

Utilization of Ethanol to Enhance Photocatalytic NO_x Oxidation and Storage on TiO₂

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Utilization of Ethanol to Enhance Photocatalytic NO_x Oxidation and Storage on TiO₂

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June 2023

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Utilization of Ethanol to Enhance Photocatalytic NO_x Oxidation and Storage on TiO₂

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Nitrogen oxides (NO_x), especially nitric oxide (NO) and nitrogen dioxide (NO₂) severely affect human health. In this regard, semiconductor photocatalysis present an appealing approach, since the only requirements for this procedure are sunlight, water and oxygen which are naturally abundant. Despite its favorable properties like chemical inertness, long-term stability and low cost, titania (TiO₂) has a lower NO_x abatement performance due to its low selectivity towards nitrites/nitrates as final product. In this work, we report a simple monohydric alcohol impregnation protocol at mild temperature range to synthesize colored TiO₂ nanoparticles for efficient photocatalytic NO_x oxidation and storage (PHONOS) application under UVA illumination. The ethanol induced coloration of commercial benchmark TiO₂ (P25) and photocatalytic activity for NO_x abatement were observed to be dependent on heat-treatment temperature; the highest activity was obtained at 150 °C. Comprehensive analyses of the optimized photocatalyst suggest the presence of surface functionalities of adsorbed formic acid and acetate. The doping of TiO₂ with these *in situ* generated impurities results in the generation of Ti³⁺ and

oxygen vacancies (V_{O} s) (intrinsic defects) which are aimed to be observed using X-Ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy and Diffuse Reflectance UV-Visible Spectroscopy (DR-UV-Vis). These fine-tuned materials demonstrated superior photocatalytic performance surpassing conventional P25 benchmark in short (1 h) and long term (15 h) evaluation studies. Special attention has been paid to the selectivity of the designed photocatalyst toward nitrate/nitrite formation and CaO was introduced as NO_x storage domains to further improve the stability of best performing photocatalysts for extended time period.

Keywords: Titanium Dioxide, Ethanol, Reduced Titania, Photocatalytic NO_x Abatement, DeNO_x Index

ÖZET

Fotokatalik NO_x Yükseltgenmesi ve Depolanmasının Etanol ile Zenginleştirilmiş TiO₂ Kullanılarak Artırılması

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Azot oksitlerin (NO_x), özellikle azot monoksit (NO) ve azot dioksitin (NO₂) insan sağlığına ciddi olumsuz etkileri vardır. Bu nedenle, yarı iletken malzemelerin kullanıldığı fotokatalitik yöntemler, bu tür zehirli gazların gideriminde ilgi çekici bir yaklaşımdır. Fotokatalitik süreçlerde, sadece doğada bol bulunan güneş ışığı, su ve oksijen kullanılması yeterlidir. Kimyasal dayanıklılığı, uzun süreli kararlılığı ve ucuz maliyetine karşın, titanyum dioksitin (TiO₂), NO_x giderim performansı ve katalitik seçiciliği düşüktür. Bu çalışmada, Degussa P25'e basit bir alkol yüklemesi yapılarak, düşük sıcaklıklarda elde edilmiş, renkli TiO₂ nanopartikülleriyle, UV-A ışıması altında, NO_x türlerinin fotokatalitik oksidasyonu ve depolanması (PHONOS) araştırılmıştır. Etanolle işlem sonucu renklen ticari TiO₂'nin (Degussa P25), NO_x gideriminde fotokatalitik aktivitesinin TiO₂'ye uygulanan sıcaklık işlemiyle değişkenlik gösterdiği bulunmuş ve en yüksek fotokatalitik aktivite 150 °C sıcaklıkta elde edilmiş örnekte gözlenmiştir. Optimize edilmiş fotokatalizörün detaylı analizi, yüzeyde adsorplanmış formik asit ve asetat fonksiyonelliklerinin varlığını göstermiştir. TiO₂'e uygulanan bu işlem sayesinde, Ti³⁺ ve

oksijen boşluklarının oluştuğu öngörölmüş ve bunun gözlemlenmesi amacıyla X-Ray Fotoelektron Spektroskopisi (XPS), Raman Spektroskopisi ve DR-UV-Vis Spektroskopisi (DR-UV-Vis) analizleri yapılmıştır. Bu şekilde zenginleştirilmiş titanya fotokatalizörlerinin, ticari olarak kullanılan P25 fotokatalizöründen hem kısa (1 saat), hem de uzun (15 saat) süreli deneylerde daha verimli çalıştığı gözlemlenmiştir. Son olarak, yüzeyde oluşan nitrat/nitrit türlerine yönelik seçiciliği arttırmak için CaO eklenmiştir ve yüzeydeki NO_x depolama alanlarının depolama kapasitelerinin arttırılması ve fotokatalitik aktivitenin uzun zamana yayılması sağlanmıştır.

Anahtar Kelimeler: Titanyum Dioksit, Etanol, İndirgenmiş Titanyum Dioksit, Fotokatalitik NO_x Arıtımı, DeNO_x indeks.

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1 Introduction

1.1 Overview on Air Pollution by NO_x

1.1.1 NO_x Emission

Nitrogen (N₂) and oxygen (O₂) are the most abundant gases in the atmosphere, compared to them, air pollutant gasses such as nitrogen oxides (NO_x), carbonaceous oxides (CO_x), sulfur oxides (SO_x) and various hydrocarbons (HCs) are in minute concentrations yet they cause serious health and environmental concerns [1]. Aforementioned pollutants can form from natural causes such as wildfires, volcanic eruptions etc., but also from anthropogenic sources such as combustion processes from power plants and transportation means which utilize fossil fuels as energy sources. Primary pollutants from these anthropogenic sources are nitrogen monoxide (NO) and nitrogen dioxide (NO₂), which both will be abbreviated as NO_x from herein, along with carbon monoxide (CO), sulfur dioxide (SO₂), ammonia (NH₃) and volatile organic compounds (VOCs). These compounds react when present in the atmosphere thereby causing secondary pollutants to evolve such as ground level ozone (O₃), sulfur trioxide (SO₃), sulfuric acid (H₂SO₄) and nitric acid (HNO₃) which are known to cause acid rains (Figure 1.1).

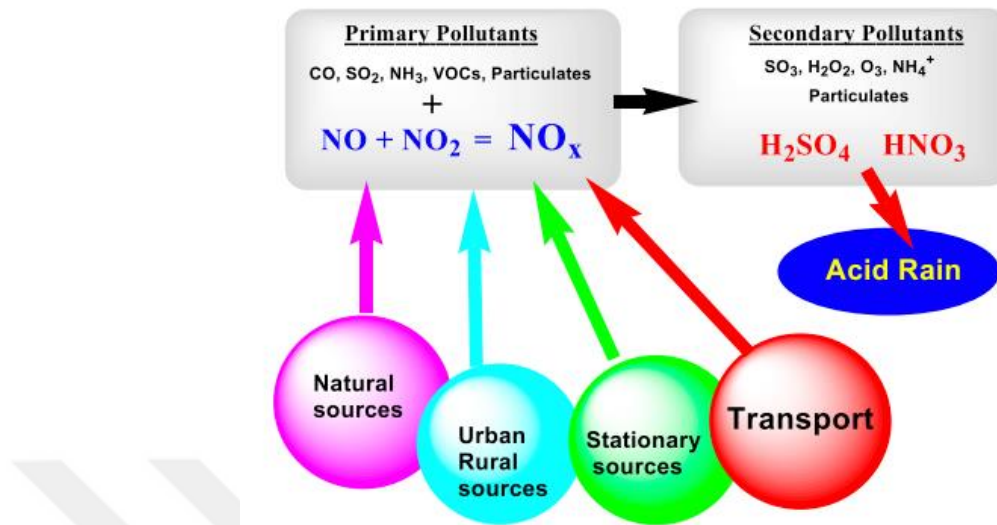


Figure 1.1: Illustration of sources of primary pollutants in the atmosphere and evolution of secondary pollutants and acid rain (Adapted from [2])

Air pollutants formed from natural sources are known to be the part of equilibrium and they are lesser concern. However, concentration of air pollutants have been known to increase in air from anthropogenic activities for last decades. That is why they were kept track in both European Union [3] (Figure 1.2) and in the United States [4] (Figure 1.3), and regulations to improve quality of the air have been implemented [5, 6].

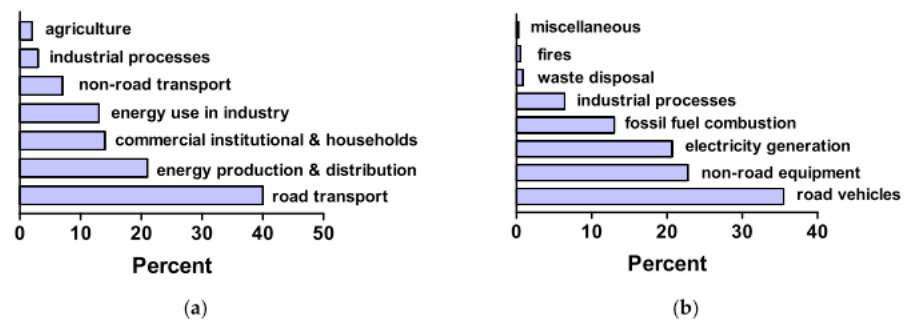


Figure 1.2: Percent emissions of NO_x gases a) 2011 year for European Union b) 2005 for the United States (Adapted from [2])

1.1.2. Generation of NO

As mentioned, NO_x species originate mainly from combustion processes, though NO species can form from oxidation of nitrogen (N₂) in the air or fuels that have nitrogen content in them (fuel-N) as NO, which is further oxidized to NO₂ in the presence of oxygen (Reaction 1-1).



Formation of NO from various sources is elaborated in this part.

