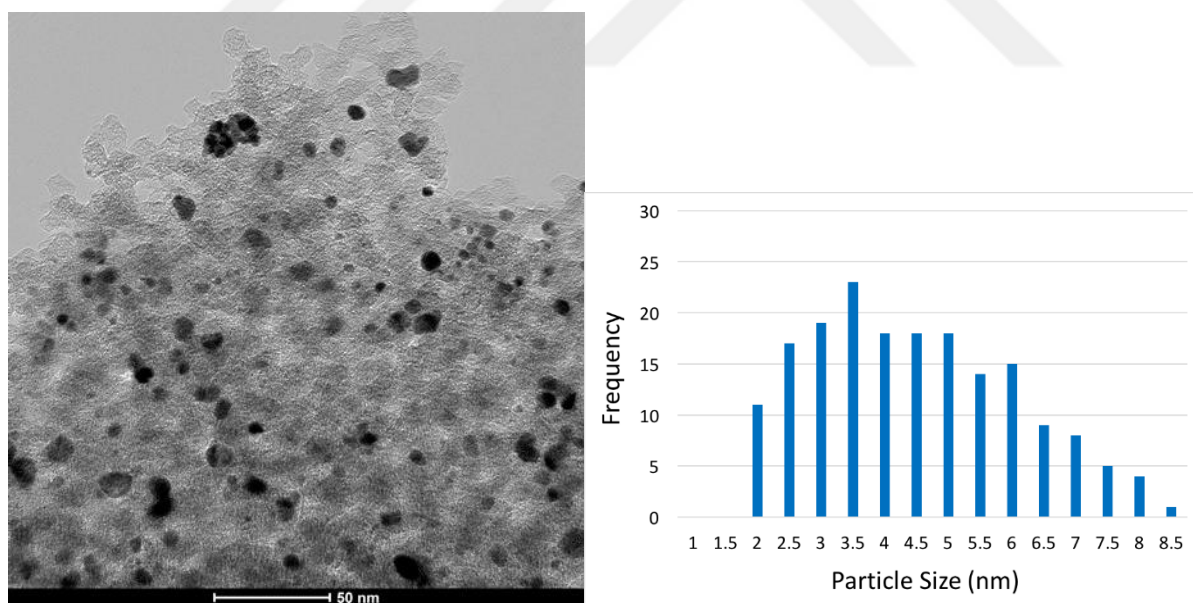
Sample	Mole Ratios (Pt:Cu)		
	XRD		XRF
Pt-Cu/CA19 Trial 1	83:17		71:29
Pt-Cu/CA19 Trial 2	90:10		49:51
Pt-Cu/CA19 Trial 3	98:2		74:26
Pt-Cu/CA19 Trial 4	89:11	46:54	70:30
	(Pt rich)	(Cu rich)	

Table 4.11 shows significant differences between the Pt:Cu mole ratios obtained from XRD and XRF for the whole set. This was expected for Trial 2 and 4 since XRD of these samples showed either individual Cu and Cu₂O or two different Pt-Cu alloy peaks (Trial 4), however, XRD of Trial 1 and 3 did not show any Cu or Cu₂O peaks so intuitively we would expect the mole ratios obtained from XRD and XRF to be approximately the same. The unalloyed Cu atoms were either in the form of atomic clusters rather than nanoparticles or in a non-crystalline structure which explains the lack of Cu or Cu₂O peaks in XRD, in spite of the difference between Pt:Cu mole ratios obtained from XRD and XRF.

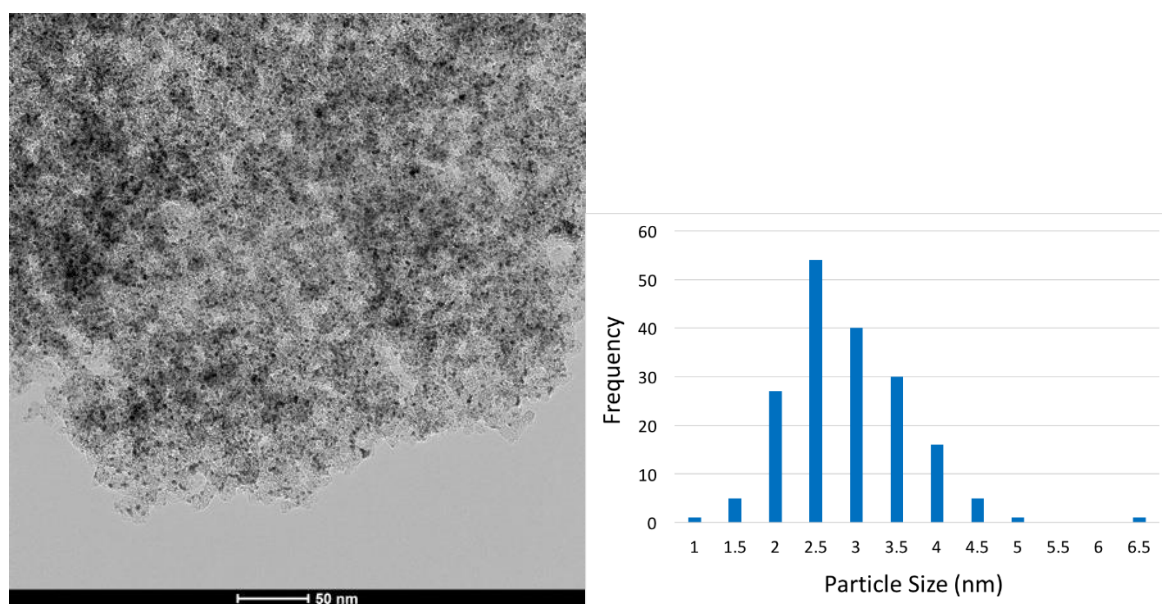
Nanoparticle morphologies of Pt-Cu/CA19 samples were characterized by high resolution TEM. Figure 4.20 shows the HRTEM images along with the particle size distribution of the Pt-Cu/CA19 samples.



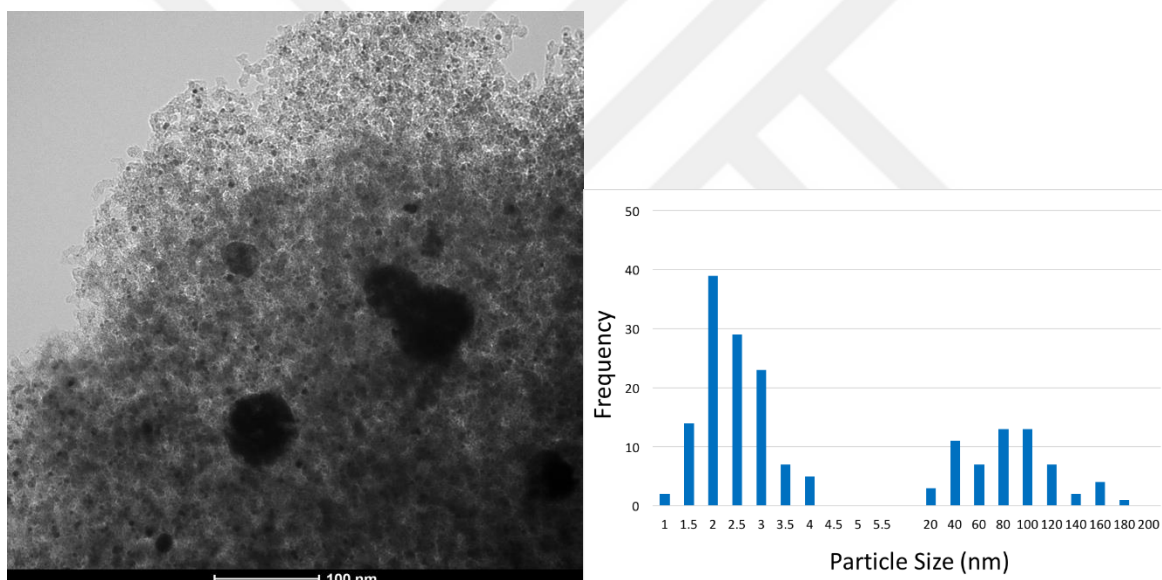
(a)



(b)



(c)

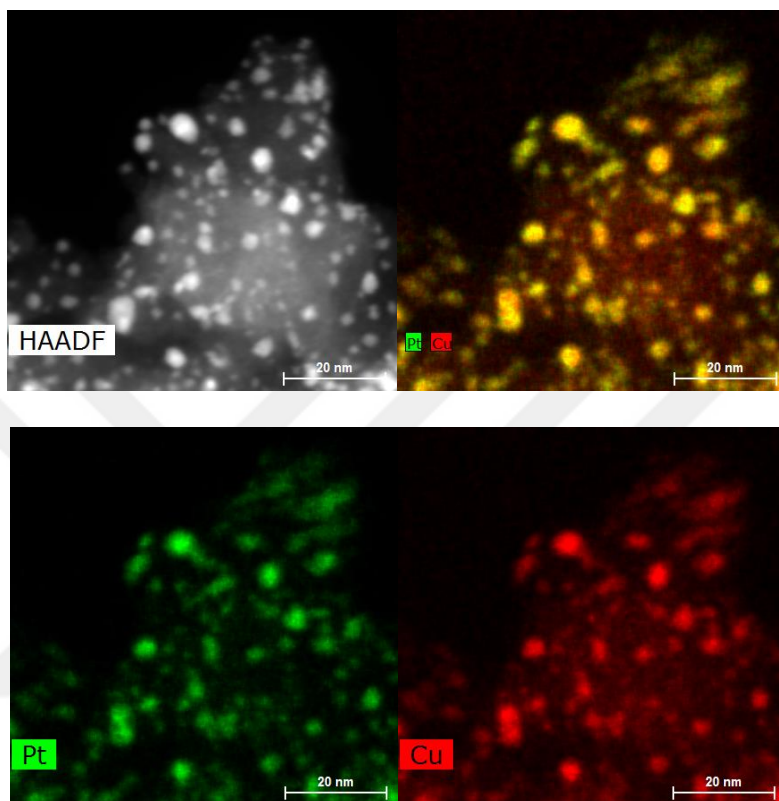


(d)

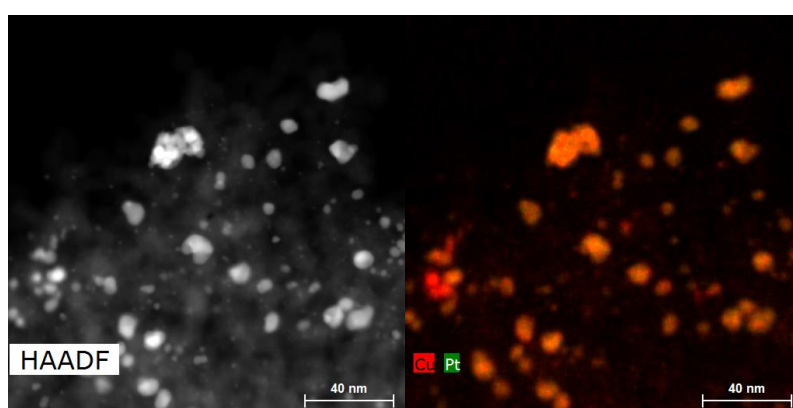
Figure 4.20: TEM images of (a) Pt-Cu/CA19 Trial 1 (simultaneous) (b) Pt-Cu/CA19 Trial 2 (sequential) (c) Pt-Cu/CA19 Trial 3 (sequential) (d) Pt-Cu/CA19 Trial 4.

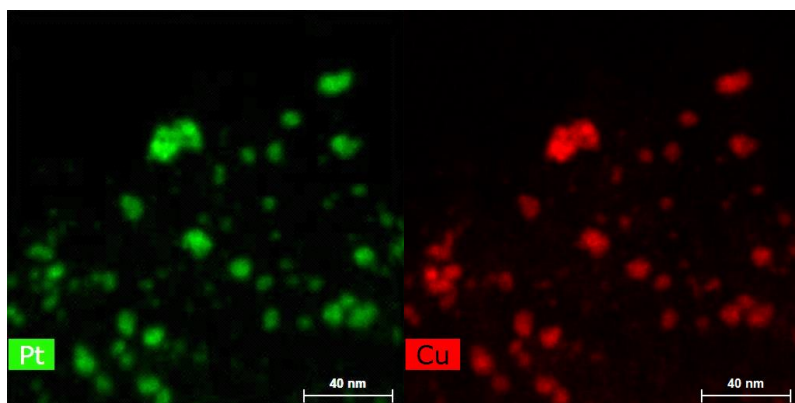
Figure 4.20 shows that except for Pt-Cu/CA19 Trial 4 all preliminary Pt-Cu/CA19 samples have homogenous distribution of Pt-Cu nanoparticles with no significant agglomeration. However, Trial 4 exhibited rather large particles which are probably the ones that are rich in Cu. Moreover, the particle size distributions of Trial 1 and Trial 3 are very

narrow, whereas, Trial 2 exhibited a broader particle size distribution most likely due to greater particle size. EDX mapping was carried out in order to determine the alloying degree in the preliminary Pt-Cu/CA19 samples. EDX and HAADF images of Pt-Cu/CA19 samples were given in Figure 4.21.

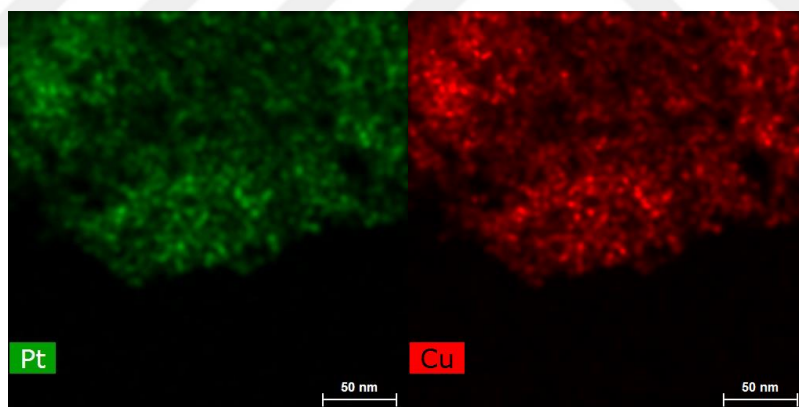
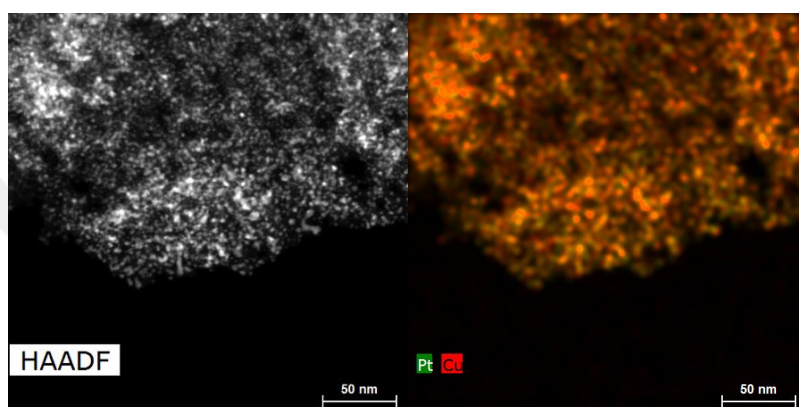


(a)

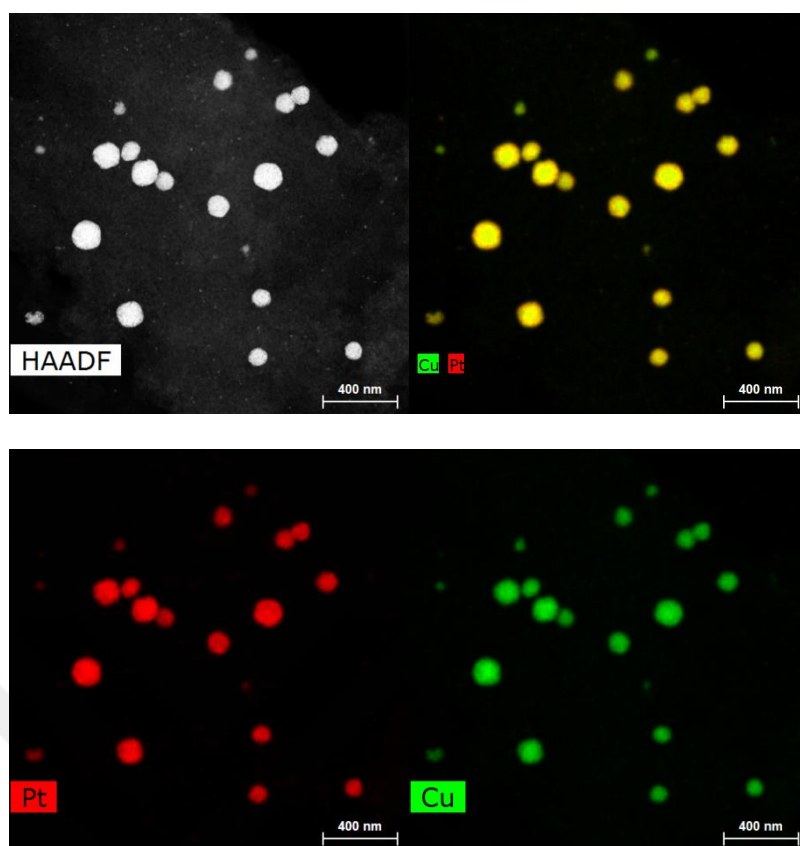




(b)



(c)



(d)

Figure 4.21: HAADF and EDX mapping images of preliminary Pt-Cu/CA19 samples (a) Trial 1 (simultaneous) (b) Trial 2 (sequential) (c) Trial 3 (sequential) (d) Trial 4 (simultaneous).

Figure 4.21 shows most of the nanoparticles are alloys of Pt-Cu. However, Pt-rich and Cu-rich regions can also be observed, particularly in Trial 4 in which XRD showed two distinctive alloy peaks. Figure 4.22 shows HAADF images and EDX mapping of two nanoparticles which are in close proximity that are shown to be Pt-rich and Cu-rich.

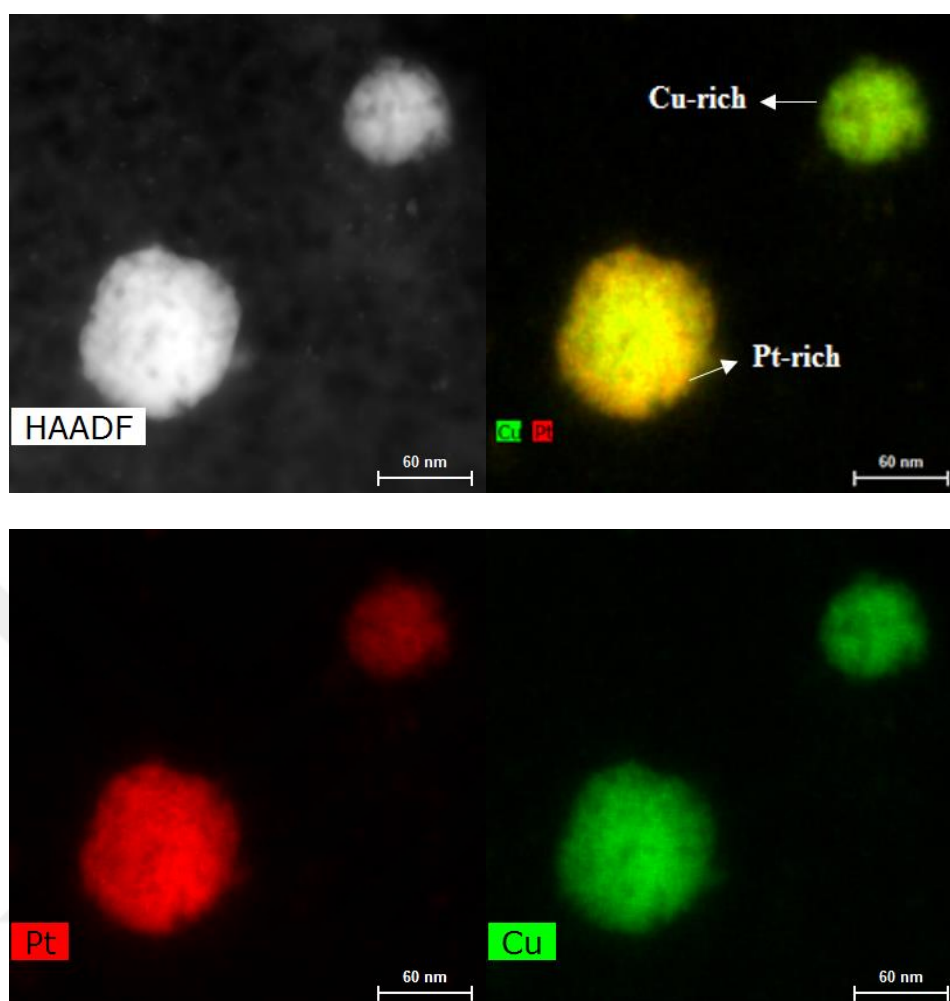


Figure 4.22: Cu-rich and Pt-rich nanoparticles in Pt-Cu/CA19 Trial 4 (simultaneous).

Figure 4.22 clearly shows the presence of two different alloy morphologies exist in Trial 4 which are in good agreement between TEM images and XRD data. Average particle sizes of the alloyed Pt-Cu nanoparticles on CA19 were determined from XRD using Scherrer Equation and $\{220\}$ plane angle and also from TEM images. The average particle sizes of preliminary Pt-Cu/CA19 samples were given in Table 4.12.

Table 4.12: The average Pt-Cu particle sizes of preliminary Pt-Cu/CA19 samples.

Sample	Particle Size (nm)			
	XRD		TEM	
Pt-Cu/CA19 Trial 1	1.9		2.1±0.7	
Pt-Cu/CA19 Trial 2	3.9		4.5±1.6	
Pt-Cu/CA19 Trial 3	1.7		2.9±0.8	
Pt-Cu/CA19 Trial 4	Pt rich	Cu rich	Average	Large
	3.4	8.9	2.4±0.6	83.5±40.7

Table 4.12 shows that the average particle sizes obtained from XRD and TEM are in good agreement and the standard deviations indicates a homogenous distribution of Pt-Cu nanoparticles on CA19, Trial 4 being the exception. TEM images revealed the presence of abnormally large particles in Pt-Cu/CA19 Trial 4. However, no such large particles were observed in XRD which suggests that these particles were not very frequent in the whole sample. Furthermore, Cu-rich Pt-Cu alloy nanoparticles observed in XRD of Trial 4 are greater in size than the ones that are Pt-rich.

Since maximum Cu content achieved with simultaneous SCD approach was 2 wt.%, we decided to continue to deposition experiment with the sequential SCD approach in which desired Cu content can be achieved by several deposition steps. Furthermore, characterization of preliminary Pt-Cu/CA19 samples revealed that after conversion, alloy formation was not complete with presence of Cu₂O nanoparticles. Our previous studies with Pt/CAs showed that Pt nanoparticles became mobile at higher temperatures, forming nanoparticles greater in size without significant agglomeration and after careful investigation of the studies involving supported Pt-Cu nanoparticles, we have seen that high temperature treatment under an inert gas atmosphere, which will be referred as annealing hereafter, after conversion favors alloy

formation [28, 125, 126]. For this purpose, two separate Pt-Cu/CA19 samples were prepared using sequential SCD approach with a Pt:Cu ratio of 1:1. These samples were subjected to annealing process after conversion where they were heated to 600 °C under flowing N₂. The only difference between the two samples was the deposition order. The detailed explanations of the two samples are given in Table 4.13.

Table 4.13: Annealed Pt-Cu/CA19 samples prepared by sequential SCD and explanation of deposition order.

Sample	Explanation
Pt-Cu/CA19 Trial 5	First Pt(cod)me ₂ (I)* on CA19 then Cu(tea) ₂ (II) on Pt/CA19
Pt-Cu/CA19 Trial 6	First Cu(tea) ₂ (II) on CA19 then Pt(cod)me ₂ (I) on Cu/CA19

*The number of deposition steps were given in parenthesis

The metal content of the annealed Pt-Cu/CA19 samples were determined gravimetrically and also using XRF analysis and given in Table 4.14.

Table 4.14: Pt and Cu weight percentages of the annealed Pt-Cu/CA19 samples.

Sample	Metal Loadings (wt. %)			
	Gravimetric		XRF	
	Pt	Cu	Pt	Cu
Pt-Cu/CA19 Trial 5	16.4	6.5	17.3	7.9
Pt-Cu/CA19 Trial 6	16.8	6.2	17.6	7.4

Table 4.14 shows that Pt and Cu metal loadings obtained gravimetrically and from XRF are quite close to each other which was expected since the results obtained from preliminary Pt-Cu/CA19 samples prepared by sequential SCD approach. Furthermore, higher Cu weight loadings on CA19 was achieved with multiple step sequential SCD (two steps for this case).

In order to determine the effect of annealing to particle size and to the alloying degree, the prepared samples were subjected to XRD. The XRD of the prepared Pt-Cu/CA19 samples are given in Figure 4.23.

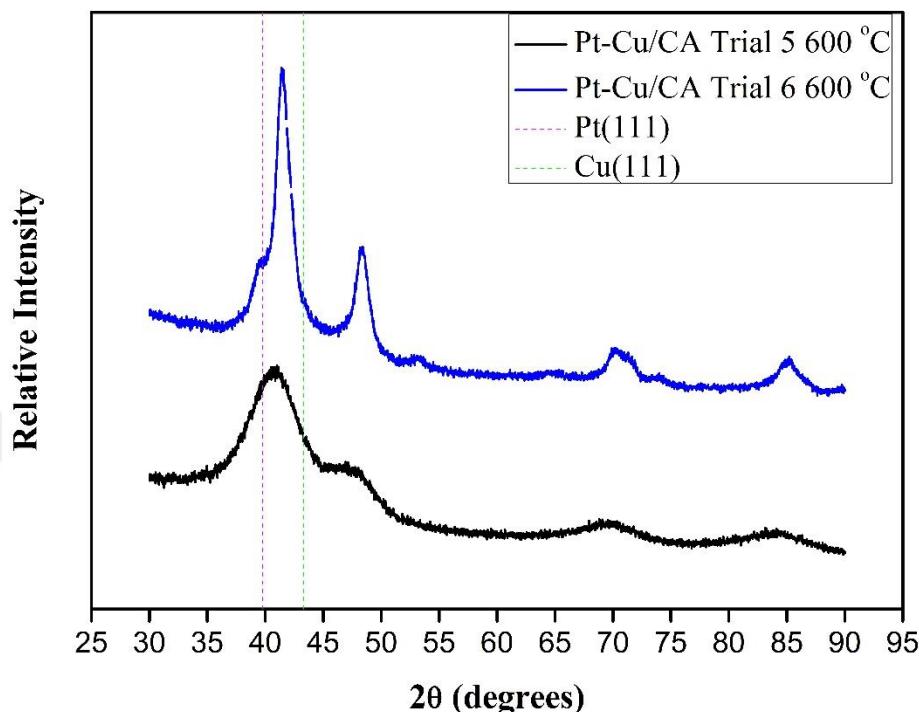


Figure 4.23: XRD of Pt-Cu/CA19 prepared via sequential SCD and annealed at 600 °C.

Figure 4.23 shows that when first Pt was adsorbed on CA19, the resulting Pt-Cu/CA19 samples exhibited only face-centered cubic Pt-Cu alloy peaks. On the other hand, when Cu was adsorbed firstly, XRD of the resulting Pt-Cu/CA19 showed the presence of two types of Pt-Cu nanoparticles on CA19 just as in Pt-Cu/CA19 Trial 4. However, since these peaks overlap rather than appear as separate peaks, the morphologies of these Pt-rich and Cu-rich Pt-Cu alloy nanoparticles probably similar to each other.

Vegard's law was used to determine the mole ratios of Pt and Cu of the Pt-Cu alloy nanoparticles from XRD. Table 4.15 summarizes the mole ratios obtained from XRD and XRF.

Table 4.15: Pt:Cu mole ratios of Pt-Cu/CA19 samples annealed at 600 °C.

Sample	Mole Ratios (Pt:Cu)	
	XRD	XRF
Pt-Cu/CA19 Trial 5	68:32	42:58
Pt-Cu/CA19 Trial 6	50:50	44:56

Table 4.15 shows that annealing promotes Pt-Cu alloy formation since the Pt:Cu mole ratios obtained from XRD are closer to the Pt:Cu mole ratios obtained from XRF than the ones for preliminary Pt-Cu/CA19 samples.

Nanoparticle morphologies of Pt-Cu/CA19 Trial 5 annealed at 600 °C was characterized by high resolution TEM. Figure 4.24 shows the HRTEM image along with the particle size distribution of the Pt-Cu/CA19 Trial 5.

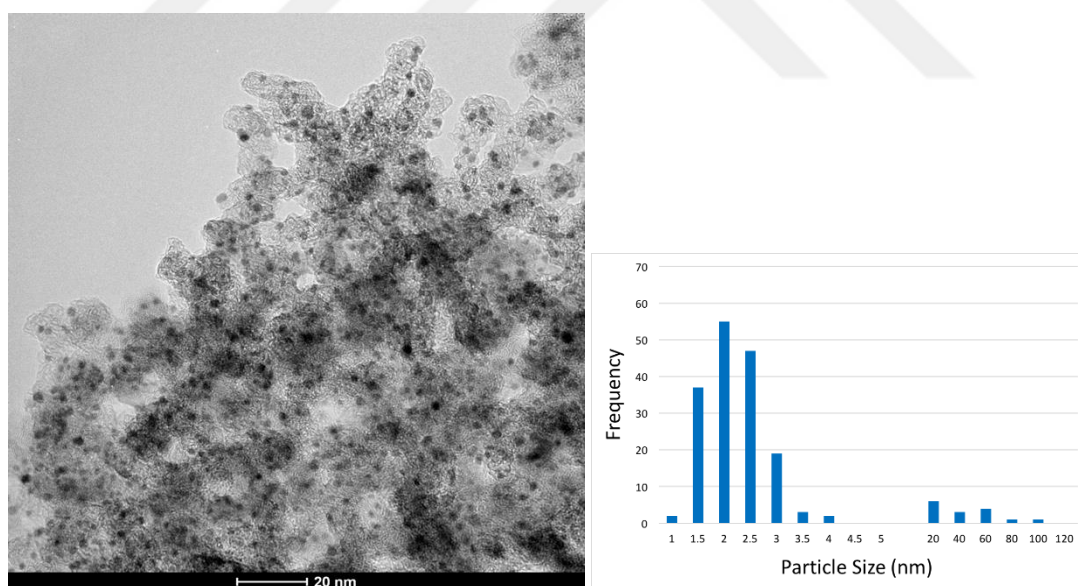
**Figure 4.24:** TEM and particle size distribution of Pt-Cu/CA19 Trial 5 annealed at 600 °C.

Figure 4.24 shows rather homogenous distribution of Pt-Cu nanoparticles on CA19 however, some abnormally large particles were observed in some of the images. Yet the frequency of these large particles are very low when compared to the ones observed at Pt-

Cu/CA19 Trial 4. In order to, determine the effect of annealing to the alloying process EDX mapping was done on Pt-Cu/CA19 Trial 5 annealed at 600 °C. EDX mapping and HAADF images of Pt-Cu/CA19 Trial 5 were given in Figure 4.25.

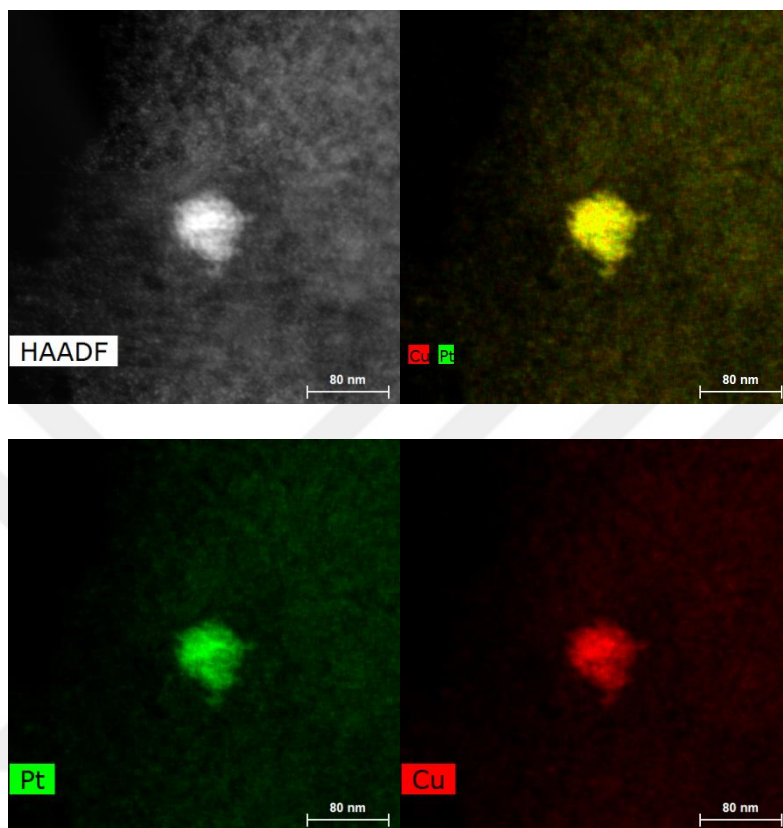


Figure 4.25: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 5 annealed at 600 °C.

Unfortunately we lack the HRTEM and EDX mapping images of Pt-Cu/CA19 Trial 6 annealed at 600 °C due to some problems during the analysis. However, the morphology of Trial 6 probably resembles the morphology of Trial 4 since we have a good agreement with XRD and TEM in all of the preliminary samples. Average particle sizes of the alloyed Pt-Cu nanoparticles on CA19 were determined from XRD using Scherrer Equation and {220} plane angle and also from TEM images. The average particle sizes of preliminary Pt-Cu/CA19 samples were given in Table 4.16.

Table 4.16: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 samples annealed at 600 °C.

Sample	Particle Size (nm)		
	XRD		TEM
Pt-Cu/CA19 Trial 5	1.8		2.2±0.6
Pt-Cu/CA19 Trial 6	Pt-rich	Cu-rich	-
	8.2	16.5	

Table 4.16 shows that when Pt was deposited on CA19 the average particle size of Pt-Cu nanoparticles was smaller than when Cu was first adsorbed on CA19 just as in the preliminary Pt-Cu/CA19 samples. Furthermore, annealing process did not result in excessive growth of Pt-Cu nanoparticles. However, we did not observe significant improvement in the alloying degree and considering the reports in the literature observations pointing out to higher degree of alloying between Pt and Cu with increased temperature during annealing [125, 126, 130], we have decided to investigate the effect of alloying degree and particle size Pt-Cu nanoparticles in the next set of Pt-Cu/CA19 at three different annealing temperatures, 600 °C, 800 °C and 950 °C.

4.2.4. Pt-Cu/CA19 Composites Prepared via Sequential Deposition Having Pt:Cu Mole Ratios of 1:1

Two sets of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:1 were prepared using sequential SCD approach. As in the preliminary samples, one set was prepared by first adsorbing Cu(tfa)_2 on CA19 and after conversion of Cu(tfa)_2 to Cu, Pt(cod)me_2 was adsorbed on Cu/CA19 composite and the other set was prepared by reversing the deposition order (i.e. First Pt(cod)me_2 on CA19, then Cu(tfa)_2 on Pt/CA19). The detailed explanations of the samples are given in Table 4.17.

Table 4.17: Pt-Cu/CA19 samples prepared by sequential SCD with Pt:Cu mole ratio of 1:1 and the explanation of deposition order.

Sample	Explanation
Pt-Cu/CA19 Trial 7	First Cu(tfa)_2 (II) * on CA19 then Pt(cod)me_2 (I) on Cu/CA19
Pt-Cu/CA19 Trial 8	First Pt(cod)me_2 (I) on CA19 then Cu(tfa)_2 (II) on Pt/CA19

*The number of deposition steps is given in parenthesis.

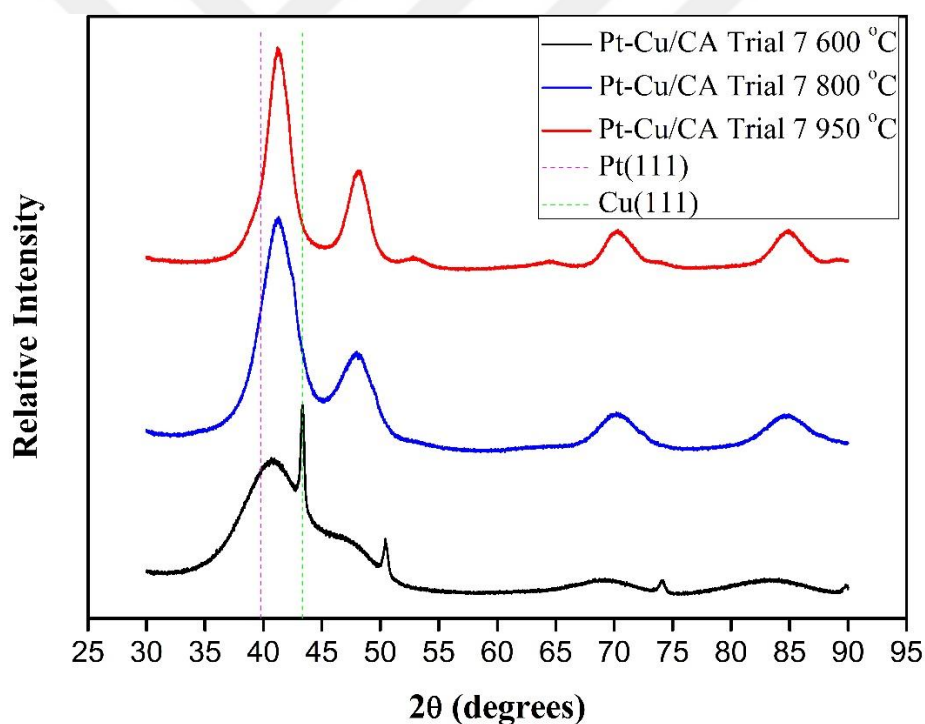
The metal content of the prepared Pt-Cu/CA19 samples were determined gravimetrically and also using XRF analysis before annealing and given in Table 4.18.

Table 4.18: Pt and Cu weight percentages of the Pt-Cu/CA19 samples before annealing.

Sample	Metal Loadings (wt.%)			
	Gravimetric		XRF	
	Pt	Cu	Pt	Cu
Pt-Cu/CA19 Trial 7	18.2	6.2	21.5	7.4
Pt-Cu/CA19 Trial 8	19.6	7.6	22.6	8.7

Table 4.18 shows that there is only a small difference between the metal contents obtained gravimetrically and the metal contents determined from XRF which was not very surprising considering comparison XRF and gravimetric results of preliminary Pt-Cu/CA19 samples were also very close to each other. This shows that the utilization of the single adsorption isotherms Pt(cod)me₂-CA19 and Cu(tfa)₂-CA19 in scCO₂ is a very good way to control the binary metal loading the sequential SCD approach.

Both Pt-Cu/CA19 samples were divided into three lots to eliminate any compositional differences and then annealed at three different temperatures, 600, 800, and 950 °C. XRD was used to determine the effect of different annealing temperatures and deposition order to particle size and to the alloying degree. The XRD of the Pt-Cu/CA19 samples are given in Figure 4.26.



(a)

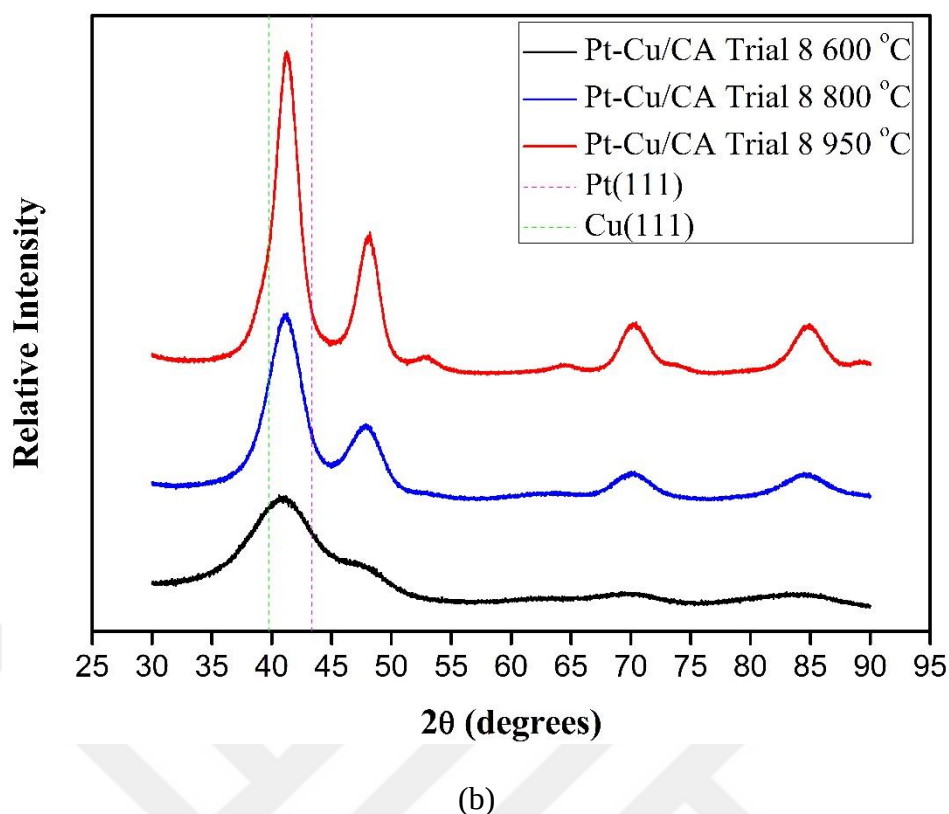


Figure 4.26: XRD of (a) Pt-Cu/CA19 Trial 7 and (b) Pt-Cu/CA19 Trial 8 with Pt:Cu mole ratios of 1:1 prepared via sequential SCD.

Figure 4.26 shows that when first $\text{Cu}(\text{tfa})_2$ was adsorbed on CA19 the resulting Pt-Cu/CA19 samples (Trial 7) exhibited separate face-centered cubic Cu peaks along with Pt-Cu alloy peaks at all three annealing temperatures. At an annealing temperature of 600 °C, pure fcc Cu peaks could clearly be observed. At higher annealing temperatures face-centered cubic Pt-Cu alloy peaks shifted to higher Bragg angle values. This indicates that when the annealing temperature is increased Pt-Cu alloying degree is increased. Furthermore, Cu peaks observed after annealing at 600 °C were very sharp whereas Pt-Cu peaks were broader indicating the particle size Pt-Cu alloy nanoparticles were significantly smaller than the particle size of separate Cu nanoparticles. At higher annealing temperatures Pt-Cu alloy peaks became sharper indicating increasing Pt-Cu particle sizes with increasing annealing temperature. Whereas, when $\text{Pt}(\text{cod})\text{me}_2$ was first adsorbed on CA19 the resulting Pt-Cu/CA19 samples (Trial 8) did

not exhibit any separate Cu peaks, only Pt-Cu fcc alloy peaks were observed on XRD. The lack of separate Cu peaks on the XRD of Trial 8 may be explained through lattice constant values of pure Pt and pure Cu. The lattice constant of Pt (3.91 Å) is greater than the lattice constant of Cu (3.62 Å), therefore, at lower annealing temperatures the diffusion of the Pt atoms into Cu lattices is difficult. This is most probably due to the formation of Cu₂O shells on Cu particles [75] once the Cu is adsorbed and contacted with air between the deposition steps. On the other hand, when Pt(cod)me₂ was adsorbed first on CA19, Pt nanoparticles do not form oxides in the ambient atmosphere, thus Cu atoms can easily diffuse through Pt nanoparticles. Similar to Trial 7, all Pt-Cu alloy peaks shifted to higher Bragg angle values with increasing annealing temperatures. The same observations about Pt-Cu alloy particle size trends for Trial 7 are valid for Trial 8, as the annealing temperature increased, Pt-Cu alloy peaks became sharper indicating higher Pt-Cu particle size.

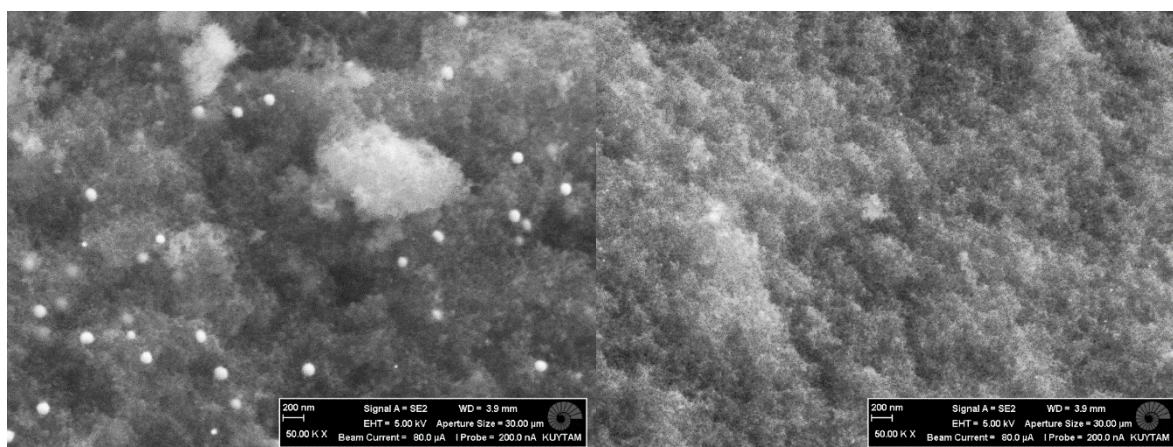
Vegard's law was used to determine the mole ratios of Pt and Cu. Table 4.19 summarizes the mole ratios obtained from XRD and XRF.

Table 4.19: Pt:Cu mole ratios of Pt-Cu/CA19 samples obtained from XRF and XRD.

Sample	Annealing Temperature	Mole Ratios (Pt:Cu)	
		XRD	XRF
Pt-Cu/CA19 Trial 7	600 °C	68:32	49:51
	800 °C	56:44	
	950 °C	55:45	
Pt-Cu/CA19 Trial 8	600 °C	68:32	46:54
	800 °C	60:40	
	950 °C	57:43	

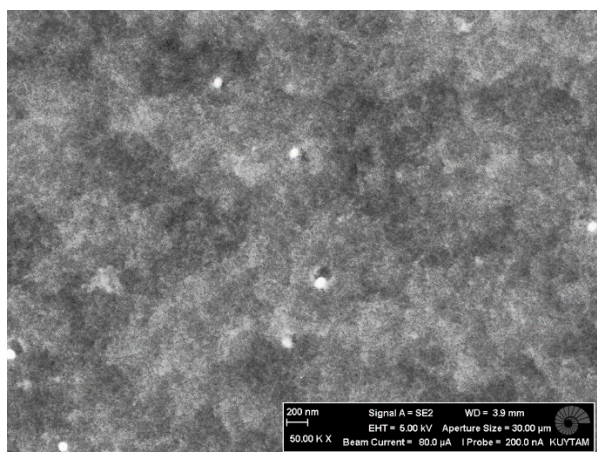
Table 4.19 shows that based on XRF, Trial 7 and Trial 8 had intended Pt:Cu molar ratios of 50:50 upon adsorption and conversion. However, as previously mentioned XRF only gives the bulk metal ratios whereas XRD can provide a good approximation of the composition of the Pt-Cu alloy nanoparticles. At lower annealing temperatures (600 °C) the difference between the Pt:Cu mole ratios obtained from XRF and XRD was more significant than the difference at 800 °C and 950 °C as expected since XRD showed the shift of reflection angles increases with increasing annealing temperatures. Furthermore, the significant difference between XRF and XRD was anticipated at Trial 7 600 °C as separate Cu reflections were present in XRD. Trial 8, on the other hand, did not exhibit any separate Cu reflections at 600 °C yet the difference between XRF and XRD was still significant. This difference indicates the unalloyed Cu is in the form of atomic clusters or have a non-crystalline structure so that they cannot be detected by the XRD.

Surface morphologies of Pt-Cu/CA19 samples were characterized by SEM EDX. Figure 4.27 and 4.28. shows the SEM images of Pt-Cu/CA19 Trial 7 and Trial 8.



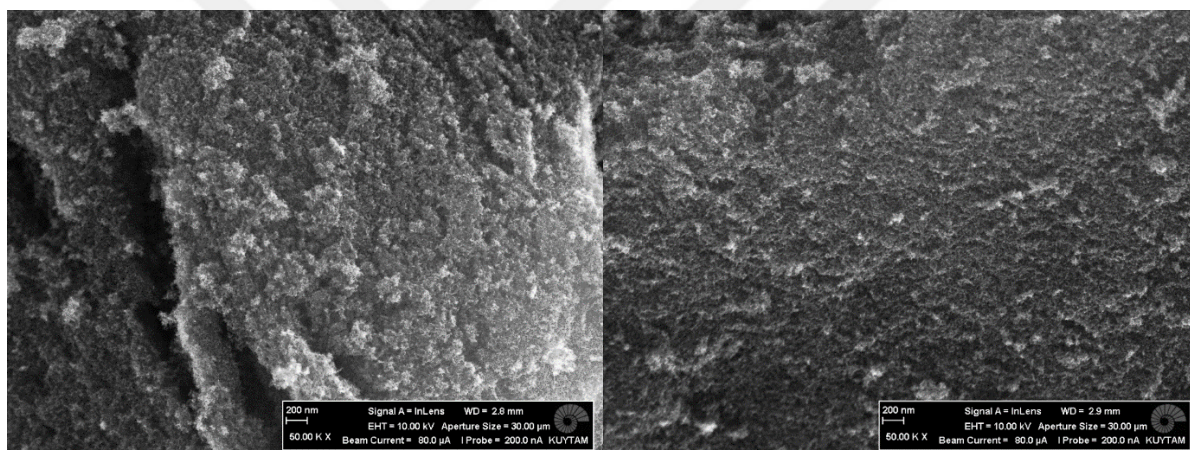
(a)

(b)



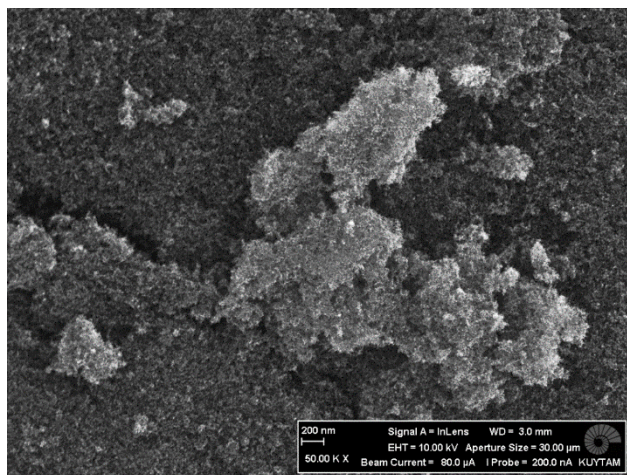
(c)

Figure 4.27: SEM images of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.



(a)

(b)

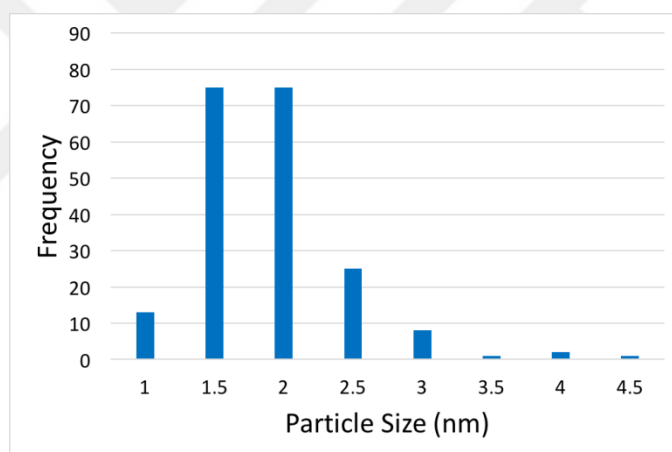
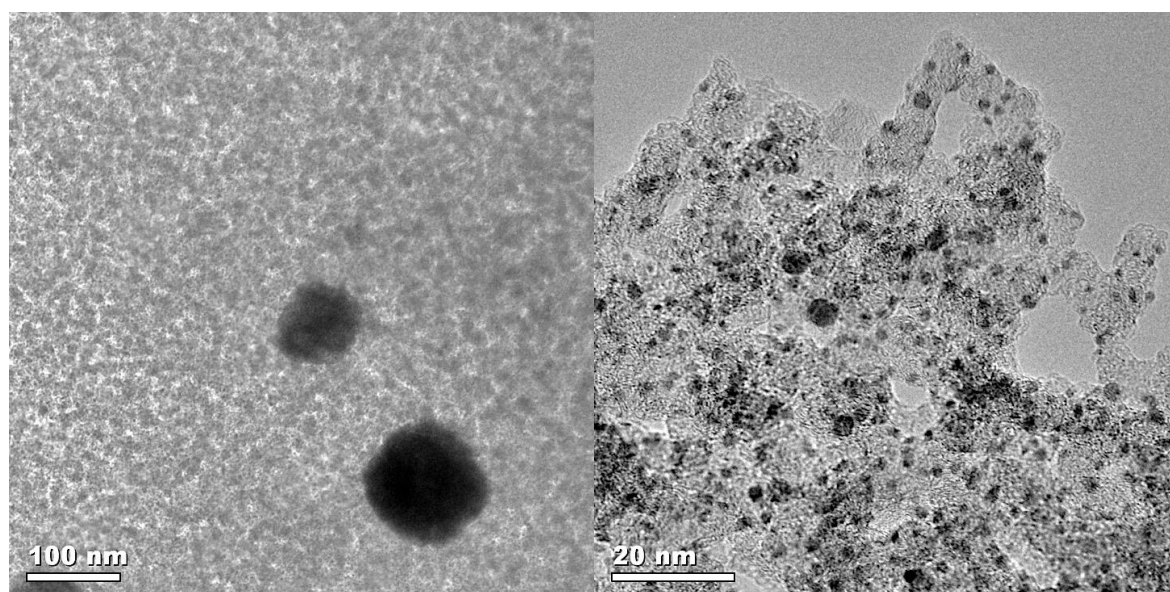


(c)

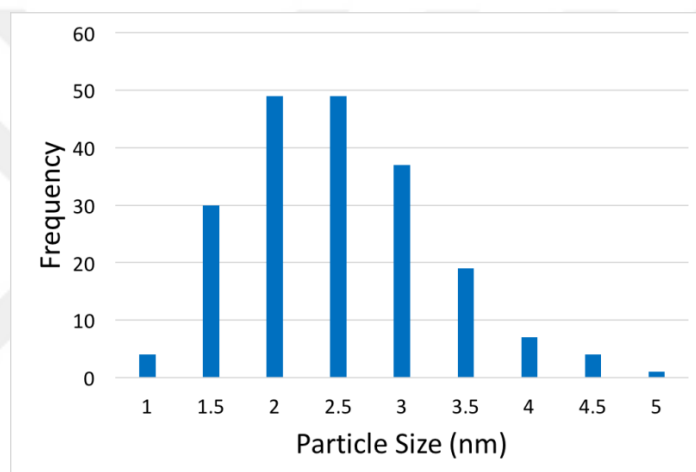
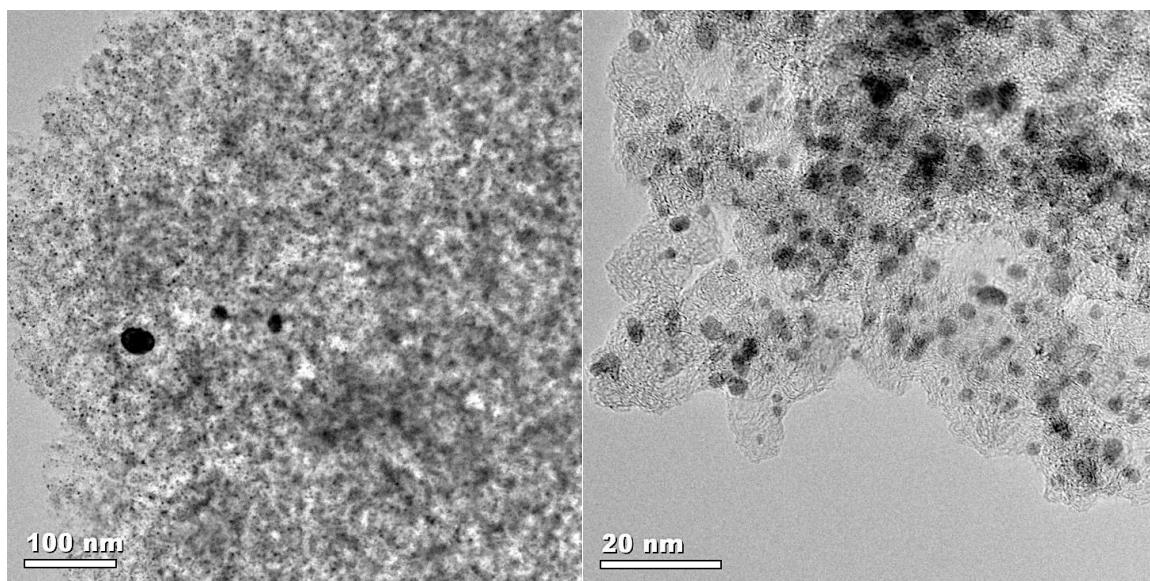
Figure 4.28: SEM images of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.