1.1.2.1 Thermal NO

When sufficient heat is present, NO is generated from the reaction between N₂ and O₂ and this NO is called “Thermal NO”. The following reactions for NO formation from N₂ and O₂ were proposed by Zeldovich [7] (Reaction 1-2, Reaction 1-3).



Zeldovich mechanism is proven to be in accordance with the experimental data above the temperatures of 2000 °C.

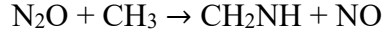
1.1.2.2 Flame Mechanism

Unlike Thermal NO mechanism, Flame Mechanism is an umbrella term in which formation of NO is caused by number of C, H, O and N containing compounds in the presence of rich flame zones. Some of these reactions are given below:

NNH Mechanism [8] (Reaction 1-4),



NO formation via N₂O [9] (Reaction 1-5),



(1-5)

1.1.3 NO_x Removal Methods

NO_x removal methods are separated into primary and secondary methods [10].

Primary methods aim to decrease formation of NO_x species directly in the combustion zone whereas secondary methods aim to decrease the concentration of NO_x species after the point of origin. An overview of NO_x removal methods is shown in Figure 1.3 [11]. This study falls under photocatalytic methods for NO_x removal which are secondary methods. Therein only photocatalytic methods will be elaborated.

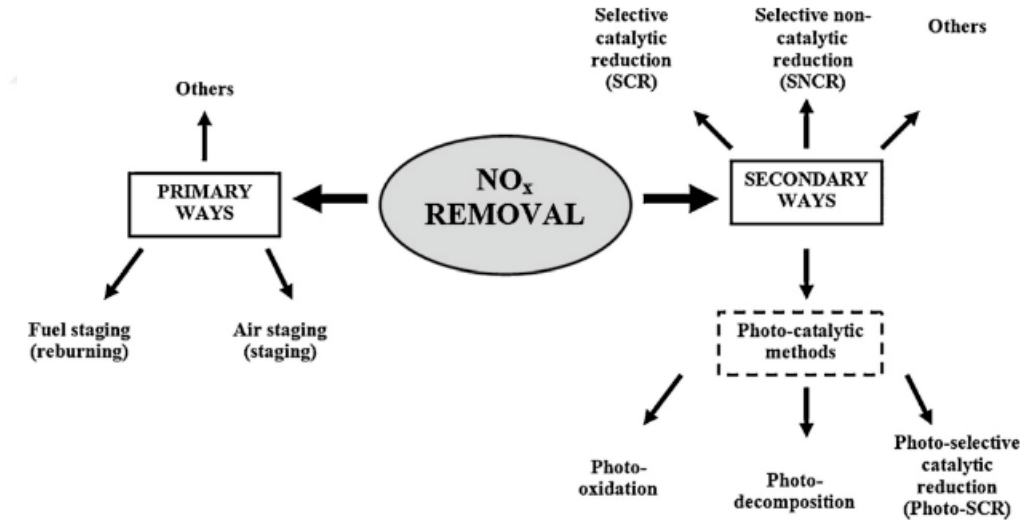


Figure 1.3: Illustration of NO_x Removal Methods (Adapted from [11])

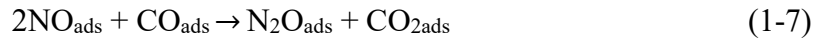
1.1.3.1 Photocatalytic Methods for NO_x Removal

There are three methods classified as photocatalytic methods for NO_x removal; photo-selective catalytic reduction (Photo-SCR), photo-decomposition, and photo-oxidation.

The first two methods aim to reduce NO_x species into N₂. The last one is an oxidation method where NO_x species are oxidized to HNO₃ on the surface of the catalyst.

1.1.3.1.1 Photo-selective Catalytic Reduction Method

Photo-selective catalytic reduction method utilizes NH₃ or carbon compounds such as carbon monoxide (CO) or propane (C₃H₈) as reducing agents where NO_x species are reduced into N₂(g) under light irradiation. It is similar to selective catalytic reduction method (not discussed here), despite this method achieves complete breakdown of NO_x species into N₂, its applications are difficult in real life [11]. Mechanisms regarding this method in the presence of CO (Reactions 1-6 – 1-9) [12] and NH₃ are given in Figure 1.4 [13].



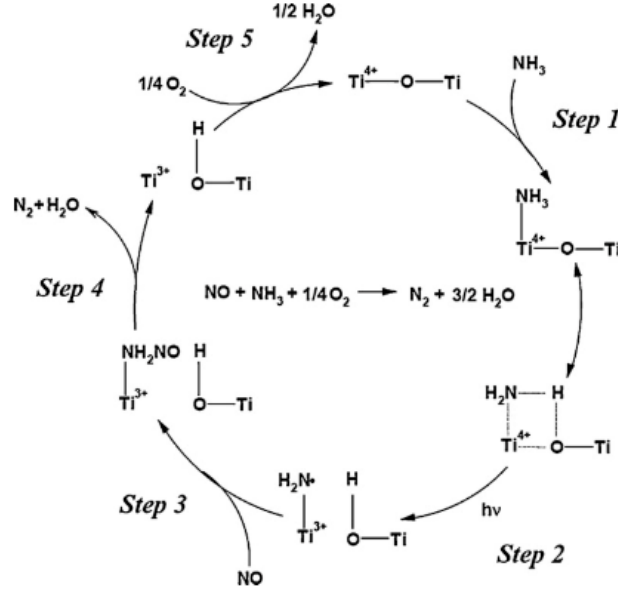


Figure 1.4: Proposed mechanisms of photo-SCR that utilize CO and NH₃ on TiO₂ photocatalyst (Taken from [13])

The photo-SCR methods are not the scope of this study, for articles about this the reader is recommended the following extensive works [14, 15, 16, 17].

1.1.3.1.2 Photo-decomposition Method

The reaction in the photo-decomposition method is given in the following reaction (1-10),

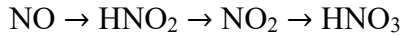


Selectivity of this process is dominated by the coordination number of Ti [18, 19, 20, 21].

1.1.3.1.3 Photo-oxidation Method

The photo-oxidation method is the method that will be utilized in this study. This method aims to oxidize NO species into HNO₃ or NO₃⁻ on the surface of the photocatalyst by

solely light irradiation. Photo oxidation mechanism of NO on the surface of TiO₂ which is the photocatalysts that will be used in this study, goes through following steps [22, 23],



Although these species are experimentally found on the surface of TiO₂, two different prominent reaction mechanisms were proposed, first being hydroxyl radical on the surface reaction acting as oxidizing species and reacting with NO_x species [24, 25], second being lattice oxygens acting as the oxidizing species for NO_x photo oxidation [26, 27]. Overview of these reactions are given in Figures 1.5 and 1.6.

Process	Reaction
Generation of charge carriers	$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(\text{h}^+ + \text{e}^-)$
Recombination of charge carriers	$\text{TiO}_2(\text{h}^+ + \text{e}^-) \rightarrow \text{TiO}_2$
Trapping of charge carriers	$\text{TiO}_2(\text{h}^+) + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{TiO}_2 + \bullet\text{OH}_{\text{ads}} + \text{H}^+$ $\text{TiO}_2(\text{h}^+) + \text{OH}_{\text{ads}}^- \rightarrow \text{TiO}_2 + \bullet\text{OH}_{\text{ads}}$ $\text{TiO}_2(\text{e}^-) + \text{O}_{2\text{ads}} \rightarrow \text{TiO}_2 + \text{O}_2^{\bullet-}$
Oxidation by hydroxyl radicals	$\text{NO}_{\text{ads}} + \bullet\text{OH}_{\text{ads}} \rightarrow \text{HNO}_{2\text{ads}}$ $\text{HNO}_{2\text{ads}} + \bullet\text{OH}_{\text{ads}} \rightarrow \text{NO}_{2\text{ads}} + \text{H}_2\text{O}$ $\text{NO}_{2\text{ads}} + \bullet\text{OH}_{\text{ads}} \rightarrow \text{HNO}_{3\text{ads}} \rightleftharpoons \text{NO}_{3\text{ads}}^- + \text{H}^+$
Adsorption-desorption equilibria	$\text{H}_2\text{O} + \text{site} \rightleftharpoons \text{H}_2\text{O}_{\text{ads}}$ $\text{O}_2 + \text{site} \rightleftharpoons \text{O}_{2\text{ads}}$ $\text{NO} + \text{site} \rightleftharpoons \text{NO}_{\text{ads}}$ $\text{HNO}_2 + \text{site} \rightleftharpoons \text{HNO}_{2\text{ads}}$ $\text{NO}_2 + \text{site} \rightleftharpoons \text{NO}_{2\text{ads}}$ $\text{HNO}_3 + \text{site} \rightleftharpoons \text{HNO}_{3\text{ads}}$

Figure 1.5: Proposed NO Oxidation mechanism on TiO₂ as hydroxyl radicals involving as the oxidizing species (Adapted from [28])

Process	Reaction
Generation of charge carriers	$\text{TiO}_2 + h\nu \rightarrow \text{TiO}_2(\text{h}^+ + \text{e}^-)$
Recombination of charge carriers	$\text{TiO}_2(\text{h}^+ + \text{e}^-) \rightarrow \text{TiO}_2$
Trapping of charge carriers	$\text{TiO}_2(\text{h}^+, \text{O}_\text{s}) \rightarrow \text{TiO}_2(\text{O}^\bullet_\text{s})$ $\text{TiO}_2(\text{e}^-) + \text{O}_{2\text{ads}} \rightarrow \text{TiO}_2 + \text{O}_2^{\bullet-}\text{ads}$
Oxidation by holes	$\text{TiO}_2(\text{h}^+) + \text{NO}_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{HNO}_{2\text{ads}} + \text{H}^+$ $\text{TiO}_2(\text{h}^+) + \text{HNO}_{2\text{ads}} \rightarrow \text{NO}_{2\text{ads}} + \text{H}^+$ $\text{TiO}_2(\text{h}^+) + \text{NO}_{2\text{ads}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{HNO}_{3\text{ads}} + \text{H}^+$
Oxidation by lattice oxygen radicals	$\text{TiO}_2(\text{O}^\bullet_\text{s}) + \text{NO}_{\text{ads}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{TiO}_2(\square) + \text{HNO}_{2\text{ads}} + \text{OH}^-\text{ads}$ $\text{TiO}_2(\text{O}^\bullet_\text{s}) + \text{HNO}_{2\text{ads}} \rightarrow \text{TiO}_2(\text{O}_\text{s}) + \text{NO}_{2\text{ads}} + \text{H}^+$ $\text{TiO}_2(\text{O}^\bullet_\text{s}) + \text{HNO}_{2\text{ads}} \rightarrow \text{TiO}_2(\square) + \text{HNO}_3^-\text{ads}$ $\text{TiO}_2(\text{O}^\bullet_\text{s}) + \text{HNO}_3^-\text{ads} \rightarrow \text{TiO}_2(\text{O}_\text{s}) + \text{HNO}_{3\text{ads}}$ $\text{TiO}_2(\text{O}^\bullet_\text{s}) + \text{NO}_{2\text{ads}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{TiO}_2(\square) + \text{HNO}_{3\text{ads}} + \text{OH}^-\text{ads}$ $\text{TiO}_2(\text{O}^\bullet_\text{s}) + \text{NO}_{2\text{ads}} + \text{H}_2\text{O}_{\text{ads}} \rightarrow \text{TiO}_2(\square) + \text{NO}_3^-\text{ads}$
Reaction of oxygen vacancies	$\text{TiO}_2(\square) + \text{OH}^-\text{ads} \rightarrow \text{TiO}_2(\text{O}_\text{s}) + \text{H}^+$
Note: $\text{TiO}_2(\text{O}_\text{s})$, and $\text{TiO}_2(\text{O}^\bullet_\text{s})$ are terminal (bridging) oxygen species at the TiO_2 surface, and $\text{TiO}_2(\square)$ represents bridging oxygen vacancies.	

Figure 1.6: Proposed NO Oxidation mechanism on TiO_2 as lattice oxygen species involving as the oxidizing species (Adapted from [28])

Though the mechanisms differ during trapping charge carrier steps, the first two steps are the same, in fact these two steps are found in many photocatalytic processes. In the charge carrier generation step, if the energy of the photon absorbed by the photocatalyst has enough energy, an electron (e^-) will be promoted from the valence band

of the semiconductor to the conduction band while leaving a hole (h^+) behind in the valence band which is illustrated in Figure 1.7 [29].

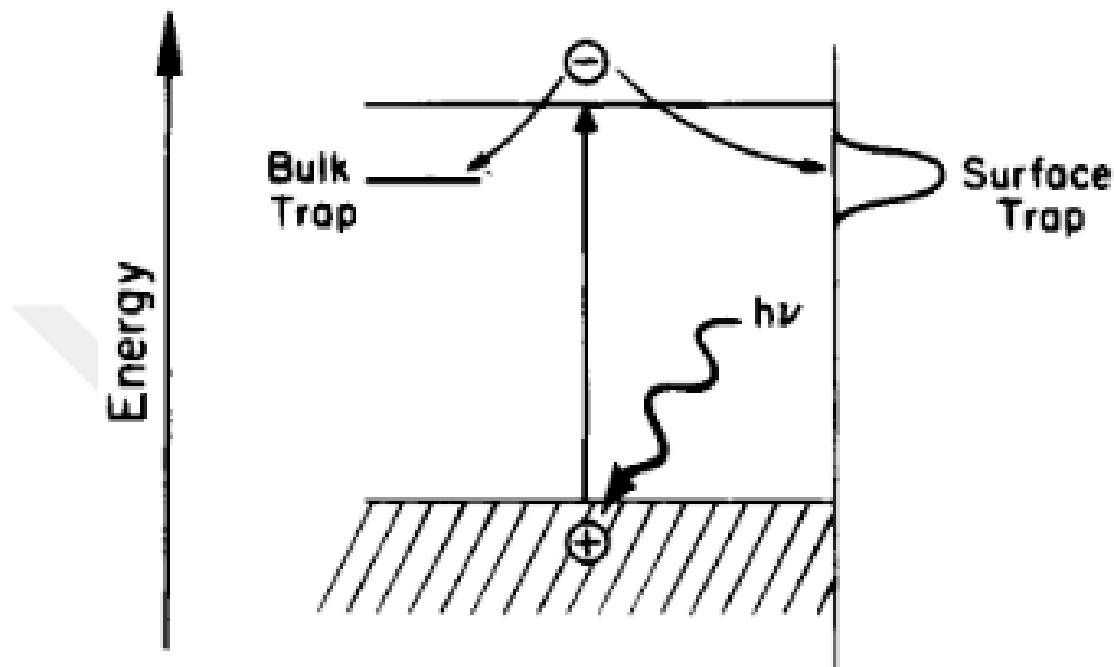


Figure 1.7: Generation of charge carriers after light absorption (Adapted from [29])

Though these generated charge carriers are known to trigger reactions on the catalyst surface, the biggest limiting factor is the recombination of them, in which 90% of the generated charge carriers recombine (TiO_2 has $\sim 10\%$ photonic efficiency), despite this TiO_2 is still considered to have a high photoreactivity [30]. Most of the generated charge carriers do not involve in photocatalytic processes but rather recombine either on the bulk or surface of the catalyst (Figure 1.8) [29].

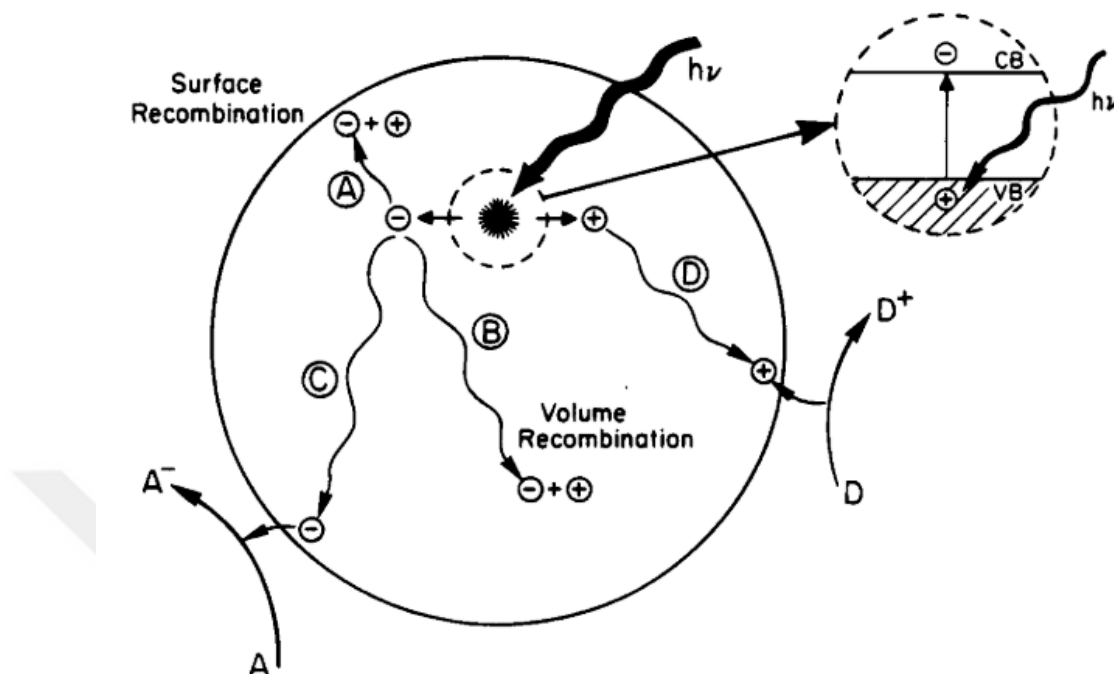


Figure 1.8: Illustration of possible deexcitation events after charge carrier generation by photoexcitation (Adapted from [29]), (A) represents generated charge carrier travels up to the surface of the catalyst then recombines, (B) represents recombination of the charge carriers at the bulk of the catalyst, (C) represents reduction induced by photogenerated electron at the surface, (D) represents oxidation induced by photogenerated hole at the surface

Photogenerated charge carriers that are not recombined are usually trapped both in the bulk and surface of the catalyst, the surface trapped ones are thought to trigger the photocatalytic processes. For the photooxidation of NO, both mechanisms given above (Figure 1.5 and 1.6) consider the photogenerated electron to be captured by an adsorbed oxygen molecule (O_{2ads}) on the surface to produce superoxide radical ($O_2^{\bullet-}$) or hydroperoxyl radical ($HO_2^{\bullet}$) which then oxidizes NO on the catalyst surface into nitric acid (HNO_3).

For trapping of the photogenerated holes, two mechanisms differ while one mechanism considers these holes are trapped as hydroxyl radicals after reacting with surface hydroxides, this was later proved to be the not the primary product, but rather lattice oxygen radicals was the primary product for hole trapping [31, 32, 33]. This does not completely falsify the mechanism proposed in Figure 1.5, but it is thought that the hole mediated NO oxidation usually follow the mechanism pathway proposed in Figure 1.6.

1.2 Properties of Titanium Dioxide (TiO₂)

Titanium dioxide (TiO₂, Titania) is one of the most prominent photocatalysts, despite it has a large bandgap of ~3.1 eV and cannot be activated by visible light, but rather only by the UV light which is known to be less than 5% of the solar spectrum [34]. The reason why TiO₂ is so prevalent is due to material being photostable, cheap, nontoxic and chemically inert [30].