Figure 4.27 shows that SEM images of Pt-Cu/CA19 Trial 7 annealed at 600 °C (a) and 950 °C (c) exhibits some large spherical nanoparticles and EDX analysis confirmed that these large nanoparticles are primarily Cu nanoparticles. SEM images of 600 °C are in good agreement with XRD results since separate Cu reflections peaks were observed. However, SEM images of Pt-Cu/CA19 Trial 7 annealed at 800 °C (c) did not show any Cu nanoparticles despite the XRD results. Since SEM represents only a very small portion of the sample, the lack of Cu nanoparticles on Trial 7 800 °C can be explained by non-homogenous distribution of these large Cu nanoparticles on CA19 and the area that was imaged did not consist any of these Cu nanoparticles although they were present. SEM images of Trial 7 950 °C showed large Cu nanoparticles were less frequent in this sample than at Trial 7 600 °C. Moreover, the Cu nanoparticles were mainly on the surface of CA19 rather than located in the pores of CA19 probably due to high particle size of the Cu nanoparticles (≥ 22.7 nm by XRD) and since the average pore size CA19 was 19 nm, Cu nanoparticles were probably cannot penetrate through the majority of the pores. SEM images of all Trial 8 samples, conversely, did not show any large Cu nanoparticles as expected considering XRD results.

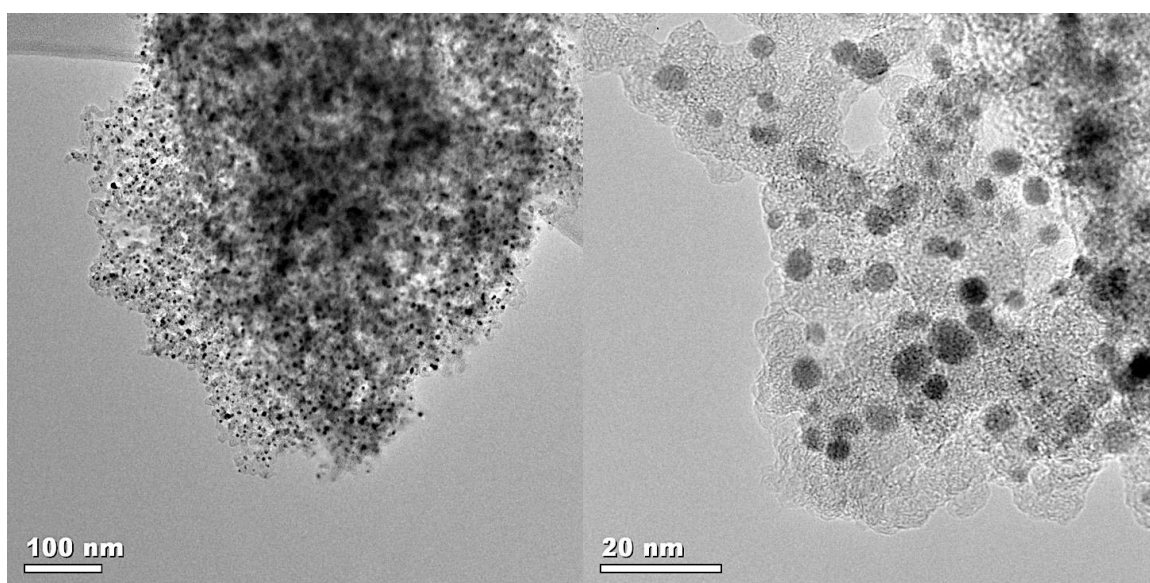
HRTEM images of Pt-Cu/CA19 Trial 7 and Trial 8 along with particle size distributions were presented in Figure 4.29 and 4.30, respectively.

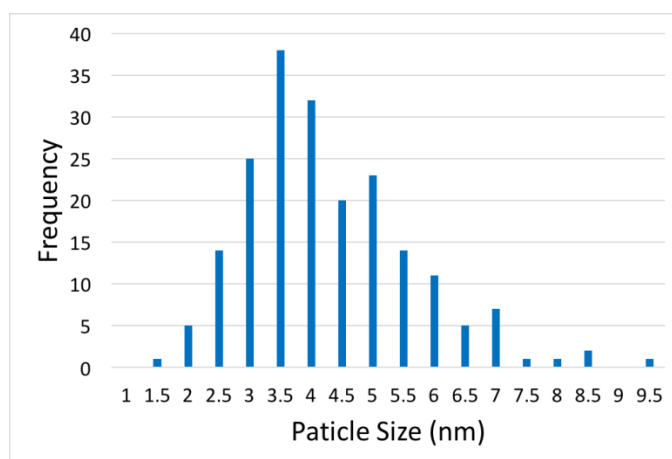


(a)



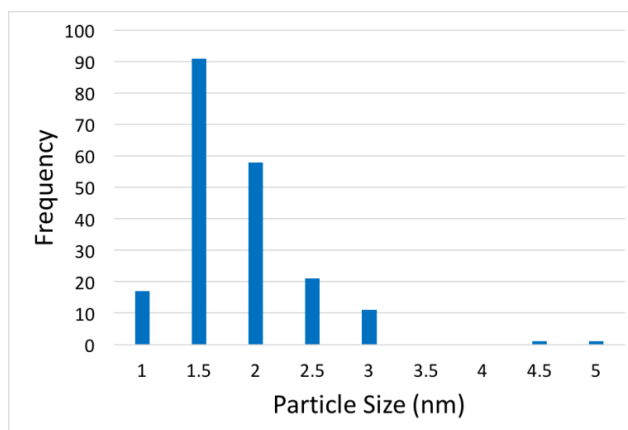
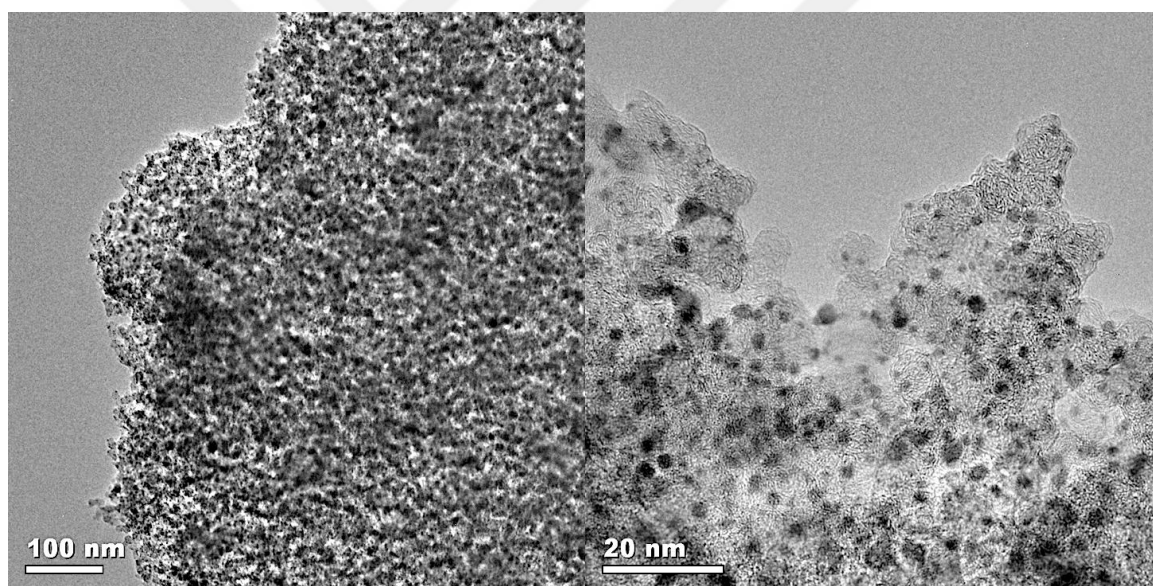
(b)



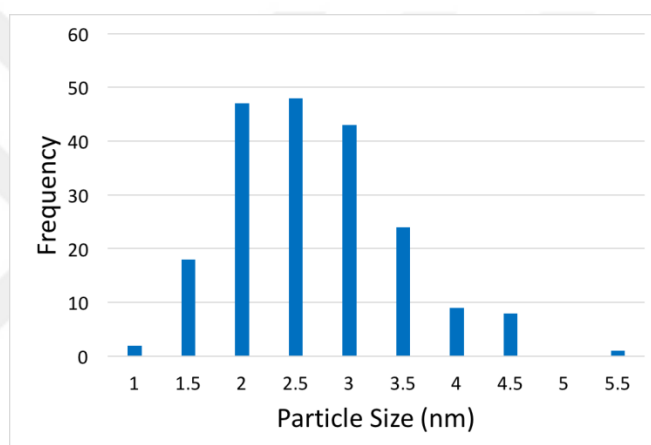
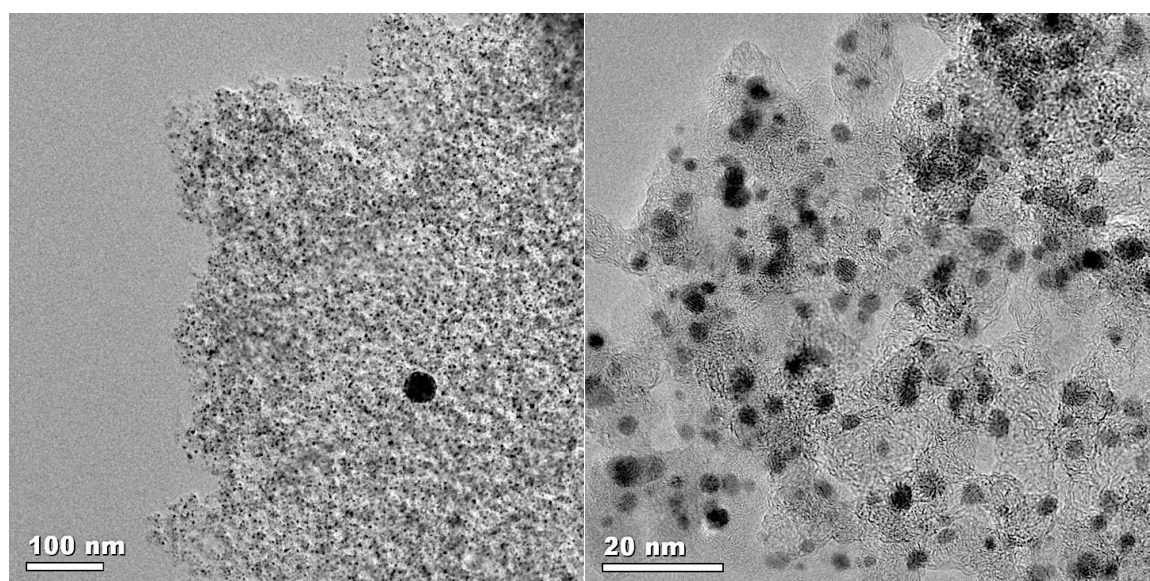


(c)

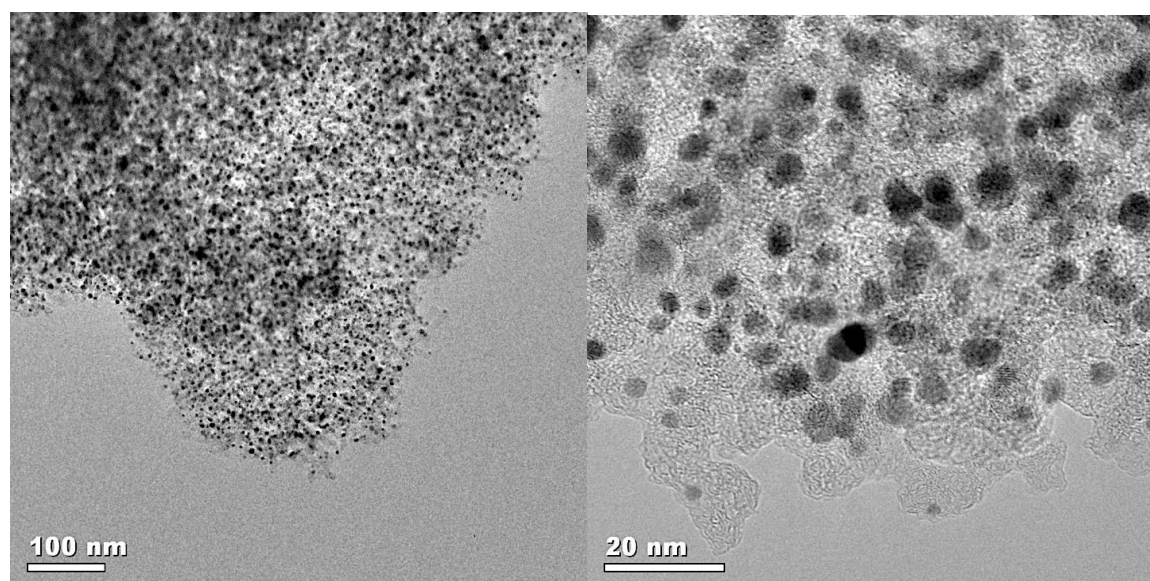
Figure 4.29: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.

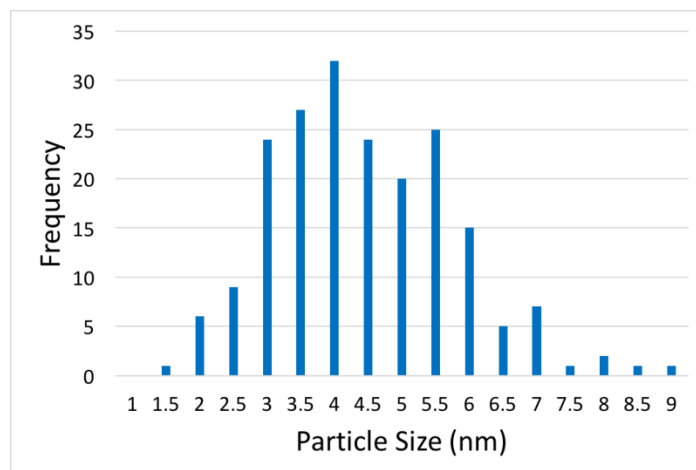


(a)



(b)





(c)

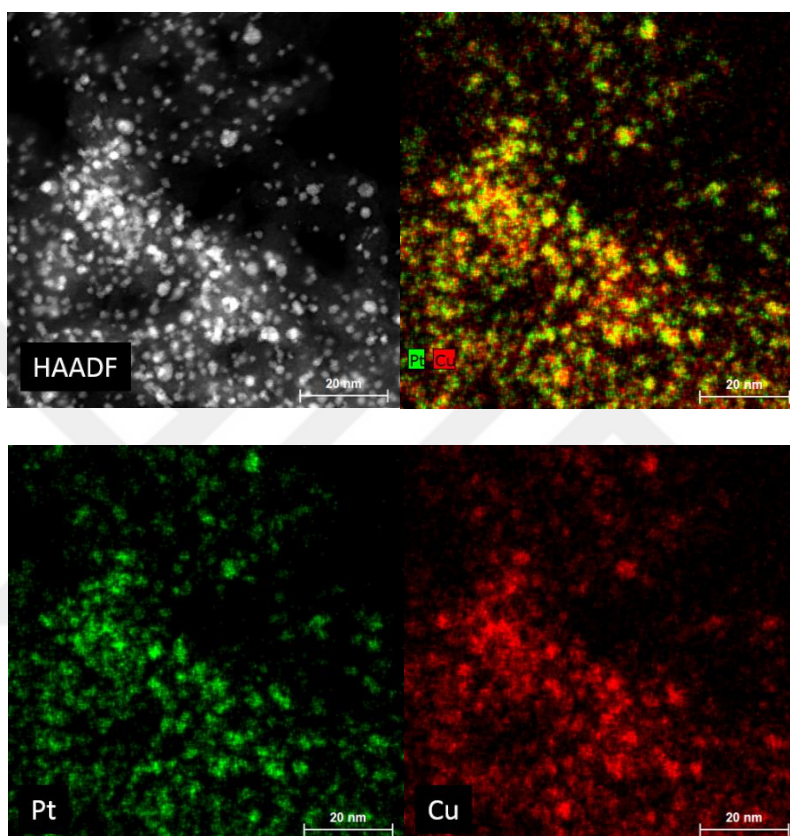
Figure 4.30: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.

Figure 4.29 (a) shows the presence of rather large particles for Trial 7 annealed at 600 °C, these are most probably the unalloyed Cu nanoparticles that were also observed at XRD. These large unalloyed Cu nanoparticles were also observed at Trial 7 annealed at 800 °C but the frequency of these are less than in 600 °C. Furthermore at 950 °C, large nanoparticles were not observed which is in good agreement with the XRD since at 950 °C, separate pure Cu reflection peaks were not observed. The distribution of Pt-Cu alloy nanoparticles (Trial 7) was quite homogenous with no sign of significant agglomeration for all three annealing temperatures.

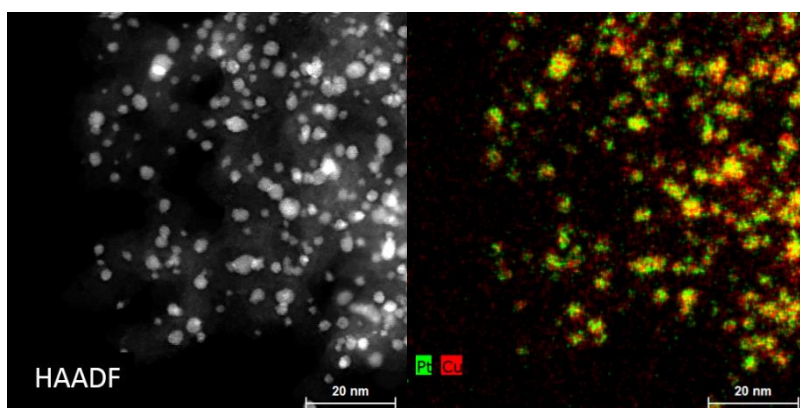
Figure 4.30 shows no evidence of large nanoparticles in Trial 8 except for 800 °C. However, the large nanoparticle observed at 800 °C was not unalloyed Cu but rather the agglomeration of smaller Pt-Cu alloy nanoparticles. The frequency of occurrence of these agglomerated Pt-Cu nanoparticles was extremely low, therefore the Pt-Cu nanoparticles had a homogenous distribution on CA19 for Trial 8. The HRTEM images of Trial 8 were also consistent with the XRD of this sample since any separate Cu reflection peaks were not observed. Moreover, for both Trial 7 and Trial 8, the particle size distributions of Pt-Cu alloy nanoparticles were very narrow for 600 °C and 800 °C. Although the particle size distributions

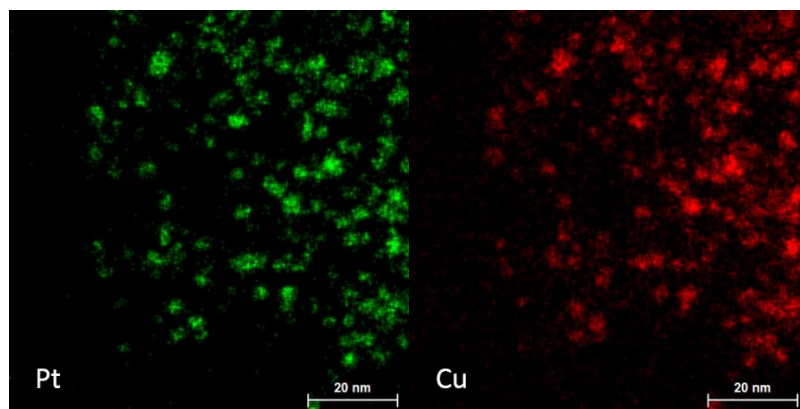
became broader at 950 °C due to larger Pt-Cu alloy nanoparticle size we did not detect any significant agglomeration in both Trial 7 and Trial 8.

In order to, determine the effect of annealing temperature to the alloying EDX mapping was done on both Trial 7 and Trial 8 annealed at different temperatures. EDX mapping and HAADF images were given in Figure 4.31 and 4.32, respectively.

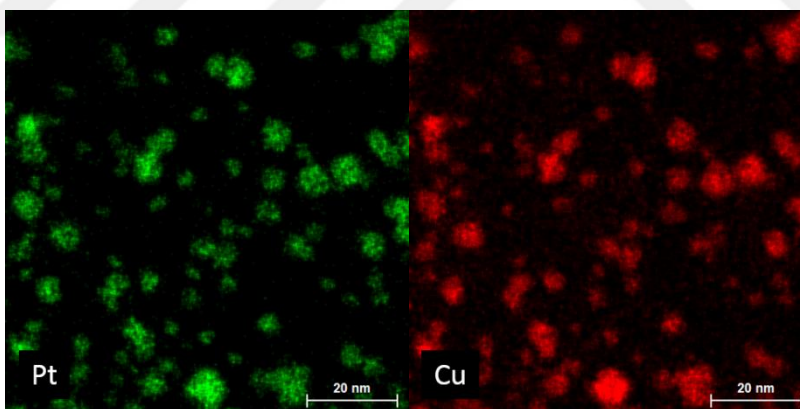
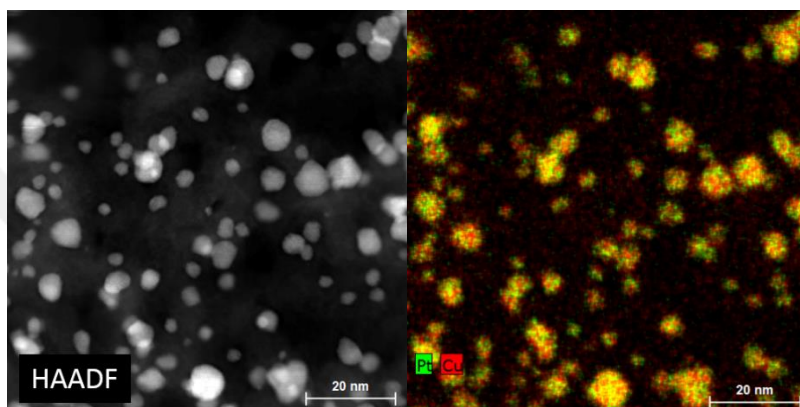


(a)



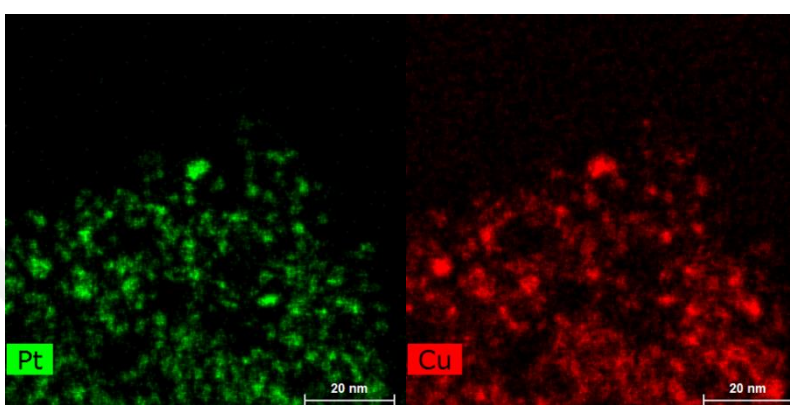
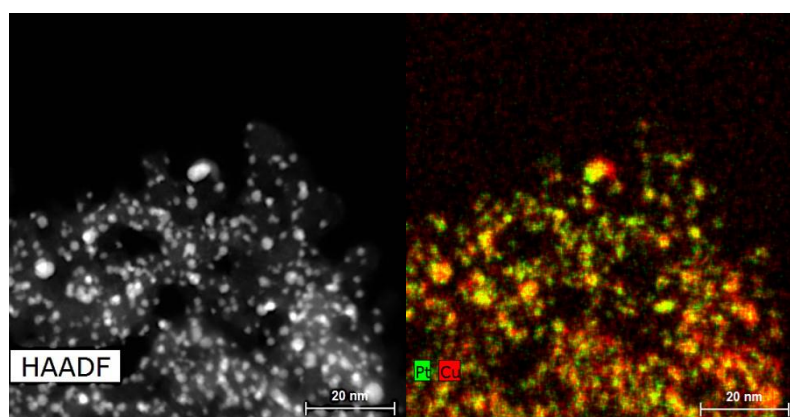


(b)

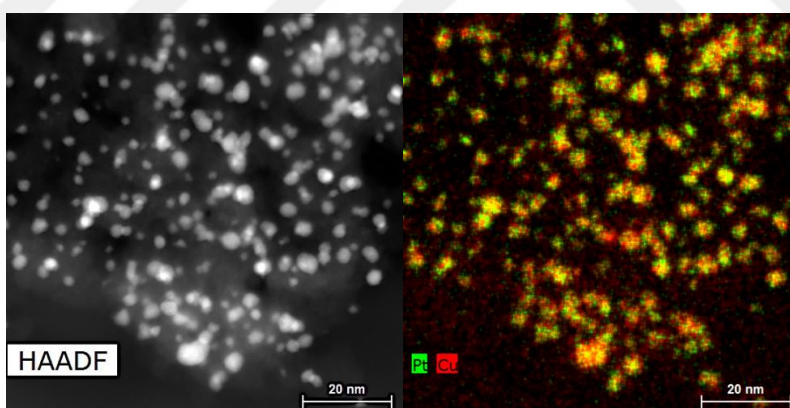


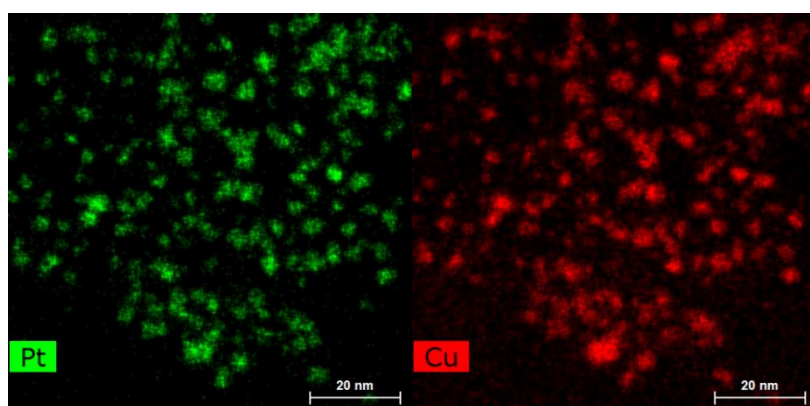
(c)

Figure 4.31: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C , (b) 800 °C , and (c) 950 °C.

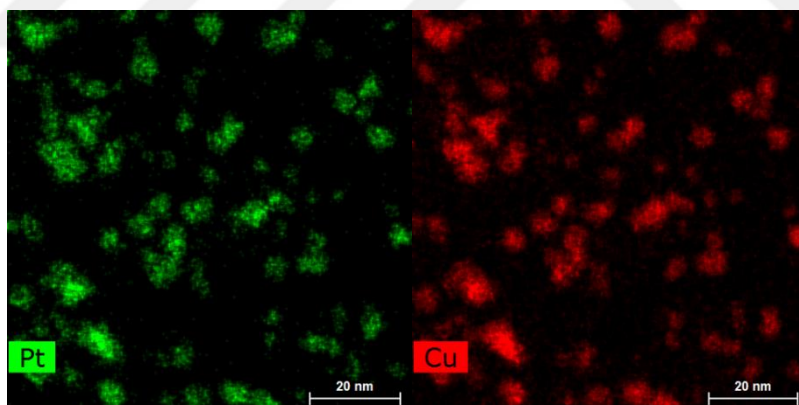
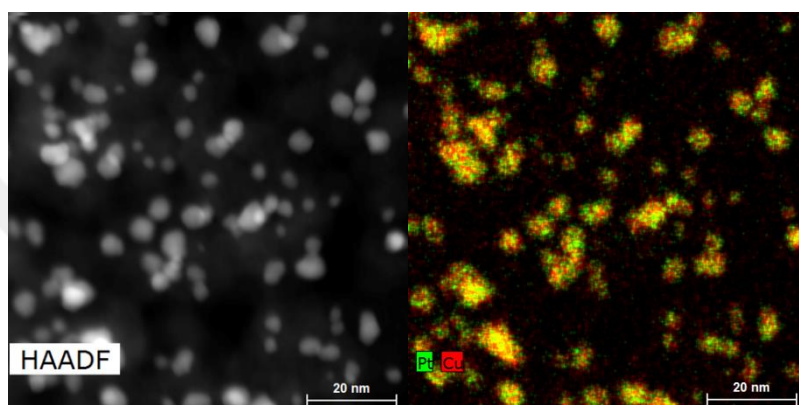


(a)





(b)



(c)

Figure 4.32: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, (c) and 950 °C.