TiO₂ found in the nature has three phases: anatase, rutile and brookite. Since brookite is rare compared to anatase and rutile and its manufacturing is difficult, most of the scientific works highlight anatase, rutile or their mixtures. Anatase is known to have superior photocatalytic activity compared to rutile despite having a higher bandgap, ~3.2 eV to ~3.0 eV. The reason for this is due to an indirect bandgap of anatase, which is thought to create better charge separation, therefore increasing the number of photogenerated charge carriers which can initiate photocatalytic processes compared to rutile. Rutile is reported to have a direct bandgap, hence less charge separation therefore lower lifetime for generated charge carriers (Figure 1.9) [35].

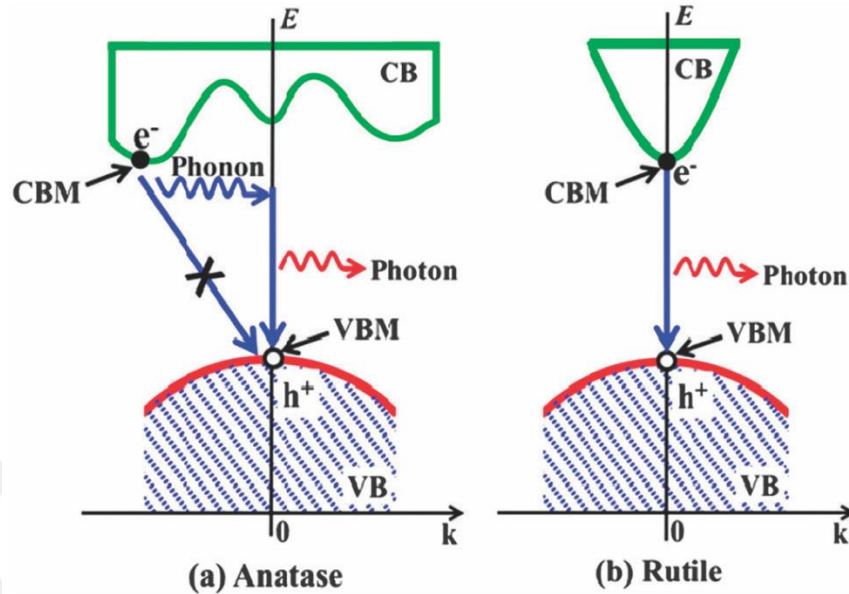


Figure 1.9: Illustration of recombination process of generated charge carriers on a) indirect bandgap anatase b) direct bandgap rutile (Taken from [35])

In terms of comparison of the thermodynamic stabilities of rutile and anatase phases, rutile is thermodynamically more stable phase whereas anatase is a metastable phase and transforms rutile above the temperature of 600 °C [35, 36].

Lastly the structures of rutile and anatase are given in Figures 1.10 and Figures 1.11 along with some other structural properties in Table 1.1 [37, 38].

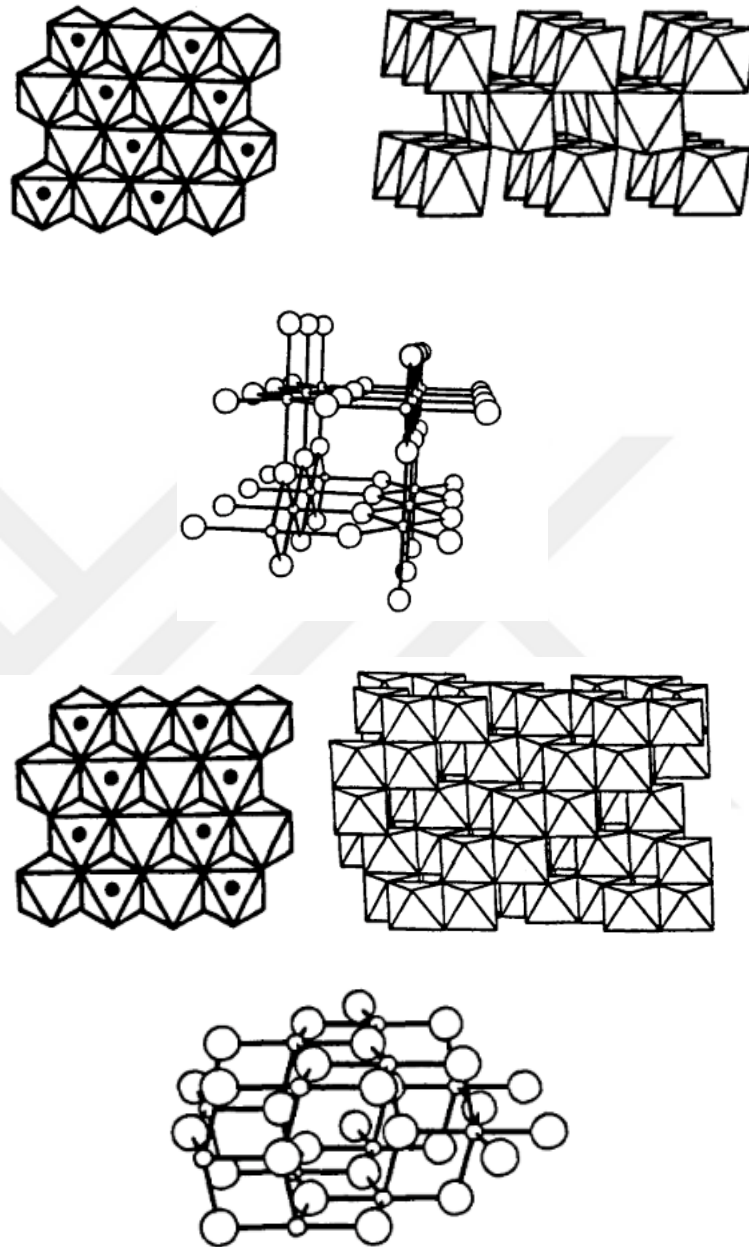


Figure 1.10: Illustrations of structures of rutile (above) and anatase (below), oxygen atoms are the large circles in right hand-side illustration (Adapted from [37])

Table 1.1 Some Structural Properties of Anatase and Rutile (Adapted from [38])

	Anatase	Rutile
Crystal Structure	Tetragonal	Tetragonal
Atoms per unit cell	4	2
Lattice Parameter (a) (nm)	0.3785	0.4594
Lattice Parameter (b) (nm)	0.3785	0.4594
Lattice Parameter I (nm)	0.9514	0.2959
Crystal Size (nm)	<11	>35
Bandgap (eV)	3.2	3.0

1.2.1 Commercial TiO₂ Photocatalyst – Degussa P25

Commercial Degussa P25 is a mixture of anatase and rutile, despite Degussa P25 is reported to be inhomogeneous, anatase is the dominant phase (78-85%) while rutile is usually in the range 14-17% and sometimes amorphous TiO₂ was observed (0-13%). Regardless of the inhomogeneity of Degussa P25, it is reported that anatase to rutile ratio was ~ 5:1 in all measurements [39].

Degussa P25 has been used as a benchmark photocatalyst since 1990s [40] for works regarding TiO₂, because this mixture has a better photocatalytic activity compared to any single polymorph of TiO₂ [39]. The reason behind such superiority in the photocatalytic activity is thought to be due to band alignment of anatase and rutile [41]. It was reported that work function of rutile is 0.2 eV lower than anatase thereby the conduction band of

rutile was thought to be located 0.2 eV above of anatase [42]. Combining this fact with the result of electron paramagnetic resonance measurements for samples of anatase and rutile mixture, it was concluded that electrons flow from rutile to anatase phase in contrast holes moved from anatase to rutile phase [43, 44, 45]. In light of these findings following band alignment was proposed (Figure 1.11) [41]. The photogenerated holes migrate into the valence band of rutile while photogenerated electrons flow to the conduction band edge of anatase phase. The process between these two phases, thought to enhance the lifetime of the carriers thus increasing the photocatalytic activity.

Since Degussa P25 is commercially available and it is known to have high photocatalytic activity, and has been used as a benchmark throughout in literature same was adopted in this study.