Figure 4.31 and 4.32 indicate that all three Pt-Cu/CA19 Trial 7 and Trial 8 samples have formed disordered Pt-Cu alloy nanoparticles. However at 600 °C, EDX mapping images of both Trial 7 and Trial 8 showed the presence of some separate Cu nanoparticles or clusters which

may explain and validate the difference between the Pt:Cu mole ratios obtained from XRF and XRD. Furthermore, in all three Trial 7 and Trial 8 samples some nanoparticles were richer in Pt and some were richer in Cu, yet as the annealing temperature increases Pt-Cu nanoparticle compositions became more uniform indicating a better Pt-Cu alloy nanoparticle structure.

Average particle sizes of the alloyed Pt-Cu nanoparticles on CA19 were determined from XRD using Scherrer Equation and {220} plane angle and also from TEM images. The average particle sizes of Pt-Cu/CA19 Trial 7 and Trial 8 annealed at different temperatures were given in Table 4.20.

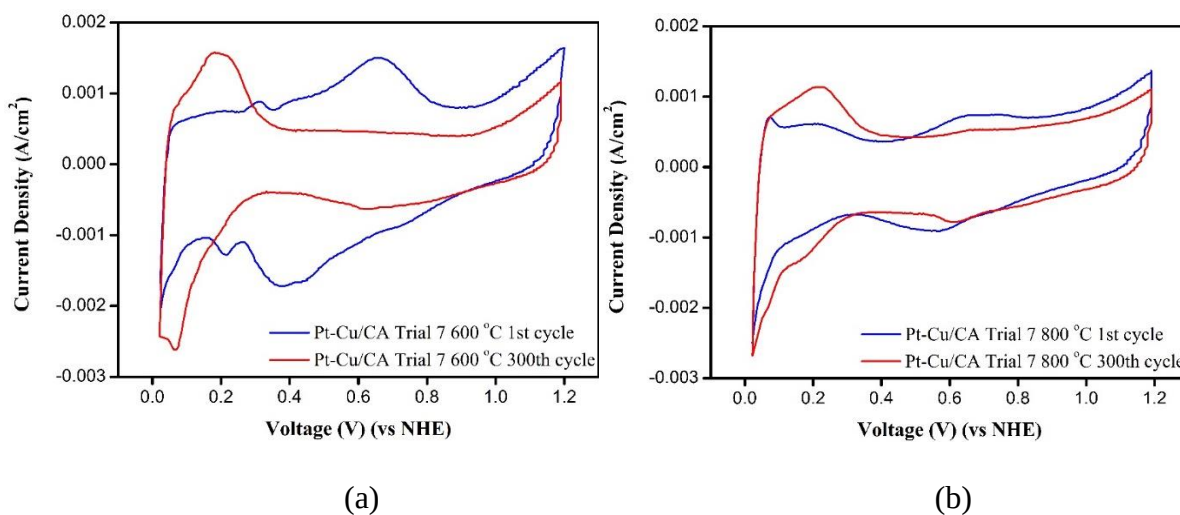
Table 4.20: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:1 and annealed at different temperatures.

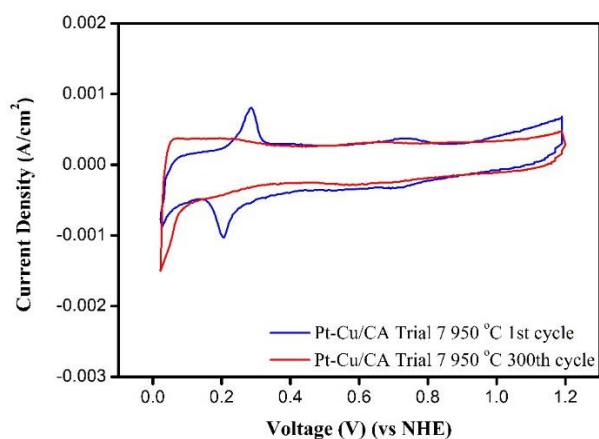
Sample	Annealing Temperature	Particle Size (nm)	
		XRD	TEM
Pt-Cu/CA19 Trial 7	600 °C	2.2	1.9±0.5
	800 °C	2.7	2.5±0.8
	950 °C	3.9	4.3±1.4
Pt-Cu/CA19 Trial 8	600 °C	2.3	1.8±0.6
	800 °C	3.2	2.7±0.8
	950 °C	3.9	4.5±1.4

Table 4.20 shows that both Trial 7 and Trial 8 had similar Pt-Cu nanoparticle sizes at corresponding annealing temperatures suggesting that deposition order did not have a significant effect on the Pt-Cu nanoparticle sizes. The average particle sizes obtained from TEM and XRD were very close to each other. However, the average particle sizes obtained from XRD were a little higher than those obtained from TEM for 600 °C and 800 °C for both Trial 7 and Trial 8, whereas at 950 °C TEM images gave higher average particle sizes than XRD for

both Trial 7 and Trial 8. The average Pt-Cu particle sizes increased with increasing annealing temperatures from 1.9 nm (600 °C) to 4.3 nm (950 °C) for Trial 9 and from 1.8 nm (600 °C) to 4.5 nm (950 °C) for Trial 10. Furthermore, the particle sizes from the TEM images are remarkably uniform with standard deviations from the averages in the range of ± 0.5 -0.8 nm except for the samples annealed at 950 °C. At 950 °C, the deviations from the average particle size increased to ± 1.4 nm for both Trial 7 and Trial 8 showing broader particle size distributions. While these particle size distributions were broader than those at 600 °C and 800 °C, they were still very narrow so that homogenous distribution of Pt-Cu nanoparticles on CA19 was attained. These particle size are actually very similar to those of Pt/CA19 samples proving that effective control of mono or bimetallic particle size on CA19 is achievable through heat treatment in an inert atmosphere.

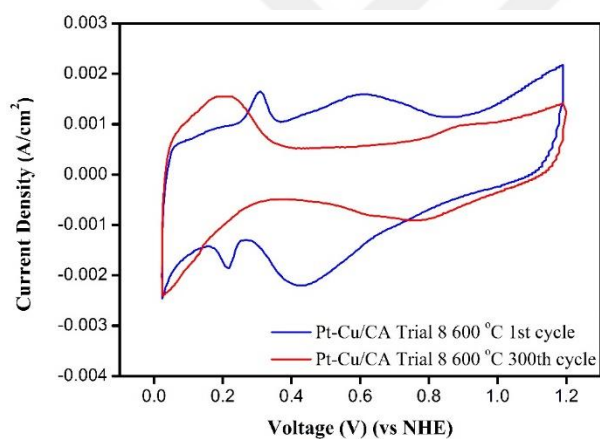
The electrochemical behaviors of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:1 and annealed at different temperatures were characterized using CV. Cyclic voltammograms taken in N₂ saturated acidic electrolyte were presented in Figure 4.33 and 4.34, respectively.



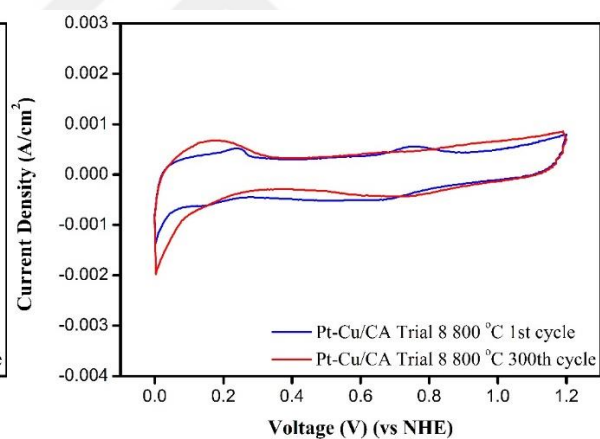


(c)

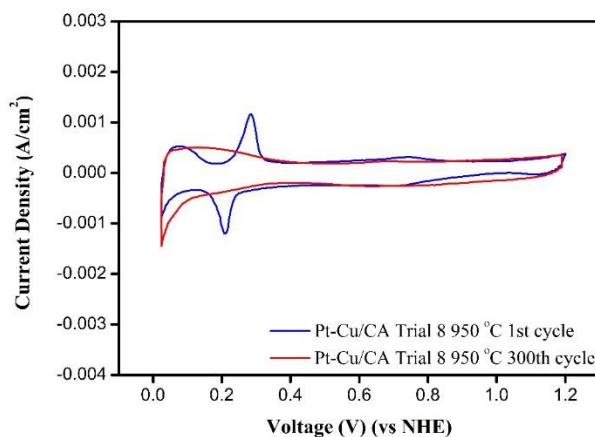
Figure 4.33: Cyclic voltammograms of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N₂ saturated HClO₄ electrolyte (1st and 300th cycles) with a scan rate of 50 mV/s.



(a)



(b)



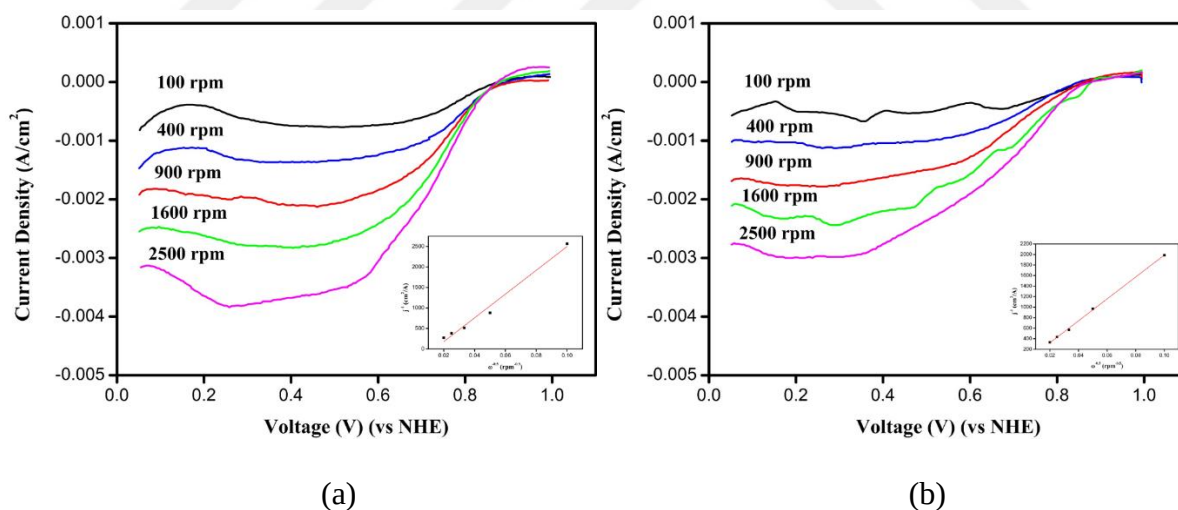
(c)

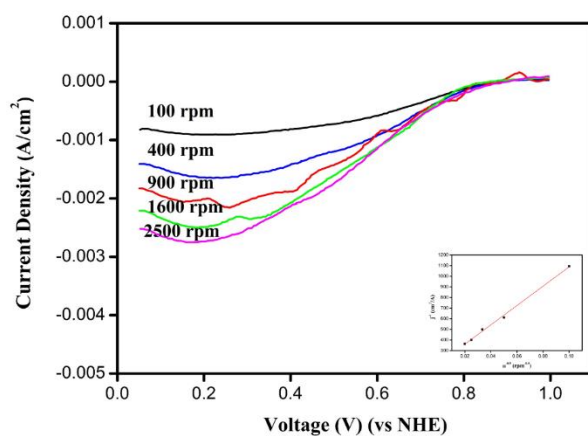
Figure 4.34: Cyclic voltammograms of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N₂ saturated HClO₄ electrolyte (1st and 300th cycles).

Figure 4.33 and 4.34 show that all Pt-Cu/CA19 Trial 7 and Trial 8 samples, except Trial 7 annealed at 800 °C, exhibited distinctive peaks at first cycle (blue lines) in between 0.2 V and 0.4 V at both directions. These peaks are associated with the bulk Cu dissolution and redeposition [125, 135]. However, Trial 7 annealed at 800 °C, did not show bulk dissolution /redeposition peaks suggesting either a different alloy nanoparticle morphology or less Cu dissolution. Moreover, all three samples showed another peaks at around 0.6 V for anodic and at around 0.4 V at cathodic directions associated with the dissolution and redeposition of Cu from the alloyed Pt-Cu nanoparticles at initial cycles [126]. Cu being a non-noble metal can easily dissolve through the acidic electrolyte with continuous cycling; a process called electrochemical dealloying. During electrochemical dealloying Cu (unalloyed or alloyed) in the samples was leached through the acidic electrolyte. Leaching of alloyed Cu from Pt-Cu nanoparticles most probably occur from the surface of the alloy nanoparticle resulting a Pt-rich shell surrounding a Pt-Cu alloy core at the end of the dealloying process [16, 27, 28, 134]. Indeed, the peaks related to Cu dissolution/redeposition disappeared with continuous cycling and at 300th cycles all six samples had cyclic voltammograms resembling to the ones of

Pt/CA19 or Pt/C with increased hydrogen adsorption/desorption peaks in the 0-0.3 V region indicating the creation of new Pt-active sites with dealloying. Also, samples having same annealing temperatures showed similar behaviors except for the ones annealed at 800 °C. Trial 8 800 °C gave lower current densities than Trial 7 800 °C most likely the result of different particle size and morphology. Furthermore, both Trial 7 and Trial 8 annealed at 950 °C exhibited much lower current densities than the other annealing temperatures due to higher Pt-Cu particle size at this annealing temperature.

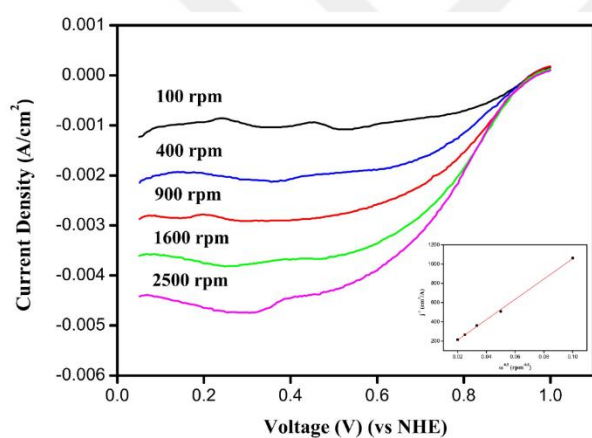
RDE experiments were conducted in an O₂ saturated environment to simulate the ORR in an acidic electrolyte after electrochemical dealloying. Mass activity and specific activity values were calculated by taking the current density value at 0.85 V at 1600 rpm to exclude the mass transport effects. The ORR curves (with Koutecky-Levich plots as inset) of Pt-Cu/CA19 Trial 7 and Trial 8 annealed at different temperatures were presented in Figure 4.35 and 4.36, respectively.



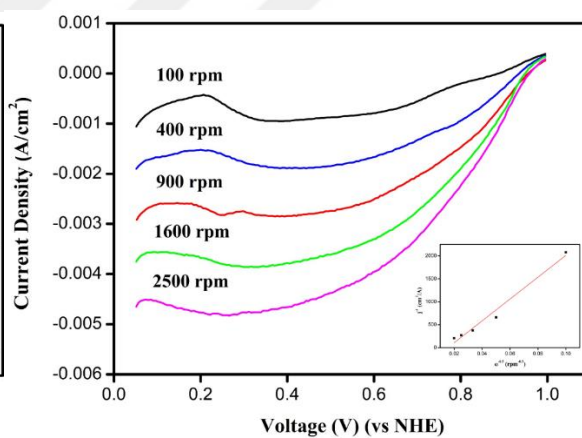


(c)

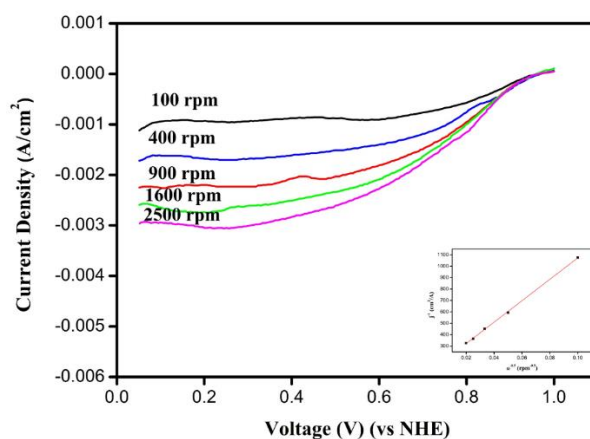
Figure 4.35: ORR curves of Pt-Cu/CA19 Trial 7 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.



(a)



(b)



(c)

Figure 4.36: ORR curves of Pt-Cu/CA19 Trial 8 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.

ORR curves from all of the samples exhibit an expected trend, namely that the current densities increase with increasing rotation speed at mass transfer controlled region (0.05 V-0.7 V). Lower current densities were observed for Trial 7 than Trial 8 for all three annealing temperatures. Moreover, amongst three annealing temperatures, 950 °C for both Trial 7 and Trial 8 resulted in the lowest current densities, indicating low activity for ORR.

Electrocatalytic properties of Pt-Cu/CA19 Trial 7 and Trial 8 annealed at different temperatures were given in Table 4.21. ESA values of the samples were calculated using 300th cycles and area under the hydrogen adsorption region.

Table 4.21: Electrocatalytic properties of Pt-Cu/CA19 Trial 7 and Trial 8 annealed at different temperatures.

Sample	Annealing Temperature	ESA (m^2/g)	MAc ($\text{A}/\text{mg}_{\text{Pt}}$)	SAc (mA/cm^2)
Pt-Cu/CA19 Trial 7	600 °C	78	0.005	0.007
	800 °C	59	0.009	0.014
	950 °C	29	0.001	0.002
Pt-Cu/CA19 Trial 8	600 °C	83	0.045	0.055
	800 °C	46	0.058	0.128
	950 °C	29	0.023	0.080

Table 4.21 shows that samples having corresponding annealing temperatures had very similar ESA values and ESA decreases with increasing annealing temperatures. Since the particle sizes increases with increasing annealing temperatures (from 1.8 nm to 4.5 nm), the decrease in ESA was expected. The highest ESA was observed for 600 °C as 78 m^2/g and 83 m^2/g for both Trial 7 (1.9 nm) and Trial 8 (1.8 nm), respectively. Whereas the lowest ESA was exhibited by 950 °C which were 29 m^2/g for both Trial 7 (4.3 nm) and Trial 8 (4.5 nm). The values of the ESAs are very similar to the ones observed in Section 4.1.4 i.e. for Pt/CA19 for the respective annealing temperatures in line with the earlier hypothesis about the formation of Pt-rich shell/Pt-Cu alloy core nanoparticles with dealloying. The similar ESA values indicates that deposition order did not affect the Pt active sites for hydrogen adsorption/desorption. However, it had a significant effect on the activities of the samples towards ORR. Trial 7 (First $\text{Cu}(\text{tfa})_2$ on CA19) showed almost no activity, mass or specific, towards ORR regardless of the annealing temperature whereas Trial 8 (First $\text{Pt}(\text{cod})\text{me}_2$ on CA19) showed promising activity values. This is most probably due to the different alloy particle morphologies of the resulting

Pt-Cu alloy nanoparticles so that Trial 7 has a Cu enriched surface resulting the blockage of the ORR active terrace sites of the nanoparticles by the unleached Cu atoms during the electrochemical dealloying of Trial 7, whereas Trial 8 has a Pt enriched surface. Further investigation is needed to determine why different deposition order results in different electrochemical activity. The mass activity values of Trial 8 samples increased from 0.045 A/mg_{Pt} (600 °C) to 0.058 A/mg_{Pt} (800 °C) and then decreases to 0.023 A/mg_{Pt} (950 °C). The specific activity had a similar trend as mass activity, increasing from 0.055 mA/cm² (600 °C) to 0.123 mA/cm² (800 °C) and decreasing to 0.080 mA/cm² (950 °C). The particle sizes of Pt-Cu alloy nanoparticles after dealloying cannot be determined since the amount of the samples deposited on working electrode was extremely low. Therefore, relating ORR activities of Trial 8 samples to the particle sizes of the Pt-Cu nanoparticles is very difficult. However, based on the ESA values reported in Section 4.1.4 i.e. for Pt/CA19 which are very similar to the ones reported in this section for Trial 7 and 8, the particle sizes of the samples do not significantly change during the dealloying. Alloying process changes the electronic structure of Pt by changing the d-band center thus the relationships established for particle size effect on carbon black or CA in terms of activity may not be valid for supported bimetallic nanoparticles. The highest mass and specific activity values, 0.058 A/mg_{Pt} and 0.128 mA/cm² respectively, were observed for Trial 8 800 °C suggesting a superior alloy nanoparticle morphology.

4.2.5. Pt-Cu/CA19 Composites Prepared via Sequential Deposition Having Pt:Cu Mole Ratios of 1:3

Two sets of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:3 were prepared using sequential SCD approach in order to determine the effect of composition of Pt-Cu nanoparticles on particle size, particle morphology and electrochemical behavior. As in the Trial 7 and Trial 8, one set was prepared by first adsorbing $\text{Cu}(\text{tfa})_2$ on CA19 and after conversion of $\text{Cu}(\text{tfa})_2$ to Cu, $\text{Pt}(\text{cod})\text{me}_2$ was adsorbed on Cu/CA19 composite and the other set was prepared by reversing the deposition order (i.e. First $\text{Pt}(\text{cod})\text{me}_2$ on CA19, then $\text{Cu}(\text{tfa})_2$ on Pt/CA19). The detailed explanations of the samples are given in Table 4.22.

Table 4.22: Pt-Cu/CA19 samples prepared by sequential SCD with Pt:Cu mole ratio of 1:3 and the explanation of deposition order.

Sample	Explanation
Pt-Cu/CA19 Trial 9	First $\text{Cu}(\text{tfa})_2$ (III)* on CA19 then $\text{Pt}(\text{cod})\text{me}_2$ (I) on Cu/CA19
Pt-Cu/CA19 Trial 10	First $\text{Pt}(\text{cod})\text{me}_2$ (I) on CA19 then $\text{Cu}(\text{tfa})_2$ (III) on Pt/CA19

*The number of deposition steps are given in parenthesis.

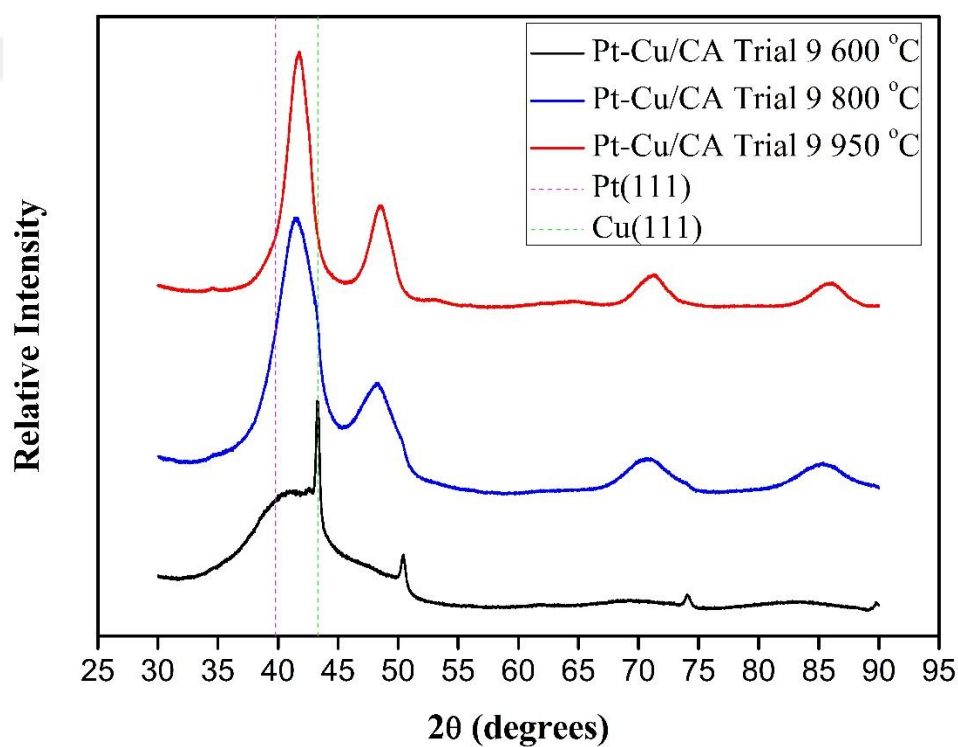
The metal content of the prepared Pt-Cu/CA19 samples were determined gravimetrically and also using XRF analysis before annealing and given in Table 4.23.

Table 4.23: Pt and Cu weight percentages of the Pt-Cu/CA19 samples before annealing.

Sample	Metal Loadings (wt.%)			
	Gravimetric		XRF	
	Pt	Cu	Pt	Cu
Pt-Cu/CA19 Trial 9	14.5	8.9	15.7	9.3
Pt-Cu/CA19 Trial 10	14.3	10.7	15.3	11.4

Table 4.23 shows that there is only a small difference between the metal contents obtained gravimetrically and the metal contents determined from XRF as in every other Pt-Cu/CA19 samples.

Both Pt-Cu/CA19 samples were divided into three to eliminate any compositional differences and annealed at three different temperatures, 600, 800, and 950 °C. In order to determine the effect of different annealing temperatures and deposition order to particle size and to the alloying degree, the prepared Pt-Cu/CA19 samples were subjected to XRD. The XRD of the Pt-Cu/CA19 samples are given in Figure 4.37.



(a)

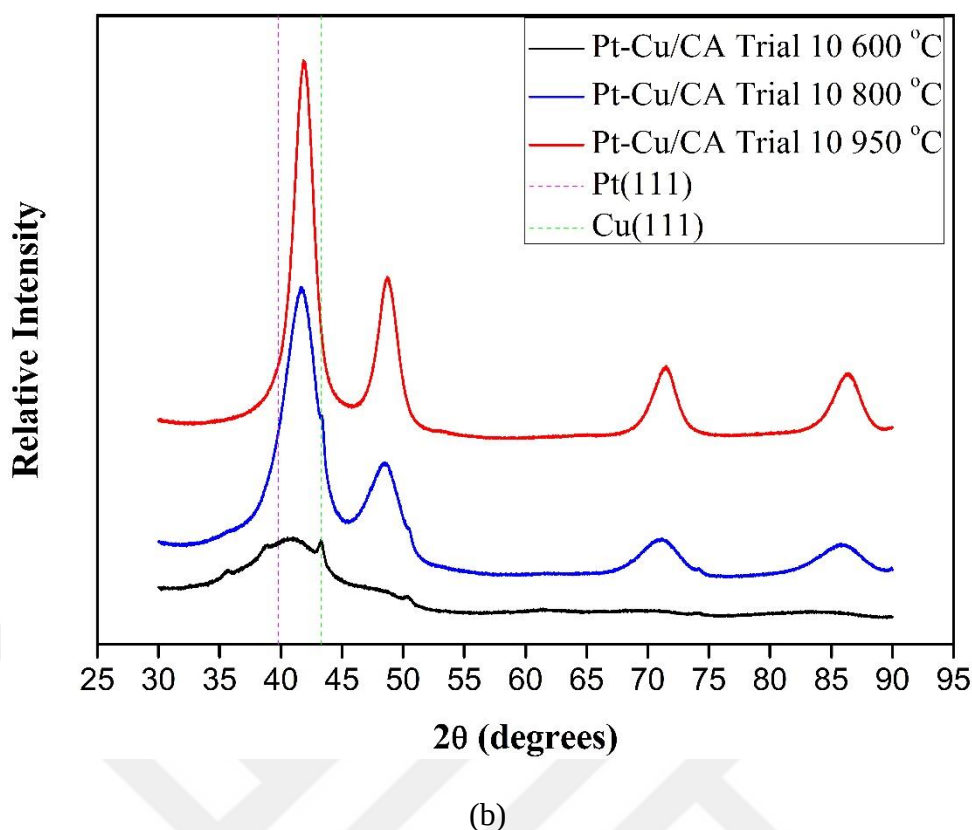


Figure 4.37: XRD of (a) Pt-Cu/CA19 Trial 9 and (b) Pt-Cu/CA19 Trial 10 with Pt:Cu mole ratios of 1:3 prepared via sequential SCD.