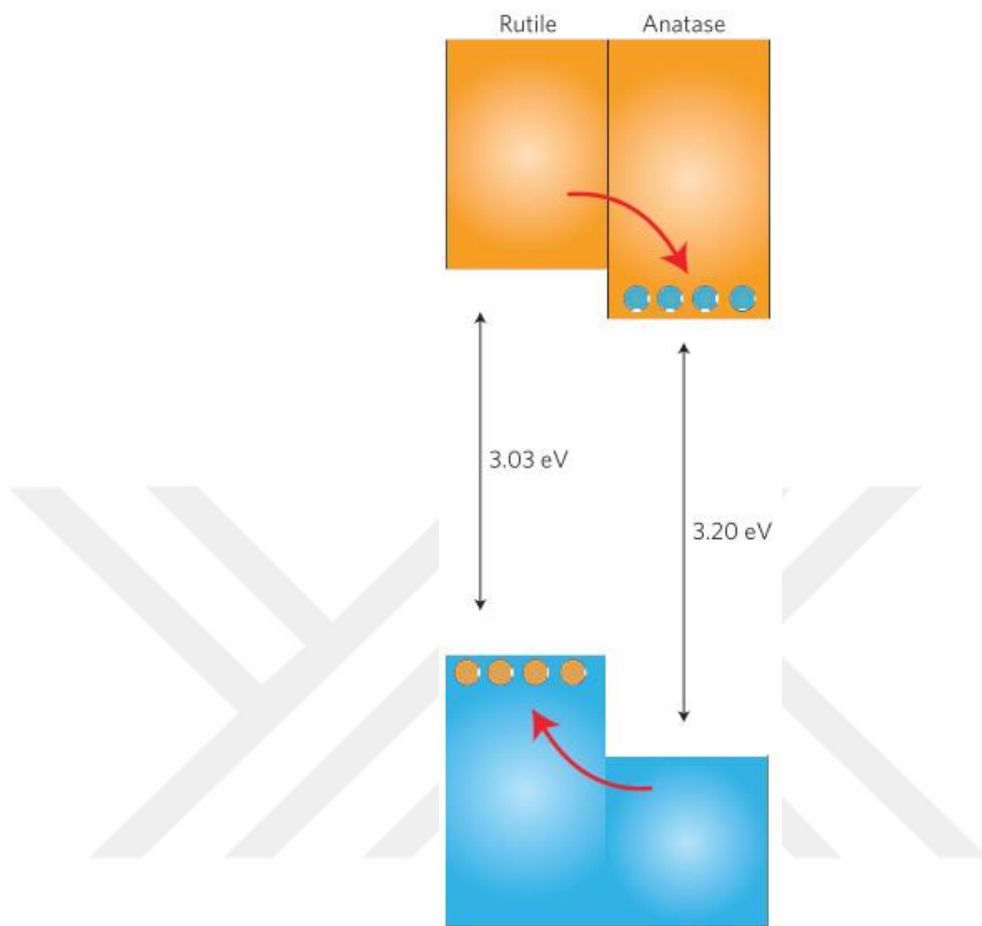


Figure 1.11: Band alignment of rutile anatase interface, orange circles represent photogenerated holes which is seen to migrate into valence band edge of rutile. In contrast it was seen that blue circles (photogenerated electrons) migrate into conduction band edge of anatase phase. (Adapted from [41])

1.3 Colored TiO₂

Since the photocatalytic activity of TiO₂ is known to be dependent on the number of photogenerated charge carriers, it is critical to increase the number of these species to enhance the photocatalytic activity. As mentioned in the previous section, TiO₂ has an electronic bandgap of 3.0-3.2 eV, thereby only UV region in the solar spectrum is able to

trigger photogenerated charge carriers [34]. Therefore, decreasing the bandgap of the TiO_2 has been investigated extensively as such would mean creation of photogenerated charge carriers after visible light absorption by TiO_2 [46].

Different approaches towards these attempts include substitution of metal ions for Ti^{4+} ions or addition of nonmetal ions to replace O^{2-} ions or combination of both to increase visible light absorption on TiO_2 [47, 48, 49, 50, 51, 52, 53, 54, 55, 56]. After doping of such metal and nonmetal ions, different colored TiO_2 materials such as yellow [51], red [57] and green were produced [58].

One important discovery in 2011 showed that intrinsic doping of TiO_2 and heat treatment under reducing conditions decreased the bandgap of the material to ~ 1.5 eV and black color was attained [59]. Since water splitting potential is 1.23 eV, this work attracted attention and different works with black TiO_2 followed [60, 61, 62]. Similar to these works under varying reducing conditions; gray, blue and brown colored TiO_2 materials were produced [46, 63, 64]. These materials are thought to have increased defect concentration in the form of Ti^{3+} and oxygen vacancies (V_{O}) which was attributed to the reason of the color change, darker color of TiO_2 was correlated with high defect concentration [65]. Such defective titania are reported to have not only enhanced photocatalytic performance in visible light region but also in the UV light region as well [66] due to changes in bandgap of these materials.

1.4 Utilization of Ethanol and Scope of the Study

In light of the studies mentioned in the previous section, it was thought that TiO_2 treated with a reducing agent such as ethanol can be used to introduce defects to the catalyst which

was hypothesized to increase the Photocatalytic NO_x Oxidation and Storage (PHONOS) activity of TiO₂. A thorough literature search on the former studies involving ethanol treated TiO₂ revealed that there are numerous publications where ethanol was utilized during the sol-gel synthesis of TiO₂, though the color of the synthesized TiO₂ was white and these works were not classified as reduced or colored TiO₂ [67, 68]. One work that utilized ethanol to reduced TiO₂ was done by a simple refluxing method [69]; where blue colored TiO₂ was produced at the end of the process, but no PHONOS work was performed (Figure 1.12).

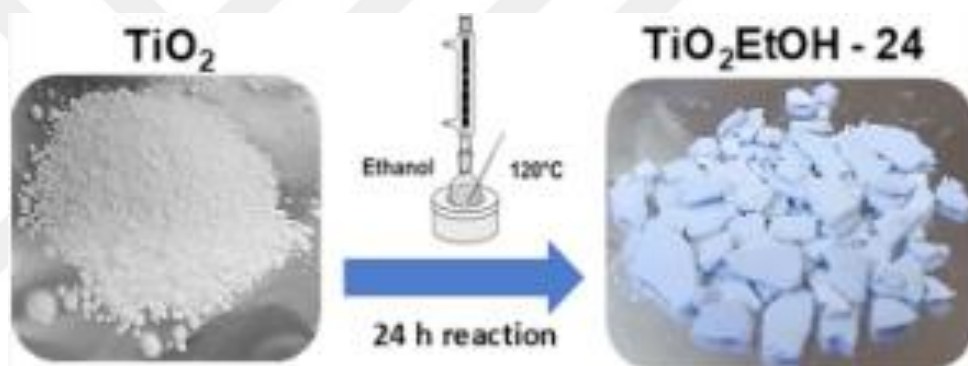


Figure 1.12: Simple ethanol refluxing treatment on TiO₂ to introduce defects (Adapted from [69])

Another way of ethanol utilization on TiO₂ to create defects is vacuum annealing. Hydrothermally synthesized TiO₂ powders were washed with ethanol and then vacuum annealed at different calcination temperatures [70, 71, 72]. These studies showed that ethanol treatment caused dark colored TiO₂ which resulted to have enhanced photocatalytic activity compared to initially synthesized “white” TiO₂ powders, but no PHONOS work was performed (Figure 1.13).

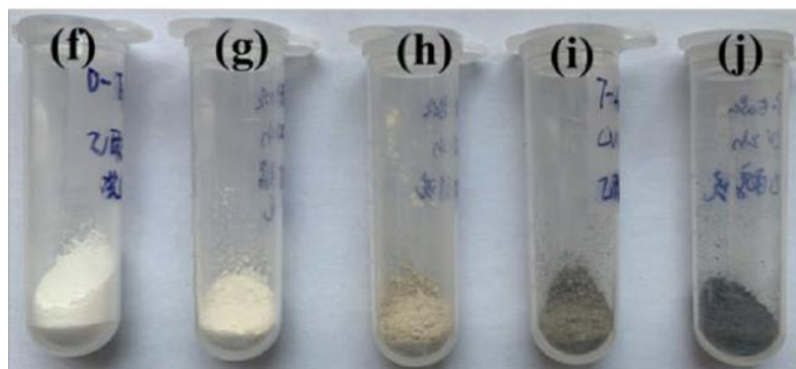


Figure 1.13: Ethanol washed samples after calcined at different vacuum annealing temperatures (Adapted from [71]).

Lastly, in another former study, impregnation of ethanol was performed on TiO_2 powder followed by calcination at different temperatures. The conclusions drawn from this work seems highly questionable and no PHONOS experiments were performed in this study [73].

Along this lines, this study is aimed to achieve a high Photocatalytic NO_x Oxidation and Storage (PHONOS) performance under UVA light with a photocatalyst that utilizes TiO_2 and ethanol. Rather than synthesizing TiO_2 in single polymorph form, Degussa P25 was utilized due to its superior photocatalytic activity and has been used a benchmark catalyst throughout the study. Utilization of ethanol on TiO_2 were done by simply mixing two components and then calcination of the mixtures in a muffle furnace. At the initial part of the study optimum ethanol loading and optimum calcination temperature were determined from 1 h long photocatalytic performance tests. Then 15 h long run tests were performed with the best performing catalyst and prolonging the viability of this catalyst in real life applications were investigated. Lastly the photocatalyst calcined at different temperatures were characterized and the relationship between PHONOS and ethanol treated TiO_2 was investigated thoroughly.

2 Experimental

2.1 Sample Preparation

2.1.1 Preparation of TiO₂-Ethanol Catalysts

For the preparation of TiO₂ based catalysts for nitric oxide (NO) oxidation, titanium(IV) oxide (commercial Degussa P25, $\geq 99.5\%$ trace metal basis, Sigma Aldrich) and absolute ethanol ($\geq 99.8\%$, Sigma Aldrich) were used throughout all experiments.

Samples were prepared by mixing Degussa P25 and ethanol in a petri dish manually for a minute, followed by calcination in a muffle furnace at atmospheric conditions for 12 h, where the total duration of the temperature ramp was 45 min in all cases.

While the amount of Degussa P25 used in all experiments was kept the same as 250.0 mg, ethanol loading and calcination temperatures were varied to determine the best photocatalytic performance among the samples prepared. The preparation of the TiO₂-ethanol catalysts with these parameters will be discussed in the following sections.

2.1.2 Optimization of Ethanol Loading on TiO₂

For the optimization of ethanol loading on TiO₂, 250 mg of Degussa P25 was mixed with six different loadings of ethanol, then the mixtures were calcined at 300 °C for 12 h. The ramp time from room temperature to 300 °C was 45 min. These catalysts were denoted as TiO₂-*X*-EtOH where *X* denotes the mL of ethanol that was mixed with TiO₂-(Table 2.1) and TiO₂-3-EtOH was found to show the best photocatalytic activity.