Figure 4.37 shows that both Pt-Cu/CA19 Trial 9 and Trial 10 exhibited separate fcc Pt-Cu alloy peaks at all three annealing temperatures. Also at 600 °C and 800 °C for both Trial 9 and Trial 10, unalloyed face-centered cubic Cu peaks were observed in XRD. However, at 950 °C the unalloyed Cu reflection peaks disappeared for both Trial 9 and Trial 10. Furthermore, similar to Trial 7 and Trial 8, face-centered cubic Pt-Cu alloy peaks of both samples shifted to higher Bragg angle values and overlapped with face-centered cubic Cu peaks. Additionally, for Trial 10 annealed at 600 °C exhibited monoclinic cupric oxide reflection peaks at 2θ of 35.5° and 38.9°. The presence of Cu and CuO reflections peaks probably the result of decreased Pt and increased Cu content in the samples. Furthermore, the intensities observed Cu peaks were higher for Trial 9 than Trial 10. Similar to Trial 7 and Trial 8, with increasing annealing temperatures Pt-Cu alloy peaks became sharper indicating higher Pt-Cu particle and all Pt-Cu

alloy peaks shifted to higher Bragg angle values with increasing annealing temperatures for both Trial 9 and Trial 10 indicating lattice contraction as compared to pure Pt thus a higher degree of alloying.

Vegard's law was used to determine the mole ratios of Pt and Cu. Table 4.24 summarizes the mole ratios obtained from XRD and XRF.

Table 4.24: Pt:Cu mole ratios of Pt-Cu/CA19 samples obtained from XRF and XRD.

Sample	Annealing	Mole Ratios (Pt:Cu)	
	Temperature	XRD	XRF
Pt-Cu/CA19 Trial 9	600 °C	54:46	35:65
	800 °C	51:49	
	950 °C	43:57	
Pt-Cu/CA19 Trial 10	600 °C	60:40	30:70
	800 °C	44:56	
	950 °C	39:61	

Table 4.24 shows that based on XRF, Trial 9 and Trial 10 had intended Pt:Cu molar ratios of approximately 25:75 upon deposition and conversion. However, the Pt:Cu mole ratios obtained from XRD were closer to 50:50 rather than 25:75 for 600 °C and 800 °C. This indicates that when Cu content is increased alloying degree decreases and this ratios are in good agreement with XRD since we observed Cu reflection peaks at 600 °C and 800 °C for both samples. The difference between XRD and XRF decreases at 950 °C as expected since XRD did not show any separate Cu peaks at this annealing temperature.

Surface morphologies of Pt-Cu/CA19 samples were characterized by SEM EDX. Figure 4.38 and 4.39. shows the SEM images of Pt-Cu/CA19 Trial 9 and Trial 10.

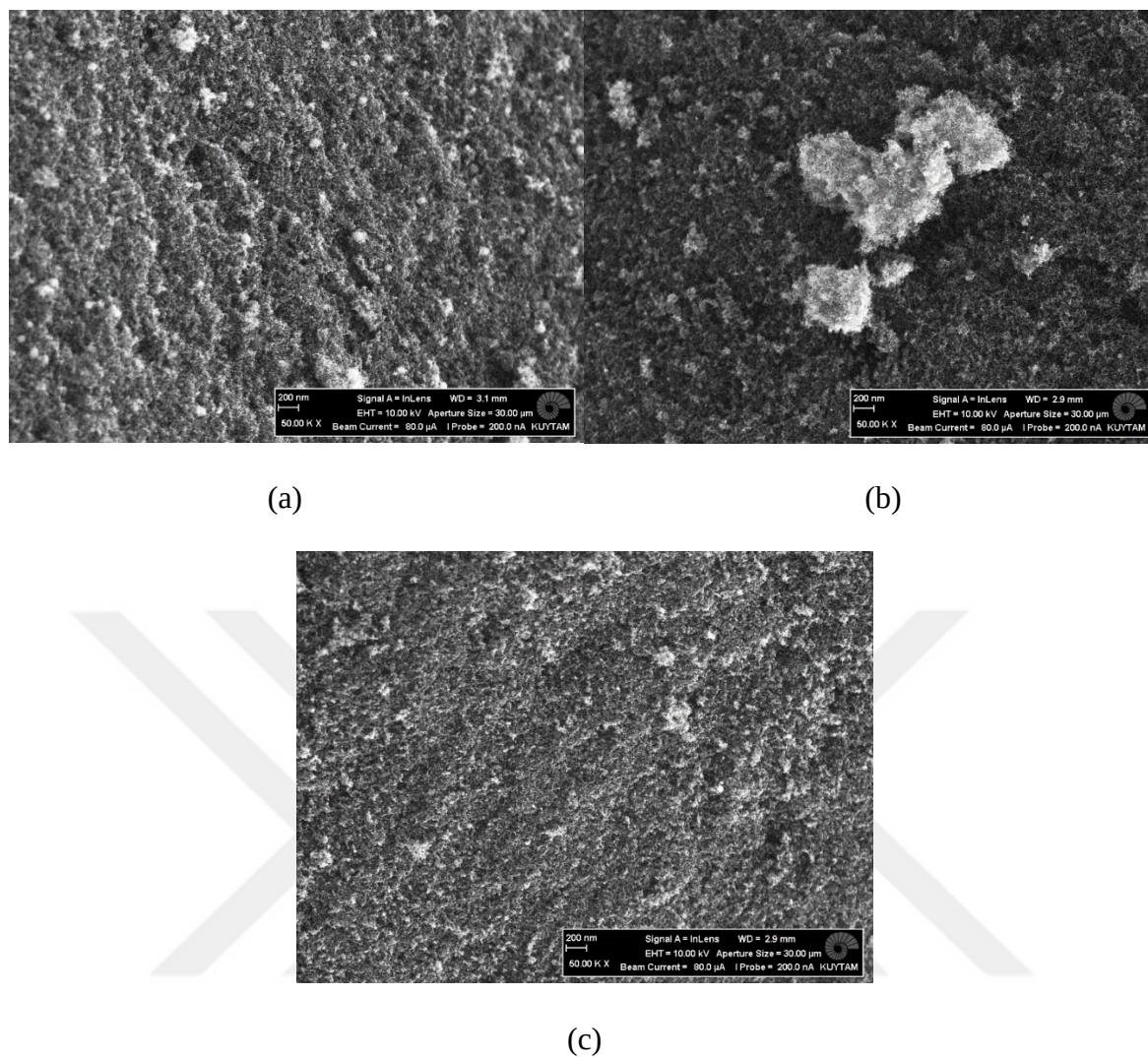
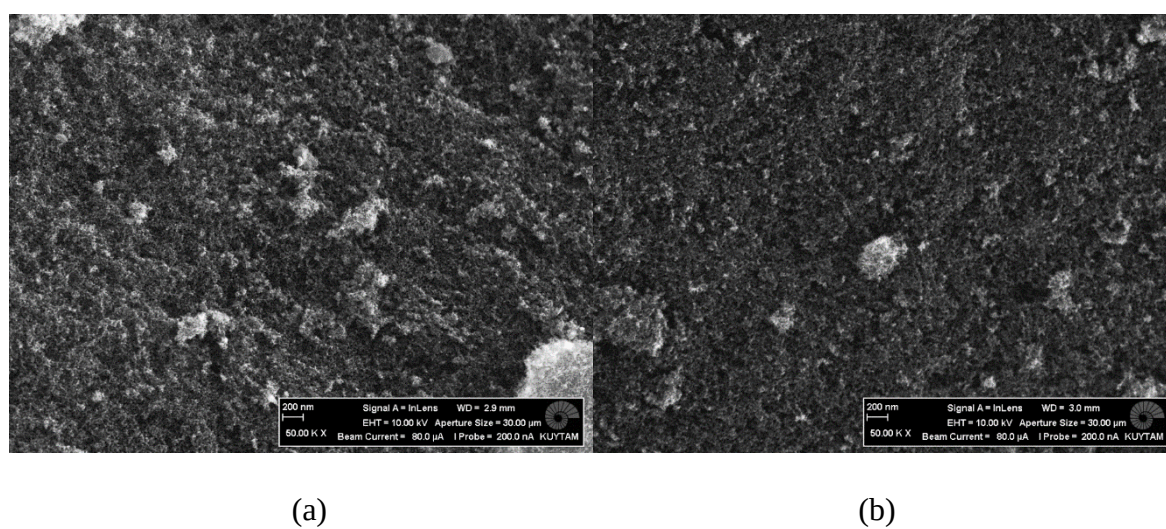
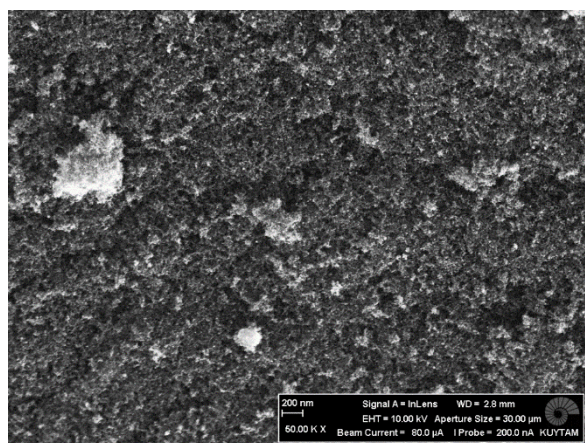


Figure 4.38: SEM images of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.



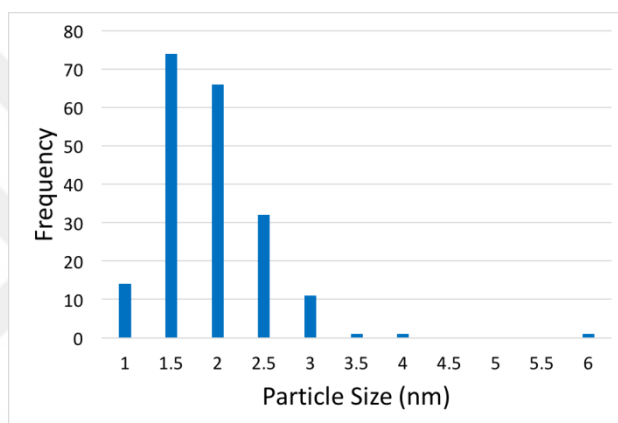
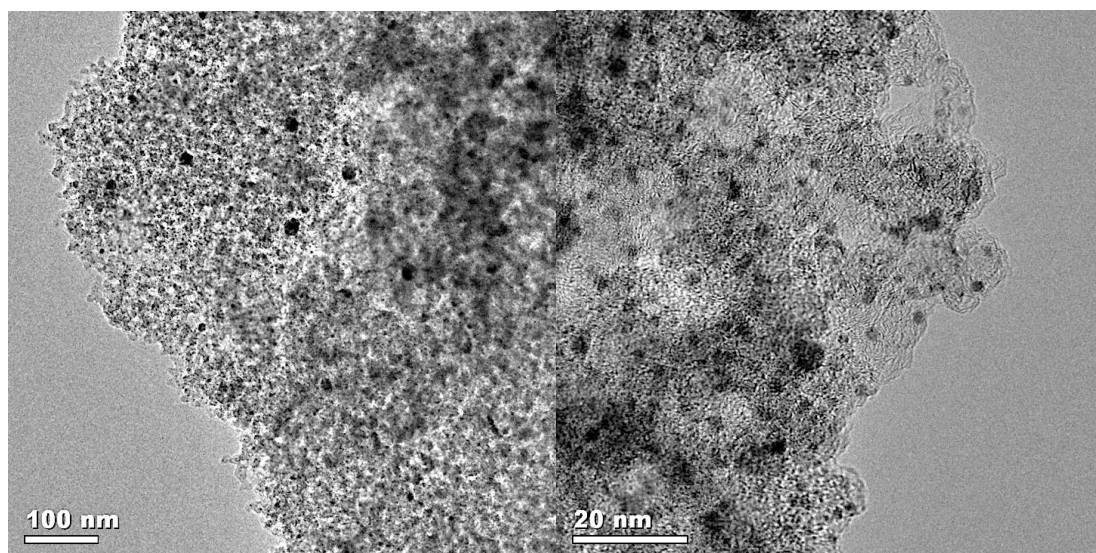


(c)

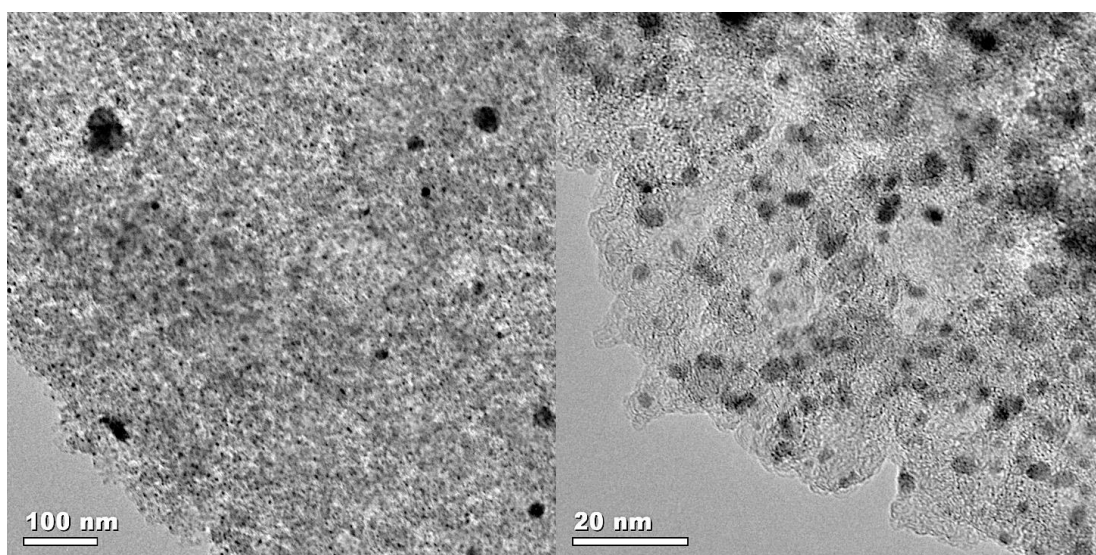
Figure 4.39: SEM images of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.

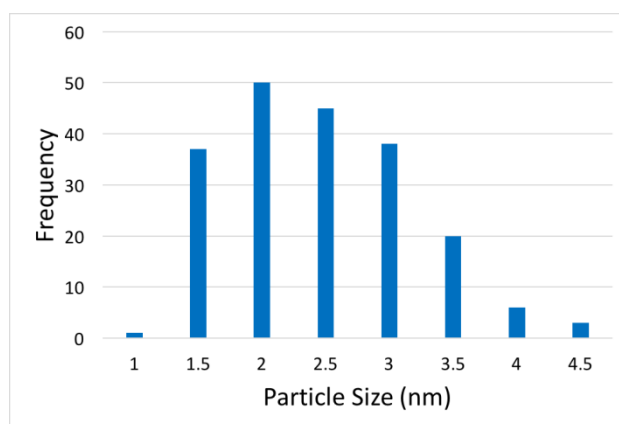
Figure 4.38 and 4.39 shows that any separate Cu nanoparticles were not observed on the SEM images of Trial 9 and Trial 10 for all annealing temperatures, although these Cu nanoparticles present in the samples, in particular at 600 °C, had rather large average particle sizes (23.6 nm for Trial 9 600 °C, 18.1 nm for Trial 10 600 °C). Again, since SEM represents only a very small portion of the sample, the lack of Cu nanoparticles, the lack of Cu nanoparticles on SEM can be explained by the very small concentration of these large Cu nanoparticles on CA19.

Nanoparticle morphologies of Pt-Cu/CA19 Trial 9 and Trial 10 were also characterized using HRTEM. HRTEM images with particle size distributions were presented in Figure 4.40 and 4.41, respectively.

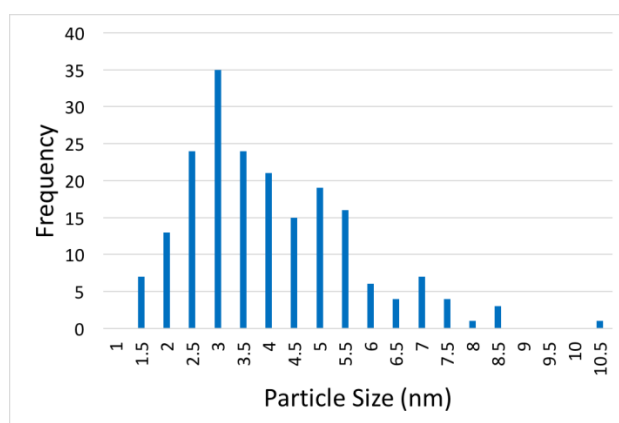
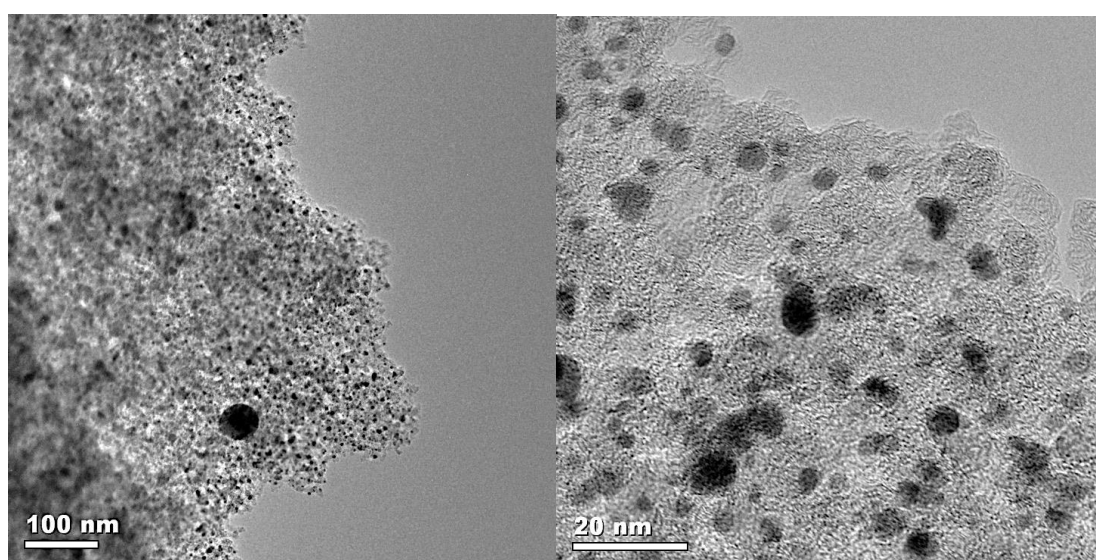


(a)



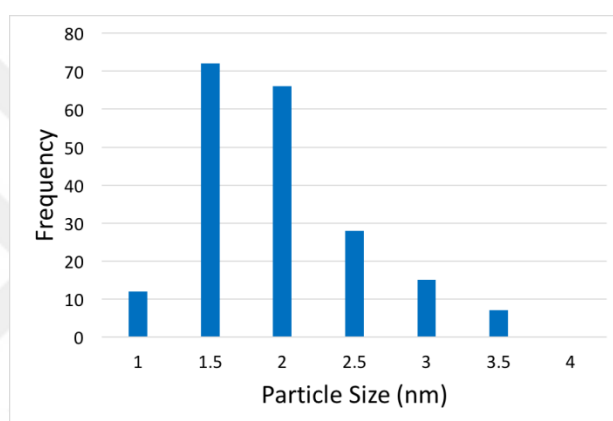
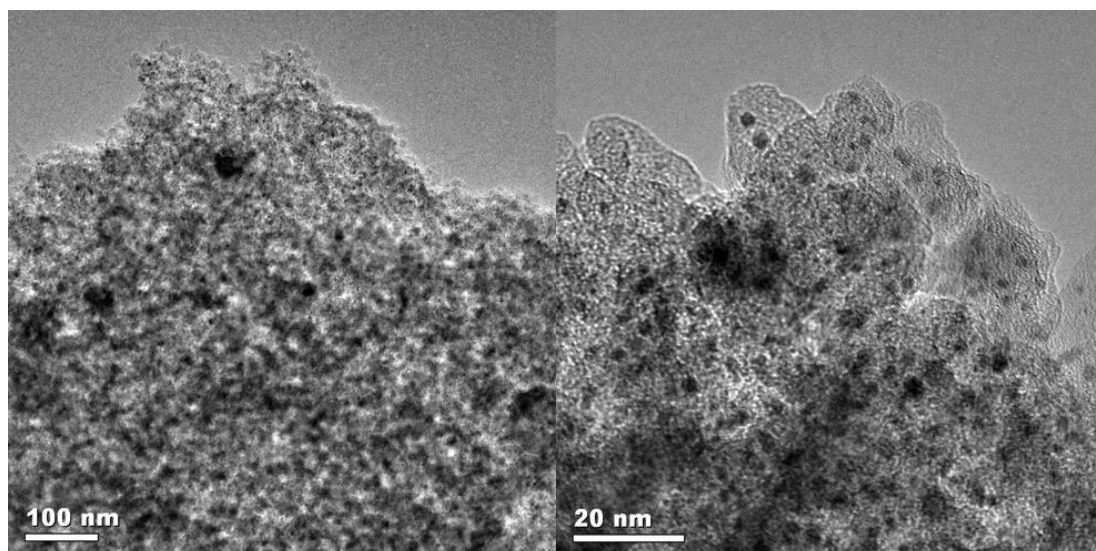


(b)

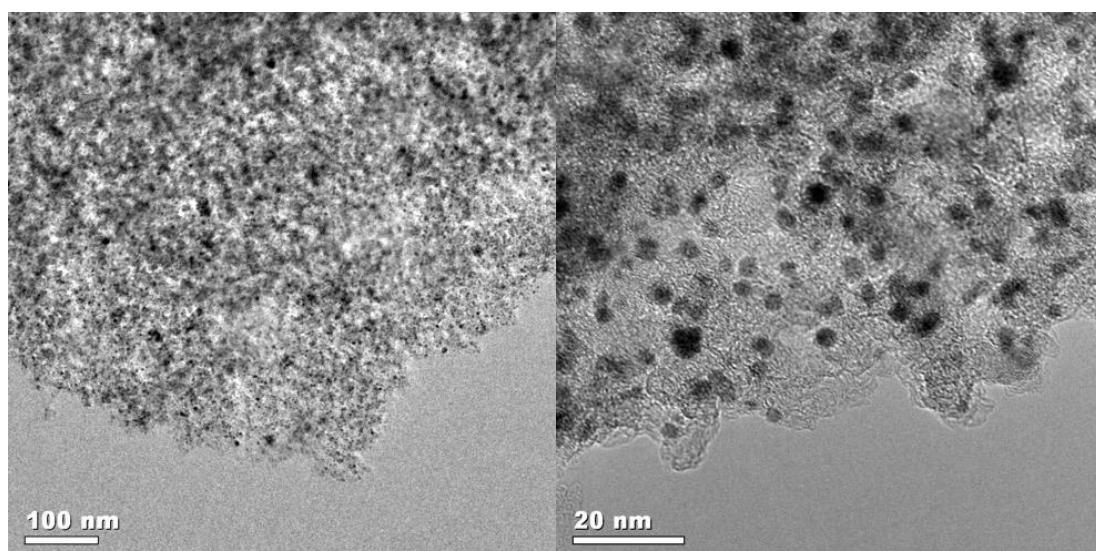


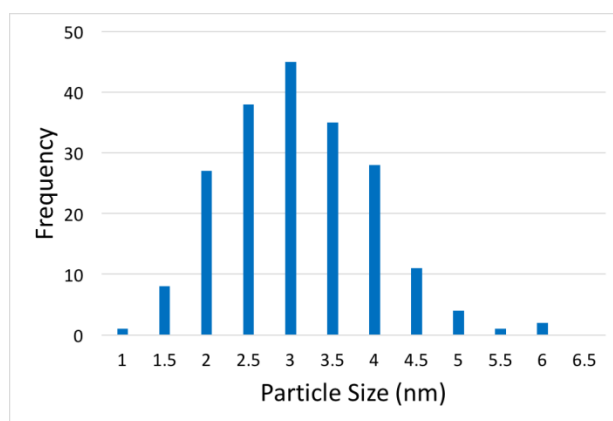
(c)

Figure 4.40: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.

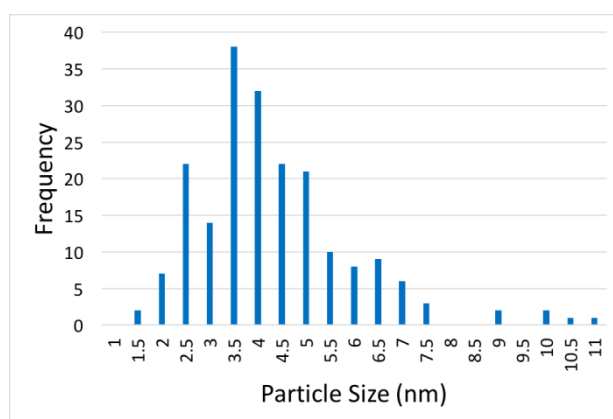
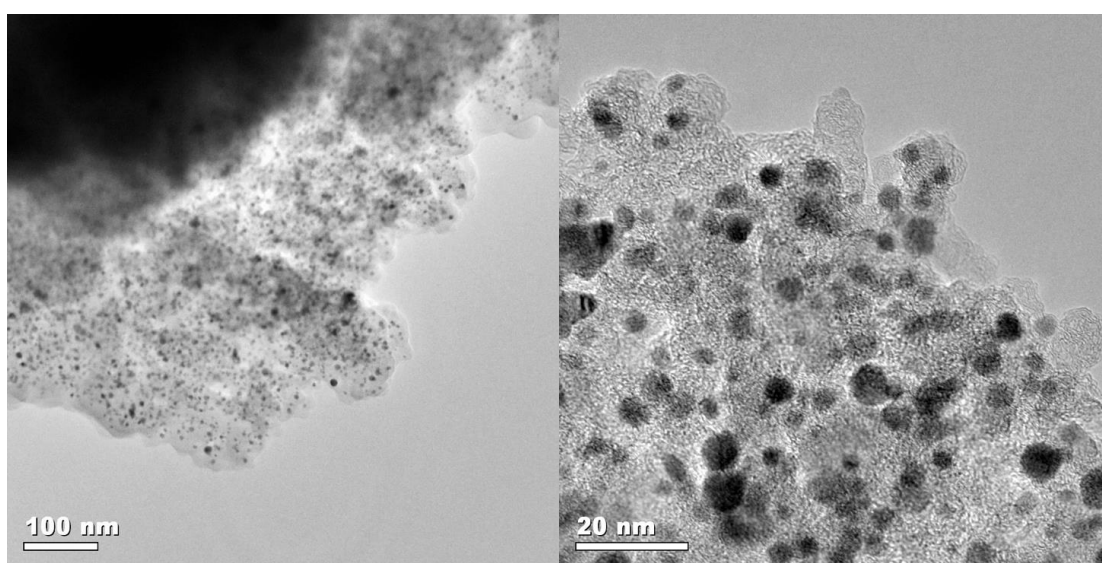


(a)





(b)



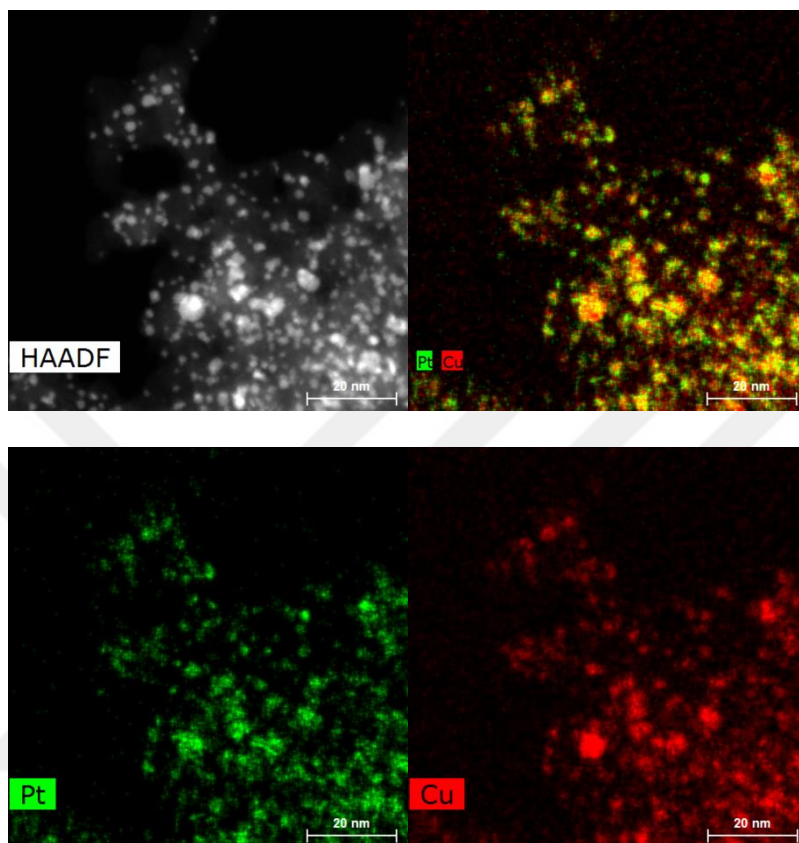
(c)

Figure 4.41: HRTEM images and particle size distributions of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C (b) 800 °C and (c) 950 °C.

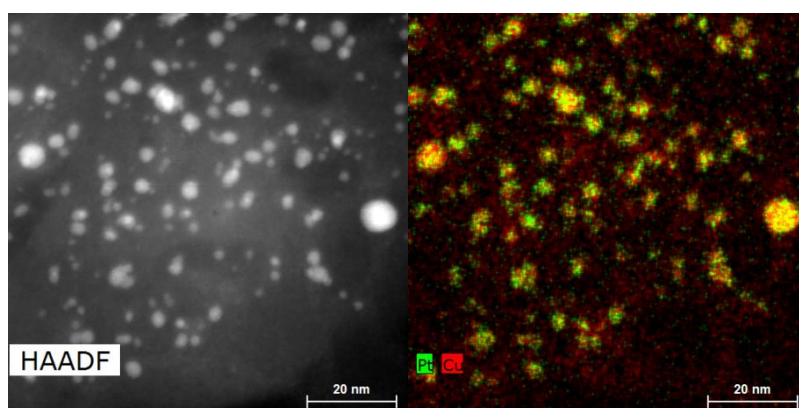
Figure 4.40 (a) indicates the presence of large particles for Trial 9 annealed at 600 °C, these are most probably the unalloyed Cu nanoparticles that were also observed at XRD (23.6 nm for 600 °C). These large unalloyed Cu nanoparticles was also observed at Trial 9 annealed at 800 °C but the frequency of these became less and less as the annealing temperature increases. Besides these large unalloyed Cu nanoparticles, the distribution of Pt-Cu alloy nanoparticles (Trial 9) was quite homogenous as in the Trial 7 and Trial 8, however, there were some nanoparticles on the TEM images of Trial 9 samples that were not consistent with the average Cu nanoparticle size obtained from XRD. Of course these can be indeed separate Cu nanoparticles (since there is higher standard deviation in size for large nanoparticles), however, these can also be agglomerated Pt-Cu nanoparticles. In any case the frequency of occurrence of these unalloyed Cu or agglomerated Pt-Cu nanoparticles was extremely low, it can be concluded that the homogenous distribution of Pt-Cu alloy nanoparticles was achieved at Trial 9 for all annealing temperatures.

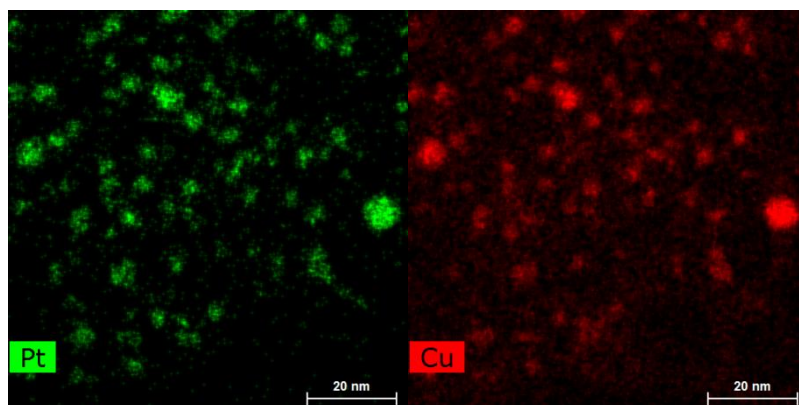
Figure 4.41 shows that in Trial 10, separate Cu nanoparticles were also observed. However, unlike Trial 9, the average particle sizes of these nanoparticles were consisted with the particle sizes obtained from XRD which suggests that these are indeed unalloyed Cu nanoparticles. Moreover, for both Trial 9 and Trial 10, the particle size distributions of Pt-Cu alloy nanoparticles were very narrow for 600 °C and 800 °C. Although the particle size distributions became broader at 950 °C due to larger Pt-Cu alloy nanoparticle size we did not detect any significant agglomeration in both Trial 9 and Trial 10. Furthermore, TEM images of Trial 9 and Trial 10 shows that even though the Cu content is higher in Trial 9 and Trial 10 than Trial 7 and Trial 8, the homogenous distribution of Pt-Cu alloy nanoparticles on CA19 was achieved indicating and homogeneity of the surface was not strongly dependent on the nanoparticle composition.

In order to, determine the effect of annealing temperature to the alloying process EDX mapping was done on both Trial 9 and Trial 10 annealed at different temperatures. EDX mapping and HAADF images were given in Figure 4.42 and 4.43, respectively.

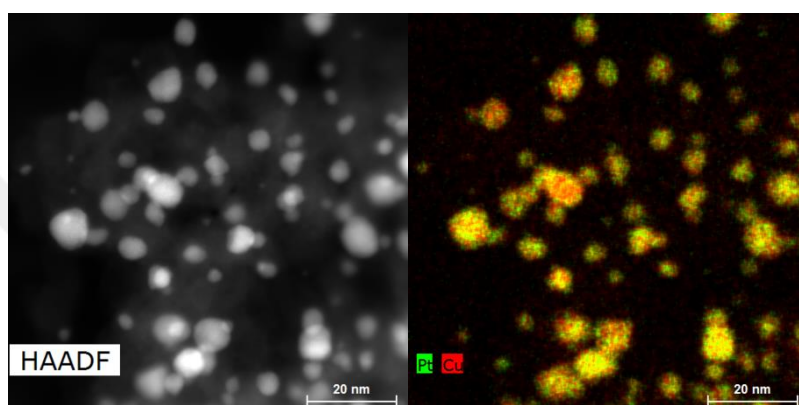


(a)



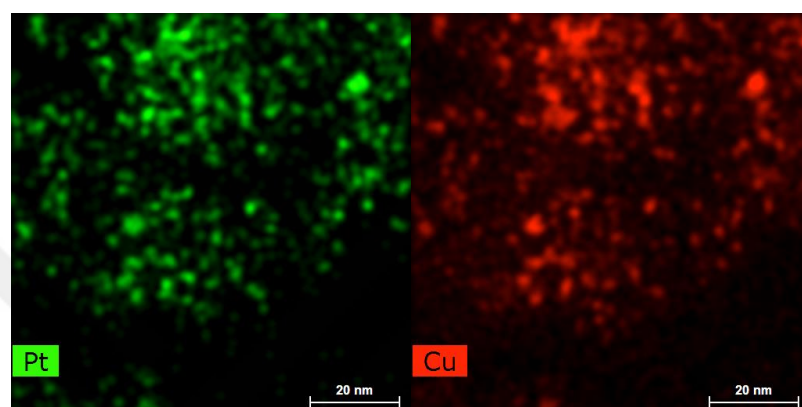
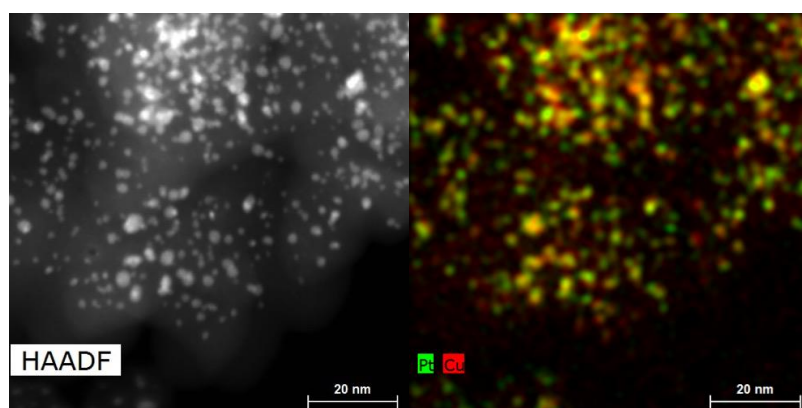


(b)

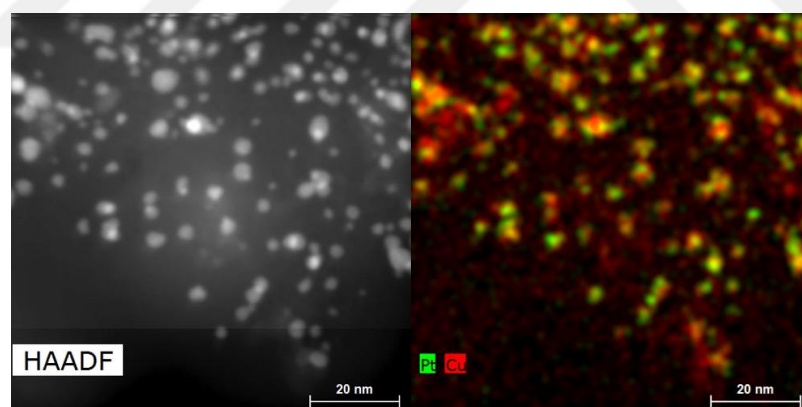


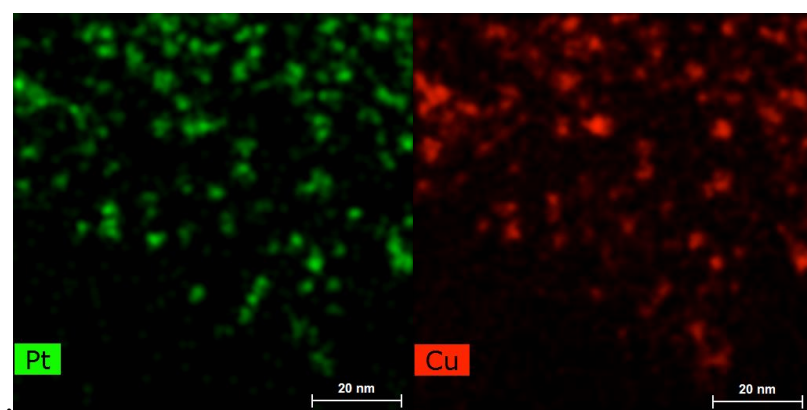
(c)

Figure 4.42: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.

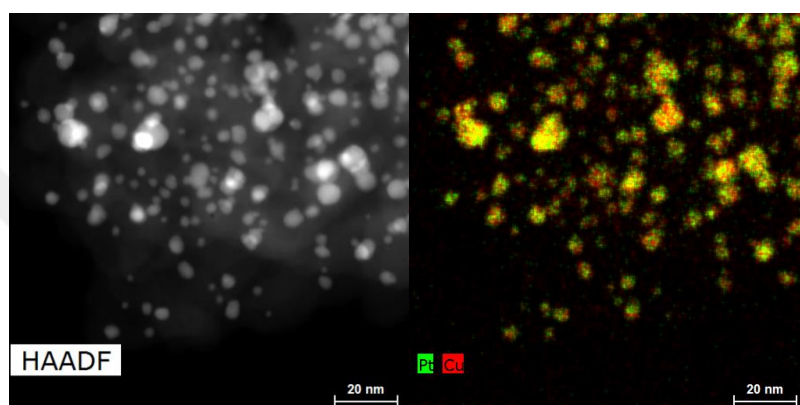


(a)





(b)



(c)

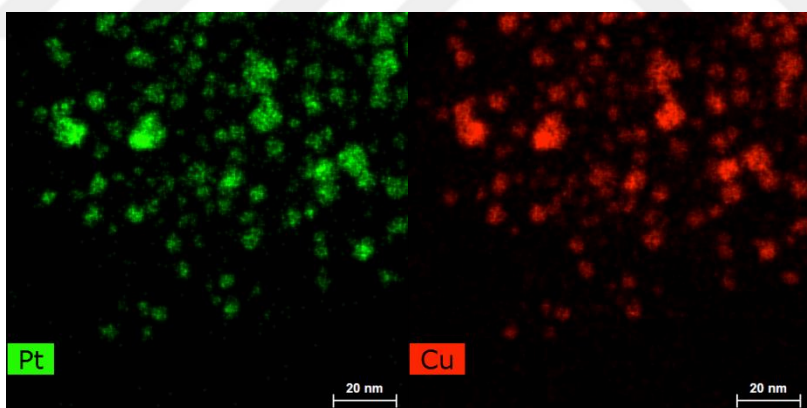


Figure 4.43: HAADF and EDX mapping images of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C.

Figure 4.42 and 4.43 indicate that all three Pt-Cu/CA19 Trial 9 and Trial 10 samples have formed disordered Pt-Cu alloy nanoparticles as in all the other samples. EDX mapping images of both Trial 9 and Trial 10 showed that the samples were consisted of Pt-Cu

nanoparticles that are non-uniform in composition, i.e. some nanoparticles observed were richer in Cu and the others were richer in Pt. However, similar to Trial 7 and Trial 8, as the annealing temperature increases Pt-Cu nanoparticle compositions became more uniform indicating a better Pt-Cu alloy nanoparticle structure. Furthermore, EDX of both Trial 9 and Trial 10 showed Cu clusters and small Cu nanoparticles which may explain the difference between the Pt:Cu mole ratios obtained from XRD and XRF.

Average particle sizes of the alloyed Pt-Cu nanoparticles on CA19 were determined from XRD using Scherrer Equation and {220} plane angle and also from TEM images. The average particle sizes of Pt-Cu/CA19 Trial 9 and Trial 10 annealed at different temperatures were given in Table 4.25.

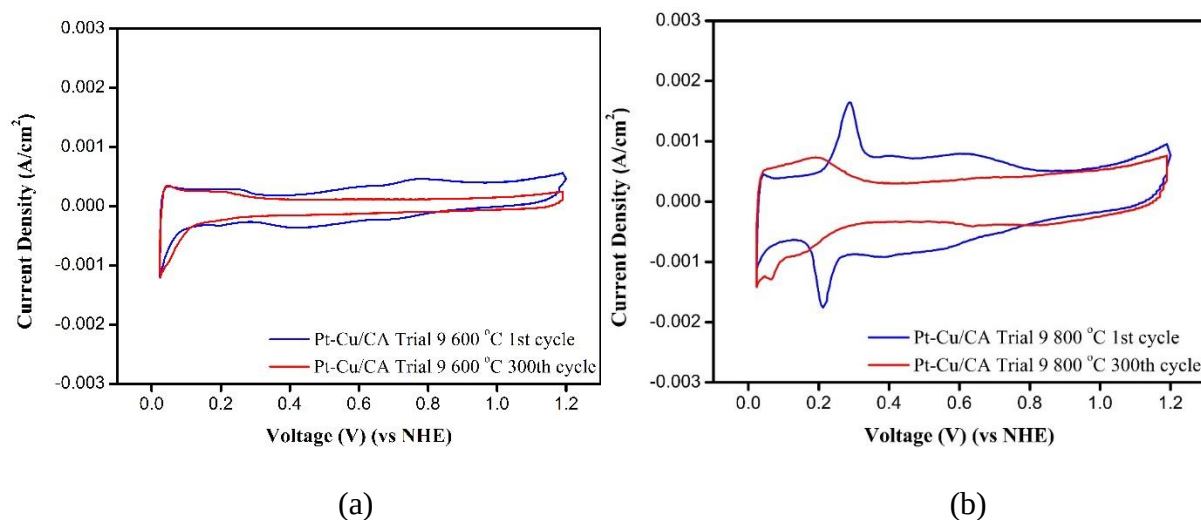
Table 4.25: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:3 and annealed at different temperatures.

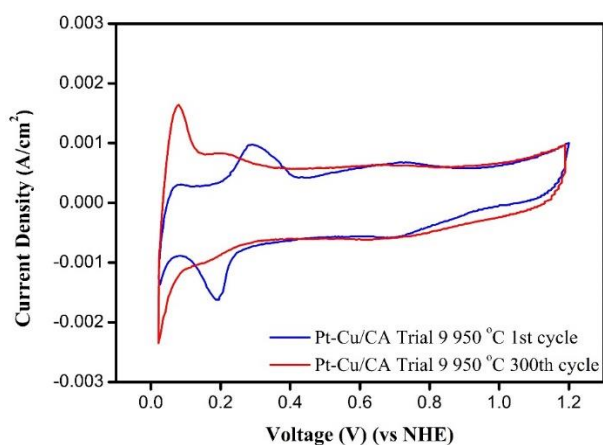
Sample	Annealing Temperature	Particle Size (nm)	
		XRD	TEM
Pt-Cu/CA19 Trial 9	600 °C	1.9	1.9±0.6
	800 °C	2.5	2.4±0.7
	950 °C	3.6	4.0±1.6
Pt-Cu/CA19 Trial 10	600 °C	1.5	2.0±0.6
	800 °C	2.7	3.1±0.9
	950 °C	4.2	4.2±1.7

Table 4.25 shows that both Trial 9 and Trial 10 had average Pt-Cu alloy nanoparticle sizes resembling to the ones of Trial 7 and Trial 8 for corresponding annealing temperatures. The average particle sizes obtained from XRD and TEM were quite close to each other. However the average particle sizes obtained from TEM were a little greater than the ones

obtained from XRD for Trial 10 600 °C and 800 °C and for Trial 9 950 °C yet the difference was not very significant. The average particle sizes increases with increasing annealing temperature from 1.9 nm (600 °C) to 4.0 nm (950 °C) for Trial 9 and 2.0 nm (600 °C) to 4.2 nm (950 °C) for Trial 10. Furthermore, the particle sizes from the TEM images for Trial 9 and Trial 10 were also remarkably uniform with standard deviations from the averages in the range of ± 0.6 -0.9 nm except for the samples annealed at 950 °C. At 950 °C, the deviations from the average particle size increased to ± 1.6 nm for Trial 9 and to ± 1.7 nm for Trial 10 showing broader particle size distributions yet the distributions were still narrow. Although the standard deviations obtained for Trial 9 and Trial 10 were higher than those of Trial 7 and Trial 8, the difference was very small. Therefore, increasing Cu content did not significantly affect the average particle sizes of the resulting Pt-Cu alloy nanoparticles [27].

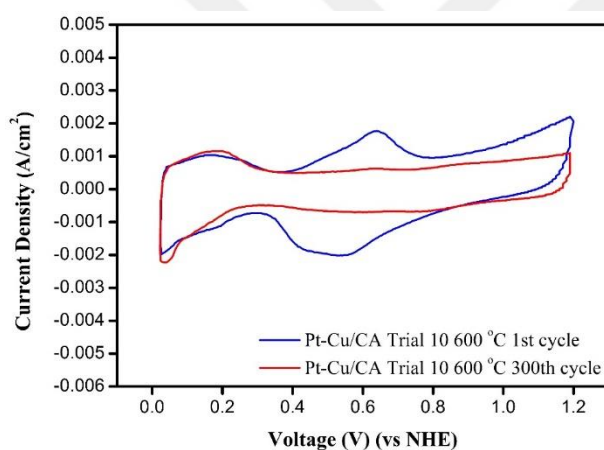
The electrochemical behaviors of Pt-Cu/CA19 samples having Pt:Cu mole ratios of 1:3 and annealed at different temperatures were characterized using CV. Cyclic voltammograms taken in N_2 saturated acidic electrolyte were presented in Figure 4.44 and 4.45, respectively.



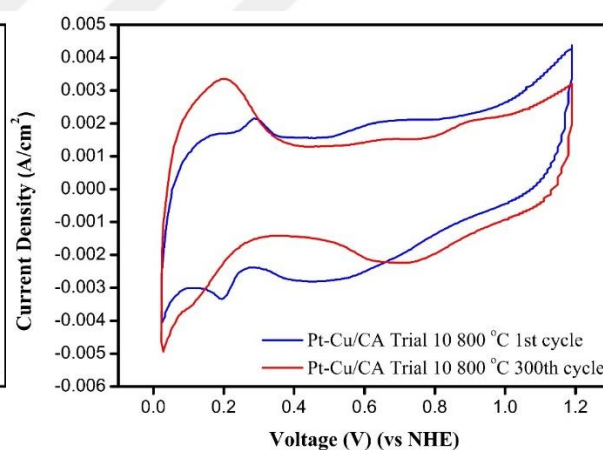


(c)

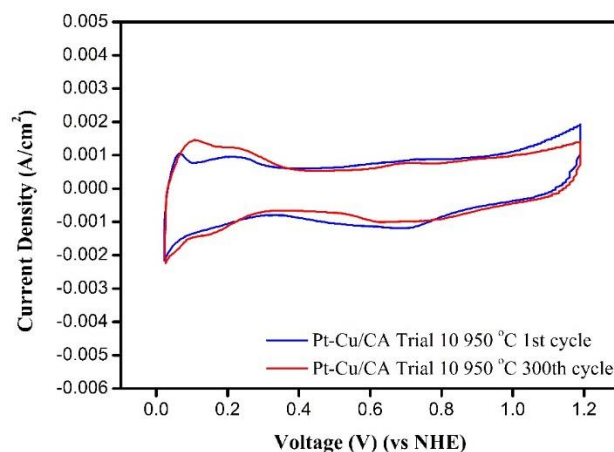
Figure 4.44: Cyclic voltammograms of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N₂ saturated HClO₄ electrolyte (1st and 300th cycles).



(a)



(b)



(c)

Figure 4.45: Cyclic voltammograms of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C taken in N₂ saturated HClO₄ electrolyte (1st and 300th cycles).

Figure 4.44 and 4.45 show that all Pt-Cu/CA19 Trial 9 and Trial 10 samples, except Trial 10 annealed at 600 °C and at 950 °C, exhibited bulk Cu dissolution/redeposition peaks at first cycle (blue lines) in between 0.2 V and 0.4 V at both directions. Trial 10 600 °C and 800 °C did not exhibit these peaks indicating a different maybe more uniform nanoparticle morphologies. Moreover, all three samples showed another peaks at around 0.6 V for anodic and at around 0.4 V at cathodic directions associated with the alloyed Cu dissolution/redeposition peaks. At 300th cycles all six samples had cyclic voltammograms resembling to the ones of Pt/CA19 or Pt/C. Trial 9 samples generally gave lower current densities than Trial 10 at corresponding annealing temperatures. Unlike Trial 7 and Trial 8, the lowest current densities obtained for Trial 9 and Trial 10 annealed at 600 °C. This indicates that changing Pt:Cu ratio from 1:1 to 1:3 results in different nanoparticles morphologies and thus different electrochemical behavior. Here, ESA increase was only significant in the Trial 9 800 °C and 950 °C, Trial 10 800 °C samples and Trial 9 600 °C, Trial 10 600 °C and 950 °C samples did not ESA increase upon potential cycling.

RDE experiments were conducted in an O_2 saturated environment to simulate the ORR in an acidic electrolyte after electrochemical dealloying. Mass activity and specific activity values were calculated by taking the current density value at 0.85 V at 1600 rpm to exclude the mass transport effects. The ORR curves (with Koutecky-Levich plots as inset) of Pt-Cu/CA19 Trial 9 and Trial 10 annealed at different temperatures were presented in Figure 4.46 and 4.47, respectively.

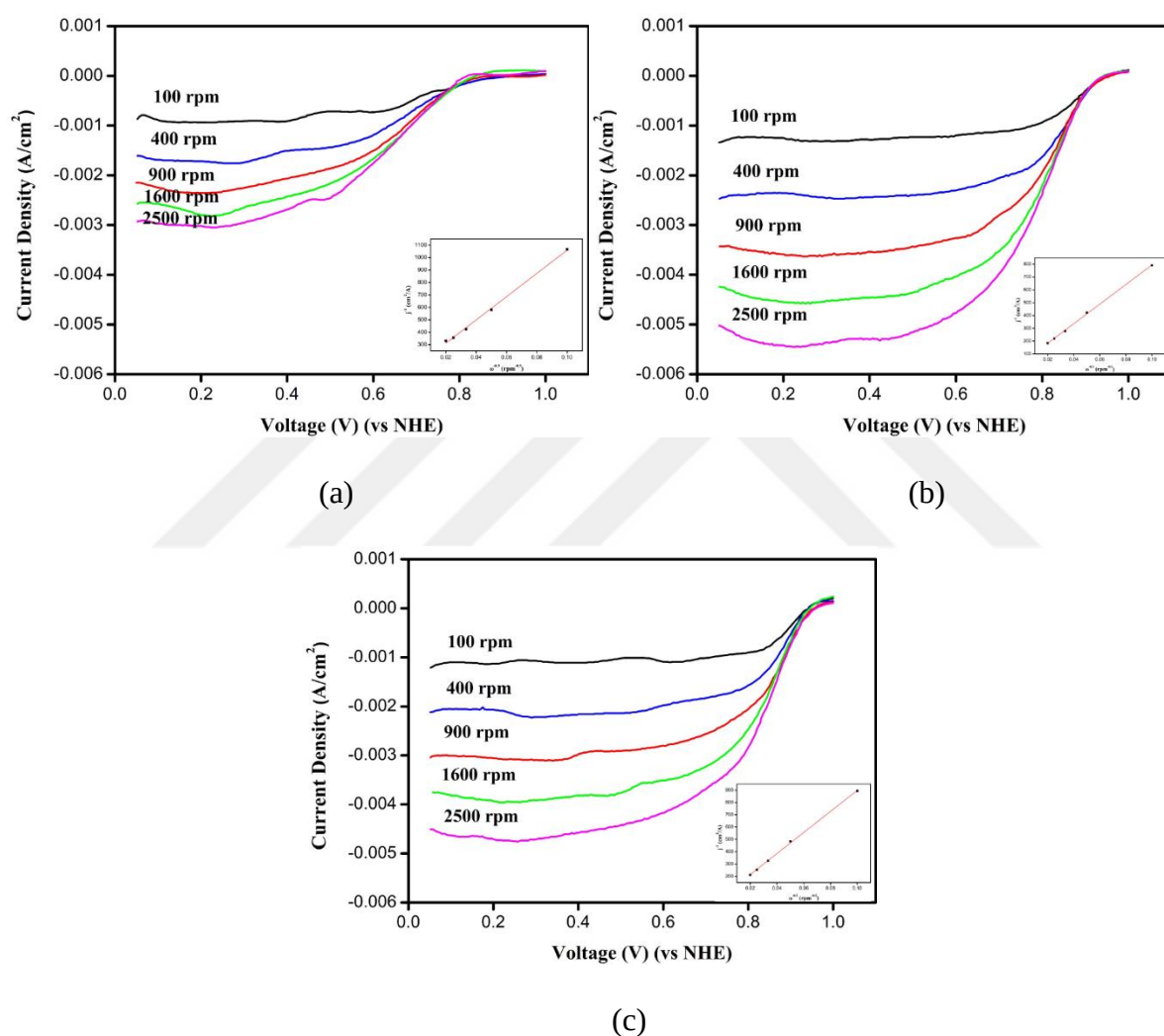


Figure 4.46: ORR curves of Pt-Cu/CA19 Trial 9 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.