Table 2.1 Ethanol Loading on TiO₂

Sample Name	Degussa P25 (mg)	Ethanol (mL)
TiO ₂ -1.5-EtOH	250.0	1.5
TiO ₂ -2.25-EtOH	250.0	2.25
TiO ₂ -3-EtOH	250.0	3.0
TiO ₂ -4.5-EtOH	250.0	4.5
TiO ₂ -6-EtOH	250.0	6.0
TiO ₂ -7.5-EtOH	250.0	7.5

2.1.3 Optimization of Thermal Treatment and Reduction Conditions on TiO₂-Ethanol Samples

After optimum ethanol loading was determined to be 3.0 mL ethanol per 250.0 mg Degussa P25 (TiO₂-3-EtOH), its thermal treatment (calcination) and reduction conditions were optimized for the photocatalytic activity. All of the samples prepared with 3.0 mL ethanol were calcined at seven different temperature for 12 h (Table 2.2). The ramp time from room temperature to any calcination temperature was 45 min. These samples are denoted as TiO₂-EtOH-*T*, where *T* denotes the calcination temperature (Table 2.2). All seven TiO₂-EtOH-*T* catalysts were tested for the photocatalysis efficiency of NO_x oxidation.

Table 2.2 Calcination Temperature on the TiO₂-3-EtOH Samples

Sample Name	Degussa P25 (mg)	Ethanol (mL)	Calcination Temperature (°C)
TiO ₂ -EtOH-100	250.0	3.0	100
TiO ₂ -EtOH-150	250.0	3.0	150
TiO ₂ -EtOH-200	250.0	3.0	200
TiO ₂ -EtOH-250	250.0	3.0	250
TiO ₂ -EtOH-300	250.0	3.0	300
TiO ₂ -EtOH-400	250.0	3.0	400
TiO ₂ -EtOH-500	250.0	3.0	500

2.2 Photocatalytic Activity Measurements of the Calcined TiO₂-EtOH catalysts

2.2.1 Flow Reactor Setup for the Photocatalytic NO_x Oxidation and Storage (PHONOS)

The photocatalytic NO_x oxidation and storage measurements were performed in a custom-designed flow reactor (Figure 2.1). To mimic polluted atmospheric conditions, three different gas cylinders each containing N₂ (99.995%, Linde), O₂ (99.5 %, Linde), and NO/N₂ mixture (90 ppm NO balanced with N₂) were used. These gas cylinders were connected to the flow reactor with ¼ -inch Swagelok stainless steel tubing and Swagelok nupro VCR valves. The amount of gas to introduce into the system was determined by

setting volumetric flow rates in Mass Flow Control Station (TRL-MFCS) which was connected to three separate mass flow controllers (MFCs). Teledyne HFC-202s (MFCs) were used to regulate the flow of the N_2 gas and NO/N_2 gas mixture while a MKS1479A (MFC) was used to regulate the flow of the O_2 gas into the system. MFC values were set to be 0.782 standard liters per minute (SLM) for N_2 -gas, 0.232 SLM for O_2 gas, and 0.012 SLM for the NO/N_2 -gas mixture. Each flow controller was calibrated specifically for the gas that flows through it and flow rates were checked periodically by using a portable Agilent Technologies ADM1000 Flowmeter. After measuring the flow rates with ADM1000 Flowmeter, the total gas flow rate was 1.20 L/min, and the concentration of NO on the inlet gas mixture was calculated as 0.90 ppm.

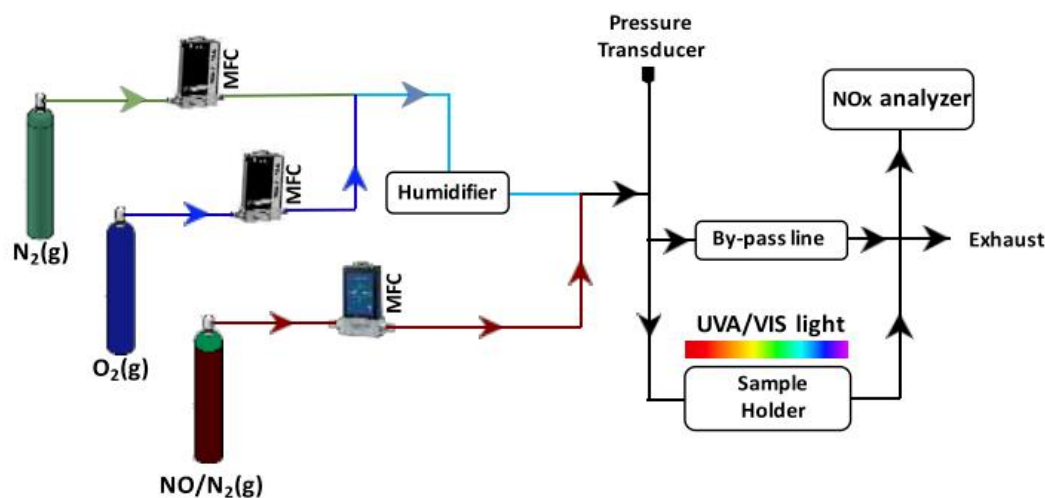


Figure 2.1: Illustration of custom-designed flow reactor for PHONOS [74].

The relative humidity percentage of the gas mixture was adjusted with water vapor. It was introduced into the gas mixture (before the inlet gas was introduced into the reactor) through the semipermeable membrane of PermSelect (PDMSXA-2500) which was

connected to a water chiller (C200-H13, Labo). The chiller was set to 12.6 °C to maintain 45% relative humidity in the reactor at 25 °C.

During catalytic measurements, the inlet gas passed through the reactor line while during other operating conditions, the gas passed through the by-pass line. The difference in the concentrations of NO, NO₂, and NO_x in the outlet gas mixture was monitored by using a Teledyne T200 chemiluminescence NO_x analyzer.

Because Teledyne T200 has only the ability to measure the amounts of NO, NO₂, and total NO_x species, the amounts of other products such as N₂O, N₂O₄, N₂ etc. could not be determined. The operation principle of a NO_x analyzer is to measure the amounts of NO and NO₂ separately then their sum gives the total amount of NO_x.

Teledyne T200 generates ozone (O₃) which reacts with NO in a gas mixture to give O₂ and excited NO₂ (NO₂^{*}) (Equation 2-1).



The excited NO₂^{*} returns to the ground state NO₂ while emitting electromagnetic radiation (photons) within the wavelength range of 600 nm to 3000 nm with a maximum intensity at 1200 nm (Equation 2-2).



The intensity of emitted electromagnetic radiation is linearly proportional to the concentration of NO when its concentration is between 0 and 20 ppm. Therefore, by utilizing a photomultiplier tube (PMT), the generated signal intensity is proportional to the concentration of NO₂^{*} hence the concentration of NO in the gas sample. In this way

the concentration of NO can be measured within the sensitivity of 0.001 ppm to 20 ppm with a measurement rate of 1.0 Hz.

The determination of the amount of NO₂ in the outlet gas mixture is achieved by utilizing a molybdenum-based NO₂ reduction catalyst at a temperature of about 315 °C. At this temperature the NO₂ molecules in the gas mixture is converted back to NO (Equation 2-3).



Therefore, there will be only NO species in the sample gas after it passes through the molybdenum-based catalyst. After the NO species in this gas is reacted with O₃, the amount of NO determined corresponds to the sum of the amounts of NO and NO₂ which gives the total amount of NO_x in the gas mixture.

With the help of pneumatic valves, measurements of the concentrations of NO and NO₂, total NO_x can be switched with small time intervals. Eventually the concentrations of NO, NO₂, and total NO_x can be determined for each second.

In this study, all photocatalytic activity measurements for NO_x oxidation were performed under UV-A light irradiation with 8W UV-A lamp (F8W/T5/BL350, Sylvania, Germany). Photon flux was measured using a photo radiometer (HD2302.0 Delta Ohm/Italy) with a UV-A probe (315-400 nm) before and after each measurement. The measured photon flux was within the range of $7.5 \text{ W/m}^2 \pm 0.3 \text{ W/m}^2$ throughout all experiments reported in this study.

For photocatalytic activity measurements, all of the catalysts were ground and then 200.0 mg catalyst packed into a 2 mm $\times$ 40 mm $\times$ 40 mm polymethyl methacrylate (PMMA) sample holder (Figure 2.2) and then the holder was placed into the flow reactor.

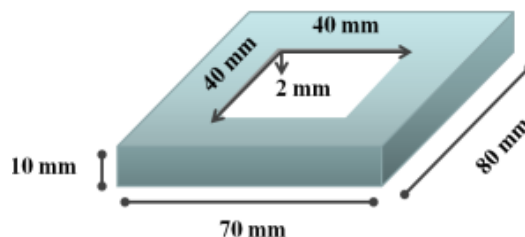


Figure 2.2: Illustration of sample holder that is used for photocatalytic performance tests.

Unless otherwise stated, all experiments were carried out through 1 h long durations, in other words the UV-A light was irradiated onto the catalyst for 1 h. An example for the NO_x concentration profile during these experiments is shown in Figure 2.3. About 0.90 ppm NO was introduced to the reactor, the initial dip before UV-A light irradiation corresponds to dark adsorption where the non-photocatalytic adsorption of NO_x species on the catalyst and on the reactor walls occurred. After this dark adsorption process, the concentration of NO rose again to 0.90 ppm and stabilized. Then UV-A light was shined upon the catalyst for 65 min and a decrease in the concentrations of NO and total NO_x and an increase in the concentration of NO_2 occurred due to the photocatalytic activity of the catalyst. At the end of 65 min, the UV-A light source was turned off and the concentrations of NO, NO_2 and total NO_x returned to initial values.