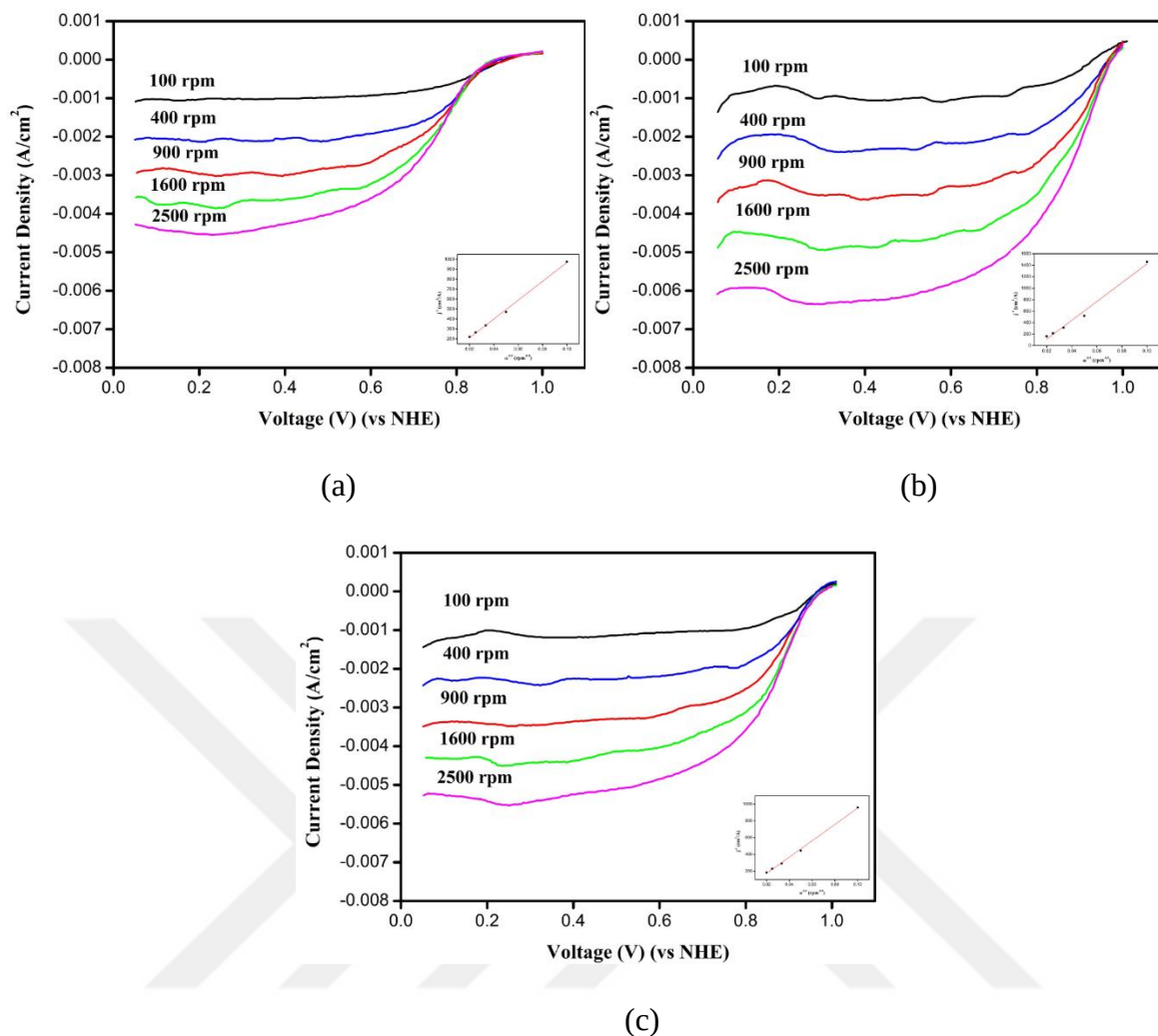


Figure 4.47: ORR curves of Pt-Cu/CA19 Trial 10 annealed at (a) 600 °C, (b) 800 °C, and (c) 950 °C after 300 cycles, recorded with a scan rate of 10 mV/s.

ORR curves from all of the samples exhibit an expected trend, namely that the current densities increase with increasing rotation speed at mass transfer controlled region (0.05 V-0.7 V). Lower current densities were observed for Trial 9 than Trial 10 for all three annealing temperatures as in Trial 7 and Trial 8. However, in contrast to Trial 7 and Trial 8 amongst three annealing temperatures, 600 °C for both Trial 9 and Trial 10 gave the lowest current densities, indicating changing Pt:Cu mole ratios changes the effect of annealing temperature on electrochemical behavior most probably due different Pt-Cu alloy nanoparticle morphologies.

Electrocatalytic properties of Pt-Cu/CA19 Trial 9 and Trial 10 annealed at different temperatures were given in Table 4.26. ESA values of the samples were calculated using 300th cycles and area under the hydrogen adsorption region.

Table 4.26: Electrocatalytic properties of Pt-Cu/CA19 Trial 9 and Trial 10 annealed at different temperatures.

Sample	Annealing Temperature	ESA (m ² /g)	MAc (A/mg _{Pt})	SAC (mA/cm ²)
Pt-Cu/CA19 Trial 9	600 °C	21	0.001	0.004
	800 °C	44	0.047	0.107
	950 °C	41	0.063	0.156
Pt-Cu/CA19 Trial 10	600 °C	62	0.010	0.015
	800 °C	131	0.123	0.090
	950 °C	61	0.102	0.169

Table 4.26 shows that Trial 10 samples had higher ESA values for all three annealing temperatures than Trial 9. Although the average particle size increased with increasing annealing temperatures, Trial 9 and Trial 10 did not exhibit decreasing ESA values with increasing average particle size unlike Trial 7 and Trial 8. This suggests that for Trial 9 and Trial 10 Cu dissolution amount is higher for 800 °C and 950 °C than 600 °C resulting much lower average particle sizes. However, the surface composition effects upon potential cycling could not be dismissed [27, 126]. The highest ESA for Trial 10 was obtained at 800 °C as 131 m²/g and for Trial 9 also at 800 °C as 44 m²/g. Whereas the lowest ESA was at 600 °C for Trial 9 which was 21 m²/g. Changing Pt:Cu mole ratios resulted in a significant difference between the ESA values of Trial 9 and Trial 10 indicating with higher Cu, content deposition order started to effect the resulting Pt-Cu nanoparticle morphologies. Changing Pt:Cu ratios also

affected the ORR activities of Trial 9 and Trial 10 after electrochemical dealloying. The mass activity values of Trial 9 samples increased from 0.001 A/mg_{Pt} (600 °C) to 0.045 A/mg_{Pt} (800 °C) and to 0.063 A/mg_{Pt} (950 °C). Trial 9 (First Cu(tfa)₂ on CA19) showed significantly improved mass and specific activity values for 800 °C and 950 °C when compared to Trial 7. This indicates that when Cu concentration is higher, Cu dissolution from ORR active sites is favored creating unblocked Pt ORR active sites most probably by the formation of Pt shell surrounding a Pt-Cu core nanoparticle. However Trial 9 600 °C did not show any activity similar to Trial 7. Since the Pt:Cu ratios obtained from XRD for Trial 9 600 °C is similar to Trial 7, the lack of activity can be explained by blocked Pt active sites due to lower Cu dissolution amount. For Trial 10 mass activity samples increased from 0.010 A/mg_{Pt} (600 °C) to 0.123 A/mg_{Pt} (800 °C) and to 0.102 A/mg_{Pt} (950 °C). Trial 10 (First Pt(cod)me₂ on CA19) 800 °C showed higher mass activity than the commercial Pt/C electrocatalyst [117] and Pt/CA19 samples presented in Section 4.1.4. This is most probably due to the shift of the d-band center of the dealloyed Pt-Cu nanoparticles creating a surface which is more active than pure Pt nanoparticle. Trial 10 950 °C showed approximately the same mass activity (0.102 A/mg_{Pt}) as the commercial Pt/C at higher average particle size [117]. The specific activity had a similar trend as mass activity, increasing for Trial 9 from 0.004 mA/cm² (600 °C) to 0.107 mA/cm² (800 °C) and to 0.156 mA/cm² (950 °C) and for Trial 10 it increased from 0.015 mA/cm² (600 °C) to 0.090 mA/cm² (800 °C) and to 0.165 mA/cm² (950 °C). The specific activity values of Trial 10 600 °C and 800 °C was lower than Trial 9 due to the higher ESA values obtained for this samples.

4.2.6. Pt-Cu/CA19 and Pt-Cu/Carbon Black Composites Prepared via Sequential *In-situ* SCD Followed by *Ex-situ* Annealing and Having Pt:Cu Mole Ratios of 1:3

In order to compare the Pt-Cu alloy nanoparticle size, nanoparticle morphology and electrochemical behaviors of carbon black and carbon aerogel, two additional samples were

prepared but this time sequential *in-situ* SCD approach was applied. Both samples were prepared by adsorbing first Pt(cod)me₂ on CA19 or Vulcan. Prepared samples were then annealed at 800 °C under flowing N₂ since the best performance obtained for Pt-Cu/CA19 samples annealed at 800 °C. The detailed explanations of the samples are given in Table 4.27.

Table 4.27: Pt-Cu/CA and Pt-Cu/Vulcan samples prepared by sequential *in-situ* SCD followed by *ex-situ* annealing with Pt:Cu mole ratio of 1:3 and the explanation of deposition order.

Sample	Explanation
Pt-Cu/CA19 <i>in-situ</i>	First Pt(cod)me ₂ on CA19 then Cu(tfa) ₂ on Pt/CA19
Pt-Cu/Vulcan <i>in-situ</i>	First Pt(cod)me ₂ on Vulcan then Cu(tfa) ₂ on Pt/Vulcan

The metal content of the prepared Pt-Cu/CA19 and Pt-Cu/Vulcan samples were determined gravimetrically and also using XRF analysis before annealing and given in Table 4.28.

Table 4.28: Pt and Cu weight percentages of the Pt-Cu/CA *in-situ* and Pt-Cu/Vulcan *in-situ* samples before annealing.

Sample	Metal Loadings (wt.%)			
	Gravimetric		XRF	
	Pt	Cu	Pt	Cu
Pt-Cu/CA19 <i>in-situ</i>	23.2	22.6	22.6	21.4
Pt-Cu/Vulcan <i>in-situ</i>	23.2	22.7	22.9	22.0

The prepared samples were subjected to XRD to determine alloying degree and average Pt-Cu nanoparticle size. Figure 4.48 shows XRD of Pt-Cu/CA and Pt-Cu/Vulcan samples prepared via sequential SCD followed by *in-situ* conversion and *ex-situ* annealing.

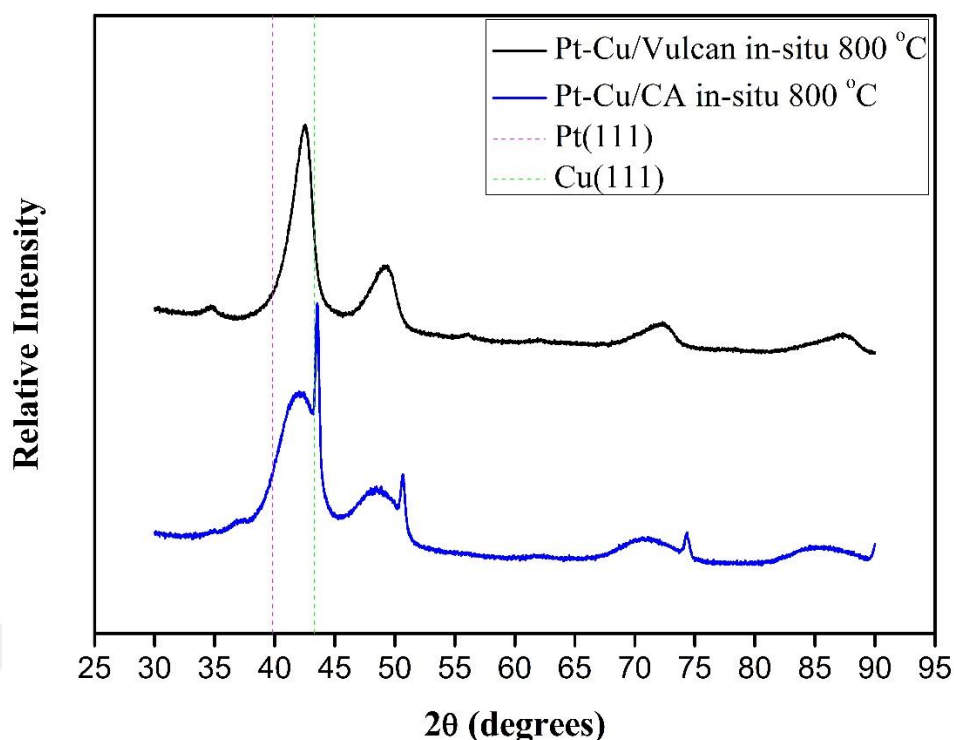


Figure 4.48: XRD of Pt-Cu/CA19 and Pt-Cu/Vulcan prepared using sequential *in-situ* SCD with Pt:Cu mole ratios of 1:3 followed by annealing at 800 °C.

Figure 4.48 shows that even though predetermined Pt and Cu contents, deposition, conversion and annealing conditions were exactly the same for both CA19 and Vulcan, the resulting Pt-Cu samples had different XRD profiles which suggests that support properties have a significant effect on the alloying process and nanoparticle morphology. Pt-Cu/CA19 sample exhibited face-centered cubic Cu reflection peaks and a small cubic Cu₂O {111} reflection peak along with face-centered cubic Pt-Cu alloy reflection peaks whereas Pt-Cu/Vulcan sample exhibited Pt-Cu alloy peaks and monoclinic CuO peak at $2\theta=35.5^\circ$. Also the shift in all Pt-Cu alloy reflections were higher at Pt-Cu/Vulcan than the shift in Pt-Cu/CA19 suggesting alloying degree is higher in Pt-Cu/Vulcan. Furthermore, the Pt-Cu alloy reflection peaks were broader for Pt-Cu/CA19 than Pt-Cu/Vulcan indicating a smaller average Pt-Cu alloy particle size.

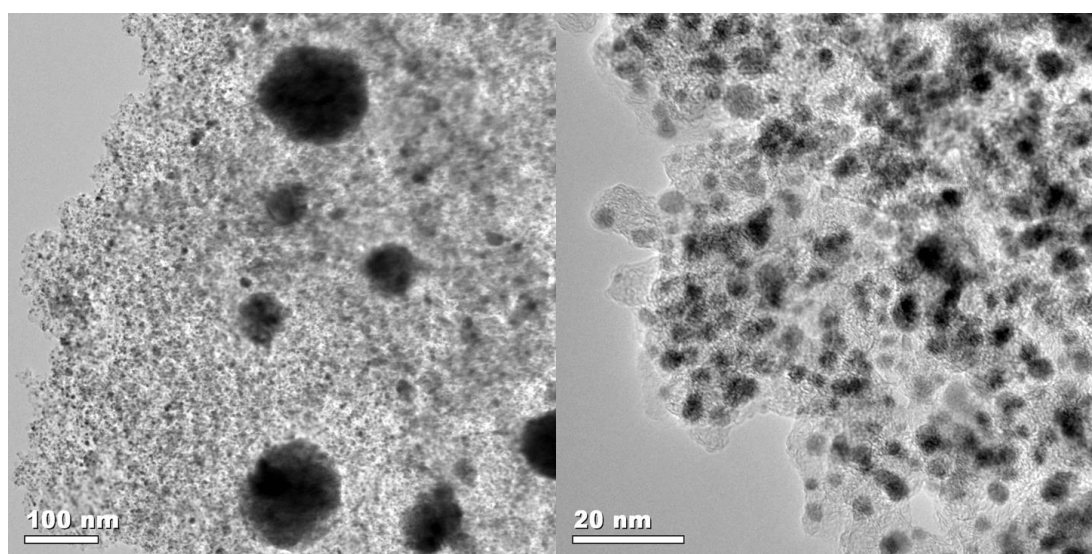
Vegard's law was used to determine the mole ratios of Pt and Cu. Table 4.29 summarizes the mole ratios obtained from XRD and XRF.

Table 4.29: Pt:Cu mole ratios of Pt-Cu/CA19 *in-situ* and Pt-Cu/Vulcan *in-situ* samples obtained from XRF and XRD.

Sample	Annealing Temperature	Mole Ratios (Pt:Cu)	
		XRD	XRF
Pt-Cu/CA19 <i>in-situ</i>	800 °C	31:69	25:75
Pt-Cu/Vulcan <i>in-situ</i>	800 °C	23:77	26:74

Table 4.29 shows that based on XRF, Pt-Cu/CA19 and Pt-Cu/Vulcan had intended Pt:Cu molar ratios of approximately 25:75 upon adsorption and *in-situ* conversion and the Pt:Cu mole ratios obtained from XRD were closer to XRF for both samples. In fact the alloying degree was the best in the samples prepared by *in-situ* SCD among all prepared Pt-Cu samples. This indicates that *in-situ* conversion may be a more suitable approach to prepare supported bimetallic nanoparticles.

Nanoparticle morphologies of Pt-Cu/CA19 and Pt-Cu/Vulcan were characterized using HRTEM. HRTEM images with particle size distributions were presented in Figure 4.49 and 4.50, respectively.



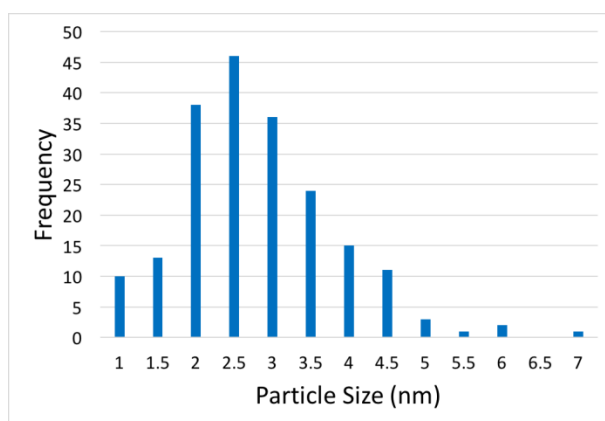


Figure 4.49: HRTEM images and particle size distributions of Pt-Cu/CA19 *in-situ* annealed at 800 °C.

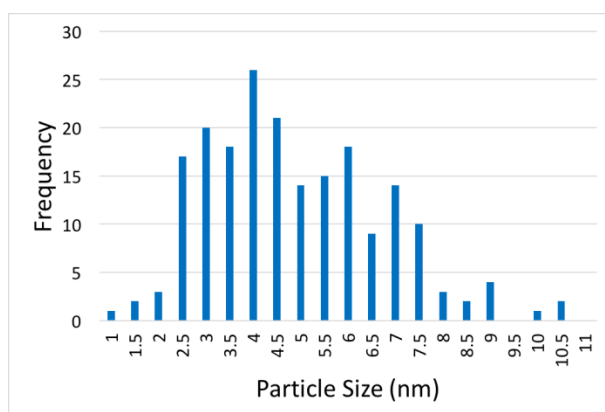
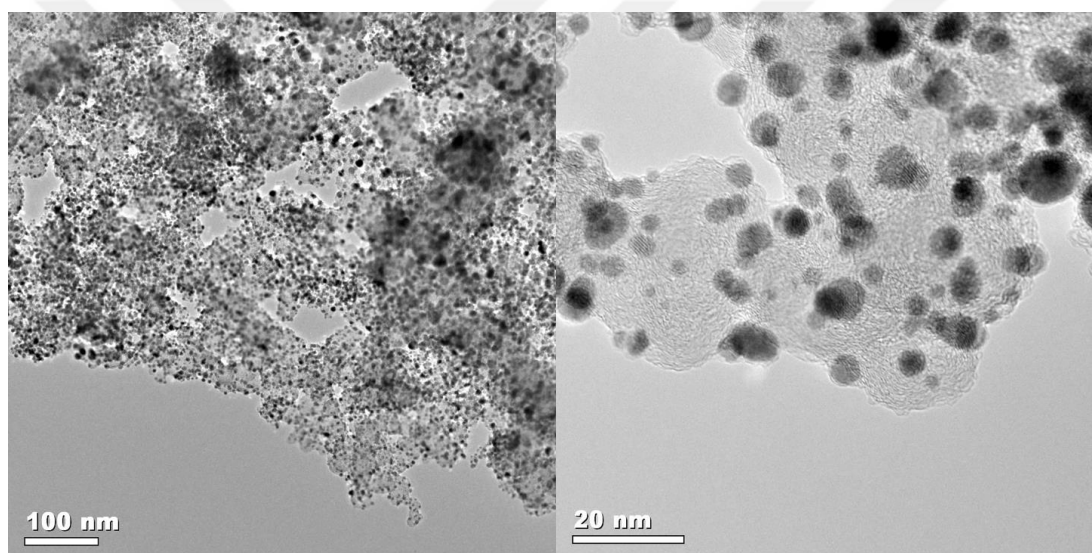
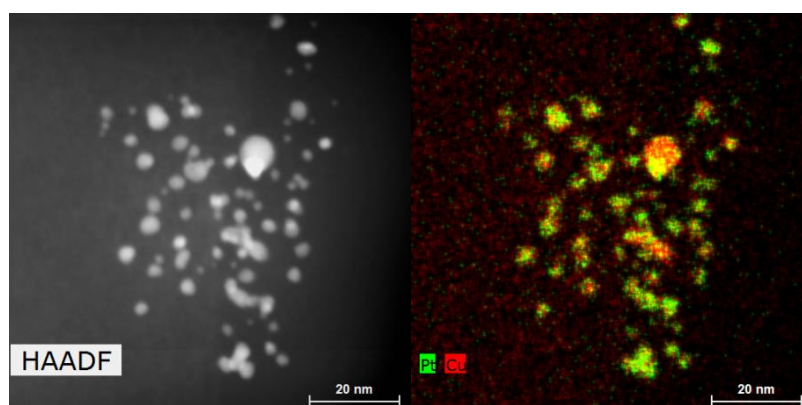


Figure 4.50: HRTEM images and particle size distributions of Pt-Cu/Vulcan *in-situ* annealed at 800 °C.

Figure 4.49 shows that Pt-Cu/CA19 sample prepared by *in-situ* conversion exhibited large particles same as previous Pt-Cu/CA19 samples prepared by *ex-situ* conversion. These large particles were probably the separate Cu or Cu₂O nanoparticles that were also visible at the XRD of the same sample which may explain the small difference between the Pt:Cu mole ratios obtained from XRD and XRF. Figure 4.50 indicates that Pt-Cu/Vulcan did not exhibit any large particles consistent with the XRD. Although Pt-Cu/CA19 showed some large particles, these were not frequent in the sample and the distribution of Pt-Cu nanoparticles on both CA19 and Vulcan were quite homogenous. Furthermore, TEM of Pt-Cu/Vulcan sample showed the particle size of Pt-Cu alloy nanoparticles was higher than the particle size of Pt-Cu/CA19 which is also in good agreement with the XRD of the samples. Moreover, the particle size distribution of Pt-Cu/Vulcan was much broader than the particle size distribution of Pt-Cu/CA19.

EDX mapping was done on the samples to determine the effect of support material to the Pt-Cu alloy nanoparticle morphology. The HAADF and EDX mapping images of Pt-Cu/CA19 were given in Figure 4.51 and Figure 4.52 and the HAADF and EDX mapping images of Pt-Cu/Vulcan were presented in Figure 4.53.



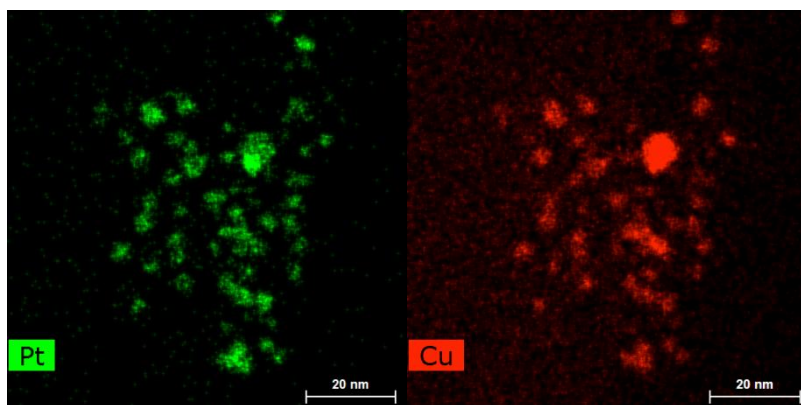


Figure 4.51: HAADF and EDX mapping images of Pt-Cu/CA19 *in-situ* annealed at 800 °C.

Figure 4.51 shows that Pt and Cu on CA19 prepared using *in-situ* SCD disordered alloy nanoparticles. Some these nanoparticles were richer in Cu and some of them were richer in Pt. However, a uniform composition of Pt and Cu was not obtained.

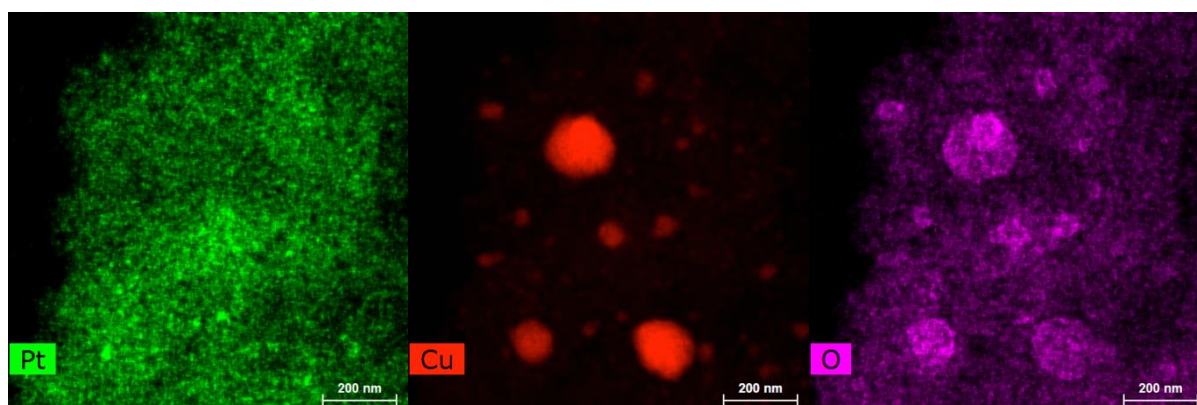
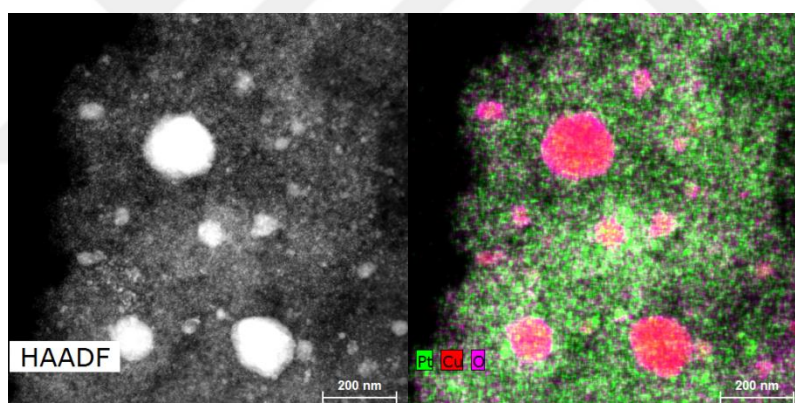


Figure 4.52: HAADF and EDX mapping images of oxide rich nanoparticles in Pt-Cu/CA19 *in-situ* annealed at 800 °C.

Figure 4.52 shows the EDX mapping images of the large particles observed on the TEM images of Pt-Cu/CA19. As suspected, EDX showed that these large particles were either unalloyed Cu nanoparticles or unalloyed Cu₂O nanoparticles. Whereas Pt nanoparticles were distributed homogenously throughout the sample in the form of Pt-Cu alloys. These EDX mappings are in very good agreement with the XRD of this sample.

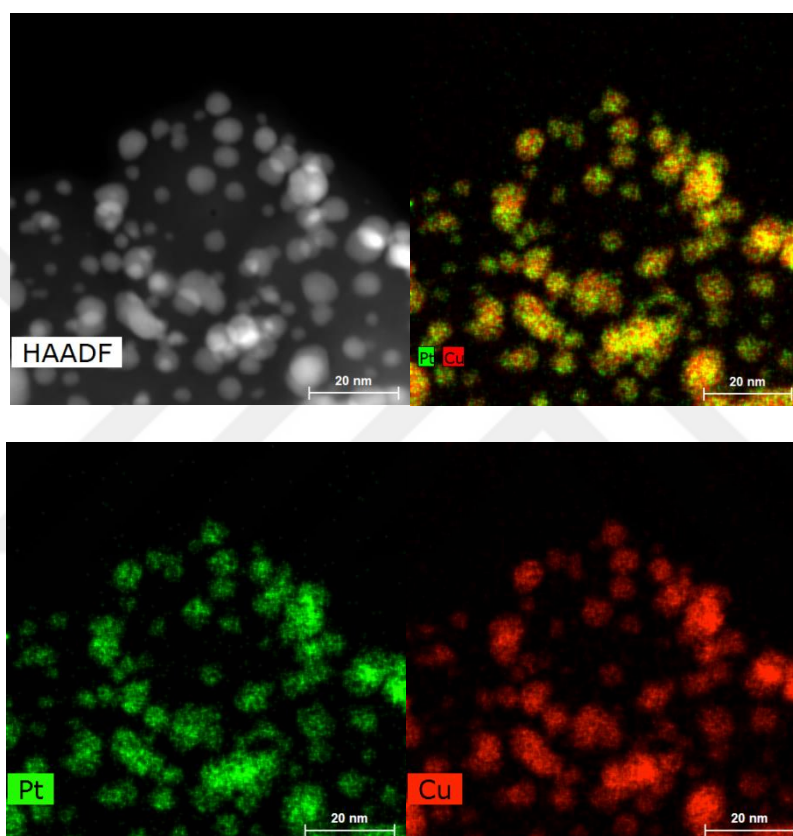


Figure 4.53: HAADF and EDX mapping images of Pt-Cu/Vulcan *in-situ* annealed at 800 °C.