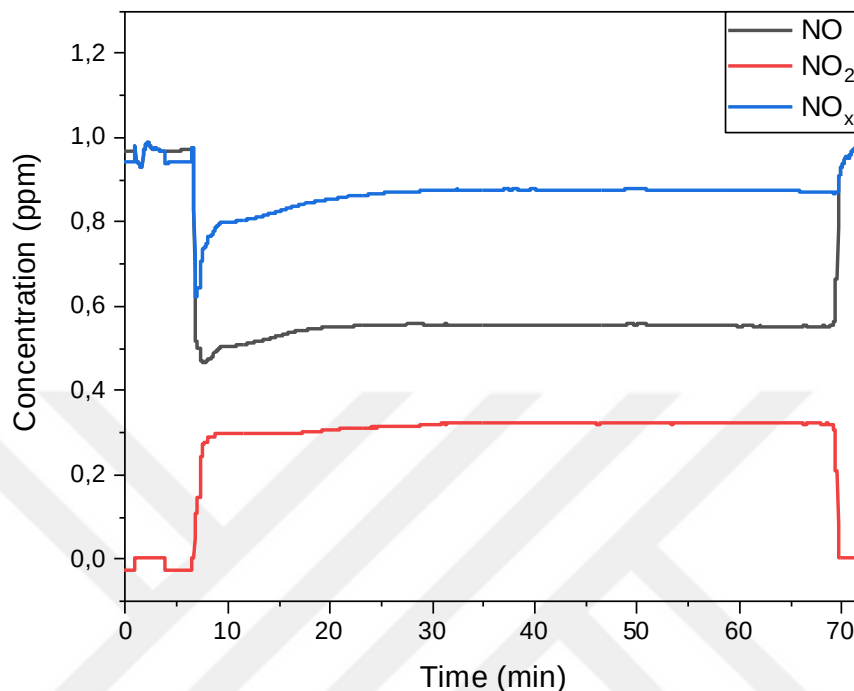


Figure 2.3: Concentration vs time profile recorded during Degussa P25-benchmark photocatalyst during the photocatalytic NO_x oxidation and storage test.

2.2.2 Photocatalytic Performance Parameters of Calcined TiO₂-Ethanol Catalysts

A number of performance parameters was tested to evaluate quantitatively the relative photocatalytic activity of different TiO₂ based catalysts. The parameters that will be reported in this study are NO Conversion Percentage (NO Conversion%), Selectivity Percentage (Selectivity%), DeNO_x Index, and Photonic Efficiency Percentage to compare the photocatalytic activities of the catalysts.

2.2.2.1 NO Conversion Percentage (NO Conversion%)

NO Conversion% is the percentage difference between the concentrations of inlet and outlet NO(g) which is given by the following equation (Equation 2-4):

$$\text{NO Conversion \%} = \frac{\int ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) dt}{\int [\text{NO}]_{\text{in}} dt} \times 100 \quad (2-4)$$

NO Conversion % indicates how much the catalyst can convert the introduced NO into other NO_x species. Therefore high NO Conversion% is desired which may yield NO₂(g), HONO(ads), HONO₂(ads), NO₂⁻(ads), and NO₃⁻(ads) [75].

2.2.2.2 Selectivity Percentage (Selectivity%)

The Selectivity Percentage gives the percentage of products of NO oxidation that are stored on the catalyst surface, which is given by the following equation (Equation 2-5).

$$\text{Selectivity \%} = \frac{\int ([\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}) dt}{\int ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) dt} \times 100 \quad (2-5)$$

This term includes both NO_x species, storage of these species is essential in a good catalyst therefore high Selectivity% is aimed. In this calculation, it is assumed that all NO_x species other than NO(g) and NO(g) are stored on the catalyst surface.

2.2.2.3 DeNO_x Index

As mentioned before, NO₂ is more toxic than NO, the short-term exposure limit reported by Occupational Safety and Health Administration, American Conference of

Governmental Industrial Hygienists, and National Institute for Occupational Safety and Health is 25 ppm whereas typically reported NO₂ values vary from 1 to 3 ppm. Due to such differences in the toxicity of NO and NO₂, Bloh et al. [76] developed an index, called DeNO_x Index, to determine whether the catalyst is purifying or poisoning the air from NO_x species. DeNO_x Index has the following formula (Equation 2-6).

$$\text{DeNO}_x \text{ Index } \% = \frac{\int ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) - 3([\text{NO}_2]_{\text{in}} - [\text{NO}_2]_{\text{out}}) dt}{\int ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}) dt} \times 100 \quad (2-6)$$

The DeNO_x Index can be used as a photocatalytic efficiency indicator. This index includes terms for both NO conversion and NO₂ formation. The DeNO_x Index values are typically within the range of -0.6 to +0.4, where a positive value indicates air being detoxified from NO_x species while a negative value indicates air being polluted by the catalyst, more toxic species are released into the air than the catalyst converts and stores.

2.2.2.4 Photonic Efficiency

The percentages of NO Conversion% and Selectivity% are greatly dependent on incident photon flux and the photocatalytic activity of catalyst, and these values can be reported after normalized by the incident photon flux. NO_x Storage % Photonic Efficiency and NO₂ Release % Photonic Efficiency values can be calculated using the following Equations 2-7 and 2-8.

$$\text{NO}_x \text{ Storage \% Photonic Efficiency } (\xi) = \frac{n(\text{NO}_x)_{\text{Stored on the catalyst surface}}}{n_{\text{Photon}}} \times 100 \quad (2-7)$$

$$\text{NO}_2 \text{ Release \% Photonic Efficiency } (\xi) = \frac{n(\text{NO}_x)_{\text{Released to atmosphere}}}{n_{\text{Photon}}} \times 100 \quad (2-8)$$

n_{Photon} (Equation 2-9) is

$$n_{\text{Photon}} = \frac{(I \lambda A t)}{(N_A h c)} \quad (2-9)$$

where I is the photon power density, λ is the mean emission wavelength of the lamp, A is the exposed surface area of the catalyst, t is the time duration of the experiment, N_A is the Avogadro constant and c is the speed of light.

By definitions NO_x Storage % Photonic Efficiency and NO_2 Release % Photonic Efficiency are the number of NO_x species stored in the solid state on the catalyst surface and the number of $\text{NO}_2(\text{g})$ molecules that are released into the air per number of photons that absorbed by the catalyst surface during the photocatalysis, respectively. In this study only UV-A light was used and the photon flux was set to be around $7.5 \text{ W/m}^2 \pm 0.3 \text{ W/m}^2$. Since photon flux was nearly stable throughout all experiments; NO Conversion%, Selectivity% and De NO_x Index values were reported and used for evaluating the performance.

2.3 Characterization Methods

2.3.1 X-Ray Diffraction

PANalytical Empyrean X-Ray Diffractometer (XRD) equipped with Cu $K\alpha$ irradiation source (40 kV, 45 mA, $\lambda = 1.5405 \text{ \AA}$) was used for determination of the crystallographic structures. The samples were scanned at 10° - 80° as 2θ operation angle at a $0.04^\circ \text{ s}^{-1}$ step resolution. The powder samples were placed onto a silicon single crystal and then pressed

before inserting into the diffractometer. Crystal structures were identified by International Centre for Diffraction Database (ICDD) crystal structure library.

2.3.2 Raman Spectroscopy

Raman Spectroscopy measurements were performed on the BWS465-532S (BWTEK) portable Raman spectrometer. Resolution of BWS465-532S was $<4.5\text{ cm}^{-1}$ at 614 nm. The laser power was adjusted to be 100 mW and time average was set to 1 for all samples. Depending on the sample behavior integration time was varied to achieve a good signal-to-noise.

2.3.3 Diffuse Reflectance-UV-A-VIS Spectroscopy

Diffuse Reflectance-UV-A-VIS (DR-UV-A-VIS) Spectroscopy was performed on the samples by using a Cary 5000 UV-A-VIS-NIR Spectrometer equipped with a Varian Cary 2500 Internal Diffuse Reflectance (DR) Accessory.

2.3.4 X-Ray Photoelectron Spectroscopy

SPECS PHOIBOS hemispherical energy analyzer was used for X-Ray Photoelectron Spectroscopy (XPS) measurements of the samples. Monochromatic Al-K α (15 kV, 400 W) X-ray excitation source was employed. The powder samples were introduced into the chamber by using an insulating tape. Charge neutralization was done with a flood gun (0.8 eV, 16.8 μA) where no differential charging was present and at a point where Ti⁴⁺ peak of

Ti 2p_{3/2} lied within an acceptable binding energy (B.E.) value (458.8 eV for Degussa P25). Spectra of all other samples were taken with the same conditions, no further B.E. referencing was performed. For core level measurements, pass energy was set to 25 eV and 50 scans were averaged for each peak, while for valence band (VB) measurements pass energy was set to 40 eV and 100 scans were average to have a lower signal-to-noise ratio (S/N).

2.3.5 *In-situ* Fourier Transform Infrared (FTIR) Spectroscopy

In-situ FTIR Spectroscopy measurements were carried out with a Bruker Tensor 27 FTIR spectrometer equipped with a batch-type custom-design spectroscopic reactor. The spectra were obtained in transmission mode, Degussa P25 was first mixed with 3 mL of ethanol, then left to dry in dark. Dried TiO₂ was pressed into a tungsten grid. Then the grid introduced into the spectroscopic reactor in the instrument. A background spectrum was taken at 30 °C after vacuum conditions were reached (10⁻³ Torr), then starting from 50 °C at each 50 °C, an FTIR spectrum was taken and then subtracted from the background. Energy resolution was set to 4 cm⁻¹ and average of 512 scans were reported.

3 Results and Discussion

In this study, efficient TiO_2 photocatalysts were synthesized to be used in NO_x removal in real life conditions. The catalysts were prepared in two steps: first, commercial Degussa P25 (TiO_2) was treated with different amounts of ethanol and these samples were tested to determine the best one for NO_x oxidation as a preliminary photocatalyst, then the sample that showed the best photocatalytic activity was calcined at different temperatures. The ethanol-treated and calcined TiO_2 photocatalysts were characterized by XRD, Raman Spectroscopy, XPS, DR-UV-vis Spectroscopy and *in-situ* Fourier Transform Infrared (FTIR) Spectroscopy. The photocatalytic performance parameters of the catalysts were determined for Photocatalytic NO_x Oxidation and Storage (PHONOS).