Figure 4.53 indicates that the composition of Pt-Cu alloy nanoparticles in Pt-Cu/Vulcan sample were more uniform than Pt-Cu/CA19 sample. This probably due to the porous structure of CA19. Most probably during first step of the sequential deposition and in-situ conversion Pt nanoparticles either located inside pores of the CA19 or on the surface of CA19 and when Cu(tfa)₂ was deposited on the second step and most likely some of the Cu(tfa)₂ cannot penetrate through the smaller pores which are already blocked by Pt nanoparticles and therefore they

remain on the surface of the larger pores of the CA19 as in the case of the unalloyed Cu or Cu₂O nanoparticles. On the other hand, Vulcan do not have a porous structure rather it is consisted of very uniform spherical carbon nanoparticles and therefore what is deposited on Vulcan stays on the surface. This probably aids the alloying process since neither Pt nor Cu can be trapped unlike CA19.

Average particle sizes of the alloyed Pt-Cu nanoparticles on CA19 and Vulcan were determined from XRD using Scherrer Equation and {220} plane angle and also from TEM images. The average particle sizes of Pt-Cu/CA19 and Pt-Cu/Vulcan annealed at 800 °C were given in Table 4.30.

Table 4.30: The average Pt-Cu nanoparticle sizes of Pt-Cu/CA19 *in-situ* and Pt-Cu/C *in-situ* samples having Pt:Cu mole ratios of 1:3 and annealed at different temperatures.

Sample	Annealing Temperature	Particle Size (nm)	
		XRD	TEM
Pt-Cu/CA19 <i>in-situ</i>	800 °C	2.7	2.8±1.0
Pt-Cu/Vulcan <i>in-situ</i>	800 °C	4.6	4.9±1.9

Table 4.30 shows that the average particles sizes obtained from XRD and TEM are in good agreement for both samples. However the average Pt-Cu nanoparticle size of Pt-Cu/Vulcan was almost two times higher than the average Pt-Cu nanoparticle size of Pt-Cu/CA19 sample although both samples were prepared under exact conditions thus the difference was most likely originated from the different support properties. Due to porous structure of CA19, Pt-Cu alloy nanoparticles probably cannot migrate through each other even at elevated annealing temperatures whereas Pt-Cu nanoparticles on the surface of Vulcan can easily became mobile and migrate through each other forming larger alloy nanoparticles at elevated annealing temperatures. The difference in the average particle sizes between Pt-

Cu/CA19 and Pt-Cu/Vulcan can also be originated from the metal-support interaction. The interaction of Pt-Cu nanoparticles and CA19 may be stronger than the interaction between Pt-Cu and Vulcan and therefore, migration of nanoparticles at elevated temperatures less likely to occur. Furthermore, the particle sizes from the TEM images for both samples were quite uniform. However, standard deviations from the average is much higher in the Pt-Cu/Vulcan (± 1.9 nm) than the standard deviations in Pt-Cu/CA19 which is ± 0.1 nm suggesting that Pt-Cu/CA19 sample had more homogenous distribution of Pt-Cu nanoparticles with a narrower average particle size distribution than Pt-Cu/Vulcan.

The electrochemical behaviors of Pt-Cu/CA19 and Pt-Cu/Vulcan samples having Pt:Cu mole ratios of 1:3 prepared via sequential deposition followed by *in-situ* conversion and *ex-situ* annealing at 800 °C were characterized using CV. Cyclic voltammograms taken in N₂ saturated acidic electrolyte were presented in Figure 4.54.

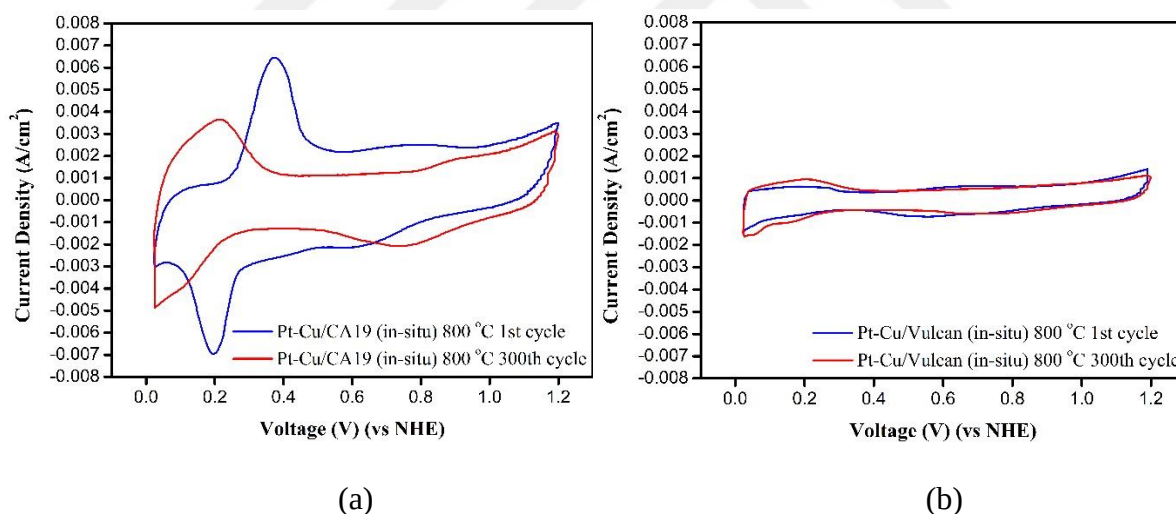


Figure 4.54: Cyclic voltammograms of (a) Pt-Cu/CA19 and (b) Pt-Cu/Vulcan annealed at 800 °C taken in N₂ saturated HClO₄ electrolyte (1st and 300th cycles).

Figure 4.54 indicates that CA19 and Carbon black (Vulcan) shows different electrochemical behaviors when used as catalyst support. Figure 4.55 (a) shows the cyclic voltammogram of Pt-Cu/CA19 sample exhibited bulk (unalloyed or excess) Cu

dissolution/redeposition peak in the potential range of 0.2 V to 0.4 V and Cu dissolution/redeposition peaks in the range 0.6 V to 0.8 V associated with the underpotentially deposited (alloyed) Cu dissolution/redeposition at the initial cycles (blue line). Whereas, cyclic voltammograms of Pt-Cu/Vulcan only exhibited the underpotentially deposited (alloyed) Cu dissolution/redeposition peaks at the initial cycles. This suggests that the two samples have different alloy nanoparticle morphologies. The Pt-Cu alloy nanoparticles present in Pt-Cu/Vulcan showed more uniform compositions throughout the nanoparticles on EDX mapping images which may explain the lack of excess or unalloyed Cu dissolution/redeposition peaks. So that the Cu only dissolved through the alloyed Pt-Cu nanoparticles creating a Pt-rich shell over a Pt-Cu core. Whereas Pt-Cu/CA19 sample had a non-uniform composition of Pt and Cu throughout alloy nanoparticles and the bulk Cu dissolution peaks were probably originated from these excess Cu present in the Pt-Cu alloy nanoparticles as well as the unalloyed Cu which was seen at the XRD of Pt-Cu/CA19. This excess or unalloyed Cu dissolution along with the Cu dissolution from Pt-Cu alloy nanoparticles most probably created similar dealloyed Pt-Cu nanoparticle morphology as in Pt-Cu/Vulcan; a Pt-rich shell over a Pt-Cu core however the shell thickness of Pt-Cu/CA19 was probably higher than the Pt-Cu/Vulcan sample. Furthermore, at 300th cycle, both samples cyclic voltammograms resembled to the supported Pt with hydrogen adsorption/desorption peaks observed in the 0 V and 0.3 V region and Pt oxidation/reduction peaks at around 0.7 V and 0.8 V for cathodic and anodic directions, respectively for both samples. Hydrogen adsorption/desorption peak increased at 300th cycle for both samples but this increase was greater for Pt-Cu/CA19 sample due to more Cu dissolution. Moreover, Pt-Cu/Vulcan sample exhibited significantly lower current densities throughout the analysis which can be explained by the higher average particle size of Pt-Cu alloy nanoparticles in Pt-Cu/Vulcan. The average particle size of Pt-Cu/CA19 was most probably less than the average particle size of Pt-Cu/Vulcan after the electrochemical

dealloying since the Cu content of the two samples were approximately the same and the Cu dissolution of Pt-Cu/CA19 was much more than the Cu dissolution of Pt-Cu/Vulcan.

RDE experiments were conducted in an O_2 saturated environment to simulate the ORR in an acidic electrolyte after electrochemical dealloying. Mass activity and specific activity values were calculated by taking the current density value at 0.85 V at 1600 rpm to exclude the mass transport effects. The ORR curves (with Koutecky-Levich plots as inset) of Pt-Cu/CA19 and Pt-Cu/Vulcan annealed at 800 °C were presented in Figure 4.55.

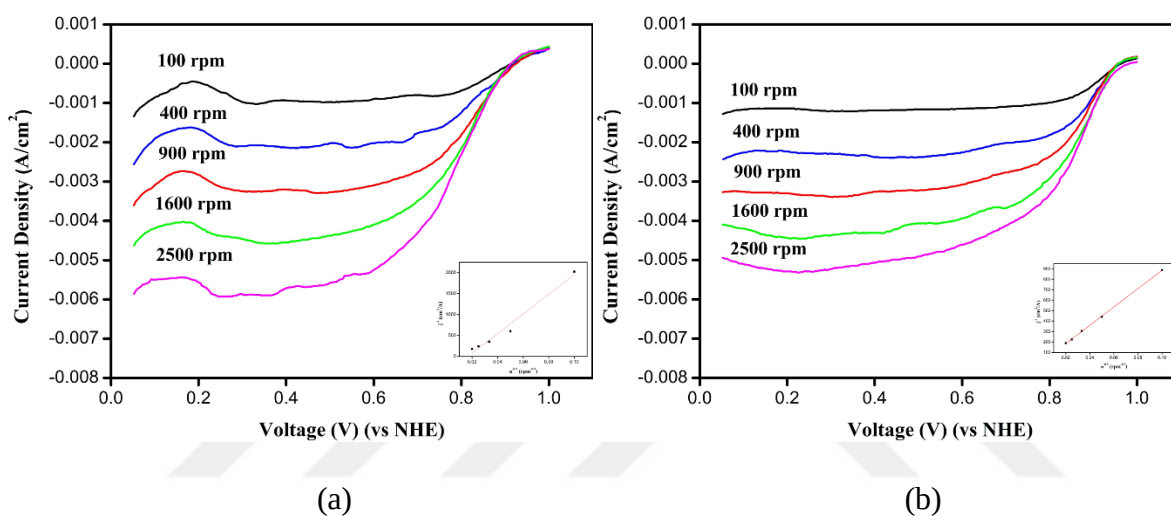


Figure 4.55: ORR curves of (a) Pt-Cu/CA19 and (b) Pt-Cu/Vulcan annealed at 800 °C after 300 cycles, recorded with a scan rate of 10 mV/s.

ORR curves of the samples exhibit an expected trend, namely that the current densities increase with increasing rotation speed at mass transfer controlled region (0.05 V-0.7 V). However, lower current densities were observed for Pt-Cu/Vulcan than Pt-Cu/CA19 at the mass controlled region. Moreover, Pt-Cu/CA19 sample showed peaks in all five rotation speeds in between 0.05 V and 0.2 V whereas Pt-Cu/Vulcan had smoother ORR curves. Also current densities decreased rapidly after 0.6 V for Pt-Cu/CA19 for all rotation speeds. On the other hand, the decrease in current densities is less significant in Pt-Cu/Vulcan indicating better catalytic activity.

Electrocatalytic properties of Pt-Cu/CA19 and Pt-Cu/Vulcan annealed at 800 °C were given in Table 4.31. ESA values of the samples were calculated using 300th cycles and area under the hydrogen adsorption region.

Table 4.31: Electrocatalytic properties of Pt-Cu/CA19 and Pt-Cu/Vulcan annealed at 800 °C.

Sample	Annealing Temperature	ESA (m ² /g)	MAc (A/mg _{Pt})	SAC (mA/cm ²)
Pt-Cu/CA19 <i>in-situ</i>	800 °C	137	0.044	0.032
Pt-Cu/Vulcan <i>in-situ</i>	800 °C	48	0.087	0.181

Table 4.31 shows that Pt-Cu/CA19 had a significantly higher ESA value than Pt-Cu/Vulcan. Since the average particle size of Pt-Cu/CA19 was nearly half of the average particle size of Pt-Cu/Vulcan (2.8 nm and 4.9 nm, respectively) before electrochemical dealloying, it was reasonable to assume the average particle size of Pt-Cu/CA19 after electrochemical dealloying (after dissolution of Cu) was still smaller than the average particle size of Pt-Cu/Vulcan hence the higher ESA value for Pt-Cu/CA19 was expected. The ESA of Pt-Cu/CA19 after electrochemical deploying was determined as 137 m²/g and the ESA of Pt-Cu/Vulcan was determined as 48 m²/g. The mass activity values obtained for Pt-Cu/CA19 and Pt-Cu/Vulcan were 0.044 A/mg_{Pt} and 0.087 A/mg_{Pt}, respectively. The mass activity of Pt-Cu/CA19 was significantly lower than the mass activity of Pt-Cu/Vulcan which was anticipated from the ORR curves. This difference in the mass activities may be the result of several factors. The metal-support interaction (MSI) is quite important in the sense that it affects the morphology of the formed nanoparticle i.e. depending on the MSI different concentration of terrace and edge sites on the outer surface of the nanoparticle may occur due to the different nanoparticle shape [93, 95]. Therefore, a different activity is obtained. Pt-Cu alloy nanoparticles may adsorbed on CA19 much strongly than on Vulcan creating less active sites for ORR giving

lower mass activity value at the same Pt:Cu mole ratios. Another explanation for the low mass activity of Pt-Cu/CA19 may be related to the average particle size of Pt-Cu nanoparticles and the shell thickness of Pt after electrochemical dealloying. If the Pt shell is thicker in Pt-Cu/CA19 than in Pt-Cu/Vulcan, the d-band center may not be lowered to the desired value and with the smaller average particle size mass activity value obtained for Pt-Cu/CA19 became lower than the mass activity value of Pt-Cu/Vulcan. The specific activity values obtained for Pt-Cu/CA19 and Pt-Cu/Vulcan were 0.032 mA/cm^2 and 0.131 mA/cm^2 , respectively. Same observations made for mass activity also valid for specific activity values.



Chapter 5: Conclusion and Future Work

For the first part of this study, Pt/CA electrocatalyst using CAs with different pore sizes (6, 8 and 19 nm) were successfully prepared via SCD. The CA pore size did not influence the Pt particle size. Increasing the precursor decomposition temperature resulted in increasing Pt particle sizes regardless of the CA employed. This increase in Pt particle size became significant after 600°C. Data obtained from both XRD and TEM were in good agreement and showed that the Pt particle sizes were between 1.1 nm and 6.3 nm. Furthermore, TEM images revealed that all of the Pt/CA samples have a homogenous distribution of Pt nanoparticles with no indication of any significant agglomeration. The ESA for Pt/CA6 400°C, Pt/CA8 400 °C and Pt/CA19 400 °C were determined using the area under the hydrogen adsorption region; in the initial cycles this approach gave values of 36, 97 and 126 m²/g, respectively. All three Pt/CAs processed at 400 °C exhibited decreasing ESA values with continuous cycling: Pt/CA8 showed the largest decrease (42%) whereas Pt/CA6 had an ESA loss of only 19%. Pt/CA19 showed a moderate ESA loss (31%) after the 200th cycle, but it still has the highest ESA. RDE analyses revealed that Pt/CA6 and Pt/CA8 had lower mass activity (0.02 and 0.03 A/mg_{Pt}, respectively) towards ORR than Pt/CA19, which had a mass activity of 0.05 A/mg_{Pt}. This latter value is consistent with the Pt particle size of 1.7 nm in this sample. Pt/CA19 samples were characterized electrochemically to determine the effect of Pt particle size. The ESAs of the Pt/CA19 samples decreased as the Pt particle size increased from 1.7 nm to 5.3 nm. However, at 1.1 nm the ESA was lower than expected, and this was attributed to incomplete nanoparticle formation at this annealing temperature (200 °C), as the XRD data showed a shift of the (220) peak towards lower Bragg angle values. ESA values of the Pt/CA19 samples starting from Pt/CA19 600 °C showed increased hydrogen adsorption/desorption current densities due to Pt dissolution to acidic electrolyte at higher Pt particle sizes. The specific activity value exhibited a 6-fold

increase from Pt particles with diameters of 1.1 nm (0.04 mA/cm^2) to 1.9 nm (0.24 mA/cm^2) and decreased slightly at 2.7 nm and 5.3 nm (0.18 mA/cm^2 and 0.16 mA/cm^2 , respectively). The mass activity showed an increasing trend with increasing particle size, exhibiting again a 3-fold increase from 1.1 nm ($0.03 \text{ A/mg}_{\text{Pt}}$) to 2.7 nm ($0.1 \text{ A/mg}_{\text{Pt}}$) and declined to $0.01 \text{ A/mg}_{\text{Pt}}$ at 5.3 nm. The Pt/CA19 600 °C sample showed the best activity and stability among all of the catalysts prepared, with a mass activity of $0.1 \text{ A/mg}_{\text{Pt}}$, a specific activity of 0.24 mA/cm^2 , and an ESA value of $78 \text{ m}^2/\text{g}$.

For the second part of the study, the adsorption isotherms of $\text{Cu}(\text{tfa})_2$ were measured in 35 °C and 10.7 MPa in scCO_2 and fitted to Langmuir adsorption model. Pt-Cu/CA19 electrocatalyst were successfully prepared via SCD. Both simultaneous and sequential SCD methods were applied, however, simultaneous SCD resulted low Cu loadings due to competitive adsorption of $\text{Pt}(\text{cod})\text{me}_2$ and $\text{Cu}(\text{tfa})_2$ on CA19. Therefore, metal adsorption measurements were continued using sequential SCD. Single component adsorption isotherms of the metal precursors were used to approximate the metal content of the samples before the adsorption experiments. The metal loadings obtained gravimetrically and from XRF were very close to each other showing that SCD is an excellent method for the control of metal content. Decomposition of the precursor were carried out thermally under flowing H_2 and preliminary samples showed that decomposition at low temperatures was not enough to complete the alloying process. Most of the preliminary samples had unalloyed Cu or Cu_2O particles and the Pt:Cu mole ratios obtained from XRD were significantly different from the ones obtained from XRF. Thermal annealing process was applied in order to promote the alloy formation. We investigated the effect of deposition order, annealing temperature and metal composition on the average Pt-Cu particle size, dispersion, alloying and electrochemical behavior. Two sets of Pt-Cu/CA19 samples were prepared with Pt:Cu mole ratios 1:1 and 1:3 and in between these sets deposition order was also changed. Samples were annealed at three different temperatures (600

°C, 800 °C and 950 °C). Increasing annealing temperatures were found to promote the alloying process for all samples. Furthermore, the average Pt-Cu particles sizes increased with increasing annealing temperatures but XRD and TEM showed homogenous distribution of Pt-Cu alloy nanoparticle sizes with narrow particle size distributions. All prepared samples had average Pt-Cu particle sizes in the range of 1.8 nm and 4.5 nm, regardless of the deposition order and metal composition. XRD and EDX mapping showed that in all samples Pt-Cu nanoparticles formed face-centered disordered alloys with alloying degree increasing with increasing annealing temperatures. All samples were electrochemically dealloyed by continuous cycling resulting a Pt-enriched shell over a Pt-Cu core. Deposition order had a drastic effect on the electrocatalytic activity. When $\text{Cu}(\text{tfa})_2$ was adsorbed on CA19 first, the resulting electrochemical activity was significantly lower than the samples prepared by adsorbing $\text{Pt}(\text{cod})\text{me}_2$ first. The metal composition also found to effect the electrocatalytic activity. The samples with Pt:Cu mole ratios of 1:3 showed higher electrocatalytic activities than the ones with mole ratios of 1:1. The enhanced electrocatalytic activity was obtained for Pt-Cu/CA19 (with Pt:Cu mole ratio of 1:3) prepared by first depositing Pt and annealed at 800 °C. The ESA value of this sample was quite high, $137 \text{ m}^2/\text{g}$) when compared other samples and pure Pt. The mass activity was determined as $0.123 \text{ A}/\text{mg}_{\text{Pt}}$ which was higher than the mass activity of all Pt/CA19 samples showing alloying process results in enhanced electrocatalytic activity. The specific activity, on the other hand, was lower than Pt/CA19 samples with similar average particle sizes due to high ESA value.

The support effect on electrocatalytic activity was also investigated. For this purpose Pt-Cu/CA19 and Pt-Cu/Vulcan (carbon black) samples were prepared using *in-situ* sequential SCD method followed by *ex-situ* annealing at 800 °C with Pt:Cu mole ratios 1:3. *In-situ* sequential SCD resulted in higher degree of alloying than *ex-situ* sequential SCD, suggesting that *in-situ* SCD may be a better way to prepared supported bimetallic alloy nanoparticles. The

support significantly affected the average Pt-Cu particle sizes; when Vulcan was employed as support the average particle size was nearly two times higher (4.9 nm) when CA19 is employed as support (2.8 nm). Both samples showed homogenous distribution of Pt-Cu nanoparticles on support, however particle sizes distributions were broader for Pt-Cu/Vulcan than Pt-Cu/CA19. Also we have seen that different supports resulted in different electrochemical behaviors. The cyclic voltammograms of Pt-Cu/Vulcan did not show any unalloyed Cu dissolution peaks whereas these peaks were quite significant in Pt-Cu/CA19. Moreover, the mass activity of Pt-Cu/Vulcan (0.087 A/mg_{Pt}) was higher than the Pt-Cu/CA19 (0.044 A/mg_{Pt}) probably due to higher average particle size of Pt-Cu/Vulcan. Conversely the ESA of Pt-Cu/CA19 was significantly higher than the ESA of Pt-Cu/Vulcan sample (137 m²/g and 48 m²/g, respectively).

In the light of this results, the prepared electrocatalysts showed promising electrocatalytic activity towards ORR and HOR. All prepared Pt-Cu/CA19 samples had disordered alloy nanoparticle morphologies upon preparation, however; after dealloying, they form Pt-rich shell over a PtCu core which show higher activity towards ORR than pure Pt/CA19 samples. Some of the Pt-Cu/CA19 samples exhibited very low activity towards ORR suggesting not all of the Cu in the PtCu alloy nanoparticles were leached and remaining Cu atoms were cover the Pt active sites resulting a low activity. However, we could not achieve Pt-shell over a Cu-core type of nanoparticle morphology in any of the samples because PtCu system tends to form disordered alloy nanoparticles in the temperature range that the experiments were conducted. This may be achieved by directed synthesis with suitable metal precursors so that the ligands of Cu precursor can anchor the Pt precursor forming the desired Pt-shell/Cu-core nanoparticle structure. However, we successfully decreased the Pt amount by nearly 50% when compared to our Pt/CA19 samples and to the commercially available 30 wt.% Pt/C and obtain higher mass activity than both Pt/CA19 and commercial Pt/C. Fuel cell testing of the prepared samples can provide more insights to the electrocatalytic activity and the samples may exhibit

higher mass and specific activities in real fuel cell environment. Furthermore, nanoparticle morphologies of the samples after dealloying can be determined using chemical dealloying approach since dealloying can be done in larger amounts with this approach. Finally, SCD is an excellent method for the preparation of supported mono or bimetallic nanoparticles with good control of the metal loading, average metal particle size and metal dispersion.



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APPENDIX

Mathcad code for the solution of Langmuir equation for single component adsorption isotherm of Cu(tfa)₂

Notations :

q	Uptake (mol/kg)
C	Concentration (mol/m ³)
Q0	Maximum uptake
K1	Equilibrium coefficient

Data :

$$q := \begin{pmatrix} 0 \\ 0.398 \\ 0.507 \\ 0.602 \\ 0.629 \\ 0.630 \end{pmatrix} \quad C := \begin{pmatrix} 0 \\ 0.513 \\ 1.471 \\ 3.697 \\ 5.984 \\ 8.390 \end{pmatrix}$$

$$Q0 := 1 \quad K1 := 1$$

$$Fa(C, Q0, K1) := \frac{K1 \cdot Q0 \cdot C}{1 + K1 \cdot C}$$

$$j := 0..5 \quad F_j := Fa(C_j, Q0, K1)$$

$$\text{Given} \quad \sum_j \left(q_j - Fa(C_j, Q0, K1) \right)^2 = 0$$

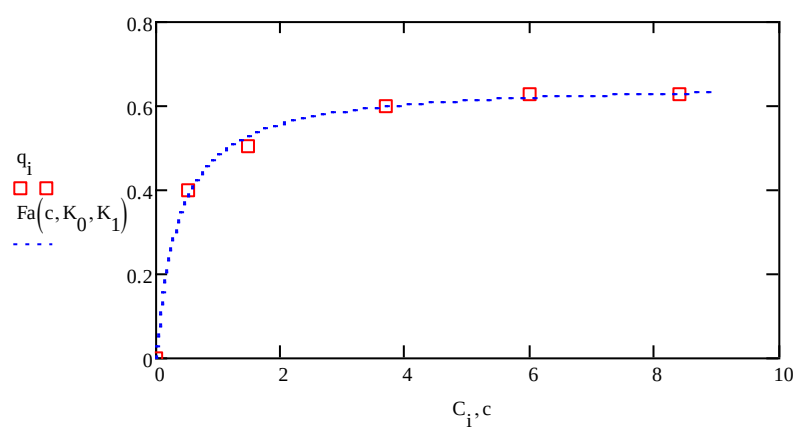
$$K_{xx} := \text{Minerr}(Q0, K1)$$

Result:

$$K = \begin{pmatrix} 0.657 \\ 2.79 \end{pmatrix} \quad 1 - \text{ERR} = 0.999$$

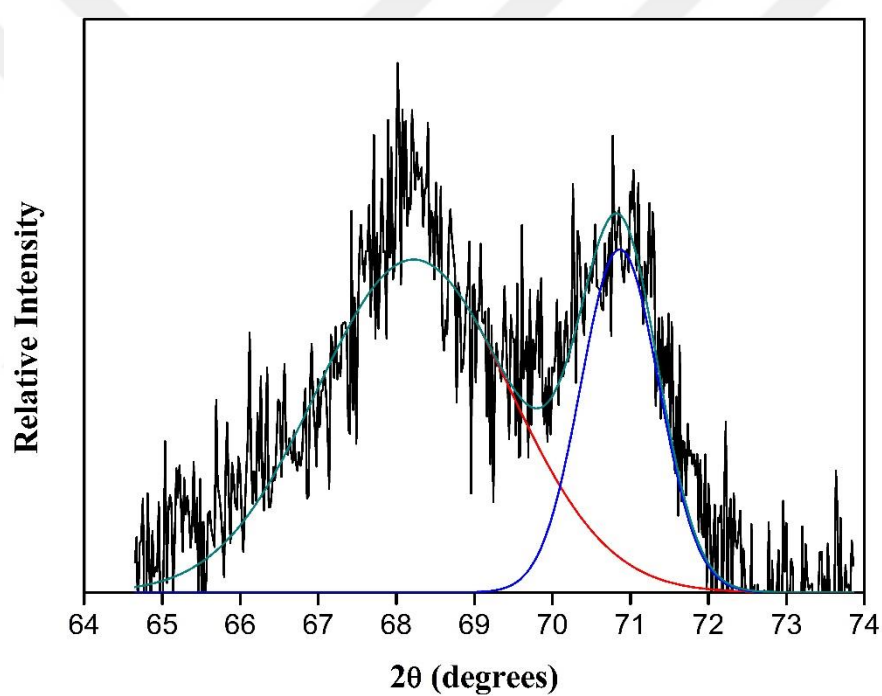
Plotting the the curve:

$$C_{xx} := 0, 0.0001..9$$



Deconvolution of XRD {220} peaks of Pt-Cu/CA19 Samples

Deconvoluted XRD of Trial 4



Deconvoluted XRD of Trial 7 600 °C