3.1 Ethanol-Treated TiO_2 Catalysts

3.1.1 Physical Appearance

As stated in the Section 1.3, colored TiO_2 were obtained after both ethanol loading (treatment) and calcination of TiO_2 samples. Compared to white Degussa P25, ethanol loading optimization samples had a slightly yellowish/darker color whereas significant color change was observed for samples after they were calcined (Figure 3.1).



Figure 3.1: Color differences on TiO_2 samples after calcination. (250 mg of Degussa P25 and 3 mL of ethanol were mixed for all samples, calcination temperatures (in $^{\circ}\text{C}$) were labeled on the vials).

Initially, the color of samples changed from white, which is the color of Degussa P25, to slightly brown and towards dark brown as the calcination temperature increased from 100 $^{\circ}\text{C}$ to 250 $^{\circ}\text{C}$. Interestingly the color of samples calcined at 400 $^{\circ}\text{C}$ and 500 $^{\circ}\text{C}$ were also almost completely white. The sample calcined at 300 $^{\circ}\text{C}$ showed a light brown color which was also the color observed for the ethanol-treated TiO_2 sample (Figure 3.1).

Color change on TiO_2 has been associated with formation of defects [59, 77, 78, 79, 80, 81]. Thus, color changes of the ethanol-treated TiO_2 samples with respect to calcination temperature are attributed to the formation of defects and disorders. Therefore, it can be argued that the amounts of defects introduced on the calcined TiO_2 samples are the greatest when the calcination temperature was 200 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$. Since the color of the samples calcined at 150 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$ showed slightly darker color, it can be argued that these samples also include noticeable amounts of defects. On the other hand, the rest of the samples calcined at 100 $^{\circ}\text{C}$, 400 $^{\circ}\text{C}$, and 500 $^{\circ}\text{C}$ had a white color indicating a limited extent of defects relative to other ethanol treated samples in this study (Figure 3.1).

Therefore, the color of the calcined TiO₂ samples is thought to provide some insight regarding the relative defect concentrations of the investigated samples.

In the following sections, the photocatalytic performance of these TiO₂ samples will be presented and the effects of the concentration of defects on their photocatalytic activity will be discussed. Furthermore, the arguments made above will be further discussed based on the results of several characterization tests carried out.

3.2 Photocatalytic NO_x Oxidation and Storage (PHONOS)

Performance Tests

Photocatalytic NO_x Oxidation and Storage (PHONOS) measurements were done to determine the optimum ethanol loading and calcination temperature for the prepared TiO₂ catalysts. For the evaluation of the photocatalytic performance of the catalysts, NO Conversion %, Selectivity %, and DeNO_x index parameters were taken into account. Benchmark catalyst was taken as Degussa P25 (named P25 from here on), and all of the comparisons regarding photocatalytic performance were made relative to P25.

After optimum ethanol loading and calcination temperature for the catalysts were determined with 1-h tests, 15-h long run test for the best catalyst was carried out. Furthermore, CaO was mixed with the best catalyst to enhance and prolong the Selectivity% of the best catalyst in the long run.

3.2.1 Photocatalytic Performance of the Benchmark Photocatalyst –P25

To have the catalytic performance values of the benchmark catalyst (P25), twenty 1-h experiments were conducted for P25 samples. The experiments were conducted as described in the Experimental Part (Section 2.2). Obtained results are given in Figures 3.2 and 3.3.

Over the course of these 20 experiments, the mean NO Conversion% of P25 was obtained as 43% with a standard deviation of 1.6% and the mean Selectivity% was 24% with a standard deviation of 3.3% (Figure 3.2). Although the NO Conversion% of P25 is sufficient to be used as a NO_x removal catalyst, its drastically low Selectivity% indicates that the product NO₂ is neither further oxidized nor stored on the catalyst but rather released into the air. Such a behavior can be explained with the limited NO_x adsorption capacity of P25.

This means that P25 produces NO₂ which is known to be more toxic than NO [76]. Thus, P25 is not a suitable catalyst for the removal of NO_x as it pollutes the air rather than detoxifying it. This is also consistent with the DeNO_x Index value of P25 revealing a quite negative value of -0.55 with a standard deviation of 0.05 (Figure 3.3).

Hence, it is crucial to enhance the Selectivity% of P25-based catalysts to achieve positive DeNO_x Index values.

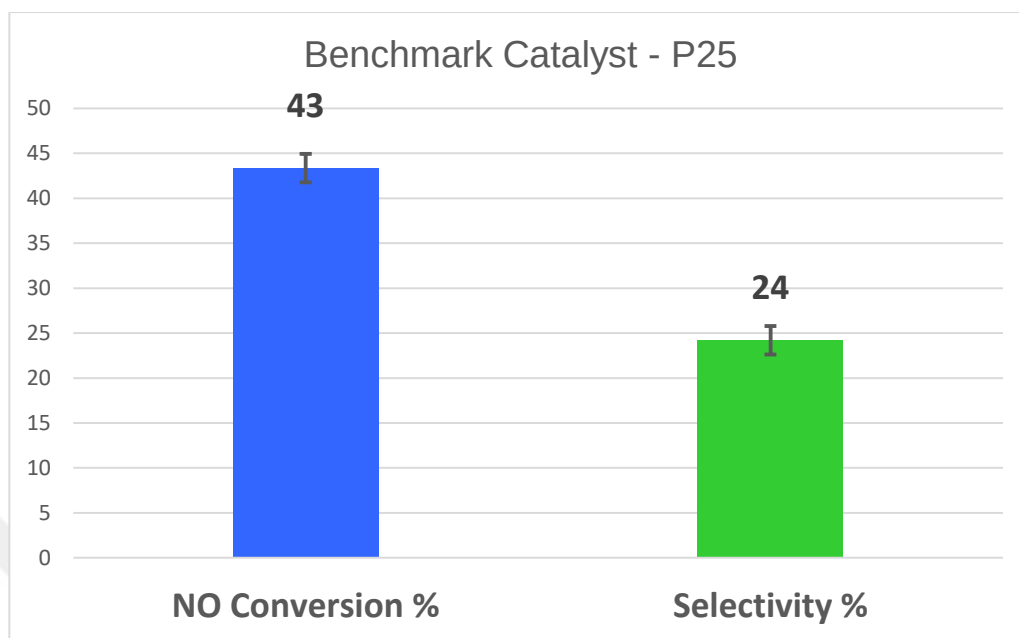


Figure 3.2: NO Conversion % and Selectivity % of Benchmark Photocatalyst –P25.

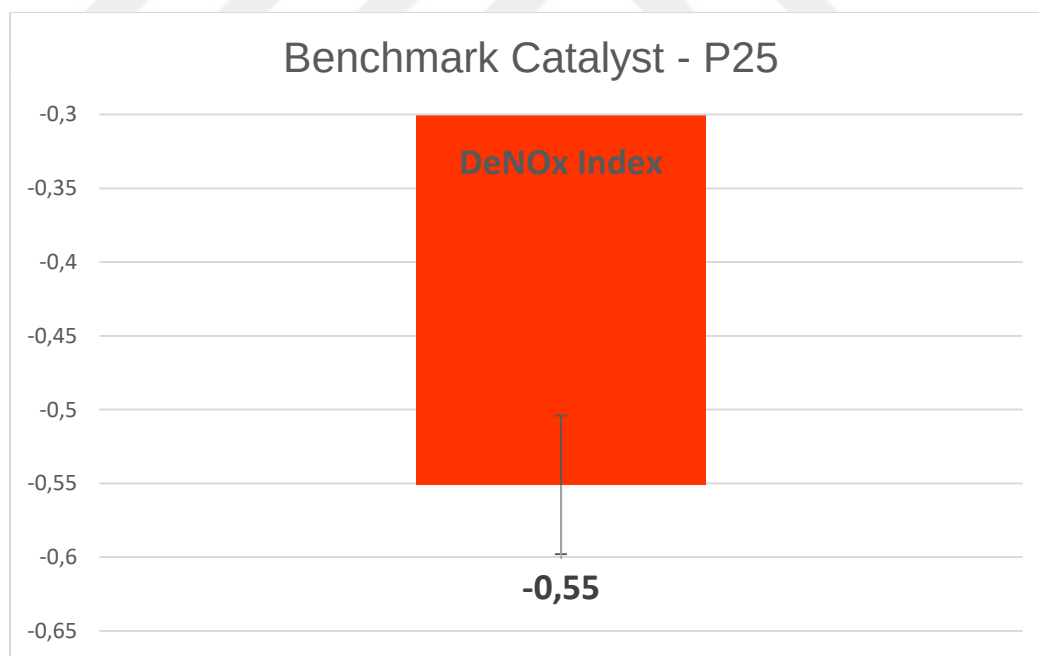


Figure 3.3: DeNO_x Index of Benchmark Photocatalyst –P25.

3.2.2 Photocatalytic Performance of TiO₂-EtOH Samples on Different Ethanol Loading

After data for the PHONOS activity of the benchmark catalyst P25 were acquired, similar tests were performed for ethanol-loaded TiO₂ samples. At least two experiments were conducted for each ethanol loading. Mean values and statistical variations in the NO Conversion%, Selectivity%, and DeNO_x Index of ethanol loaded TiO₂ samples are shown in Figures 3.4, 3.5, and 3.6. It should be noted that the experiments in this part were carried out using a different setup for the flow reactor in comparison to the rest of the experiments in this study. Hence rather than quantitative explanation for the NO Conversion%, Selectivity%, and DeNO_x Index values for these samples, only the qualitative trend will be focused on in this section.

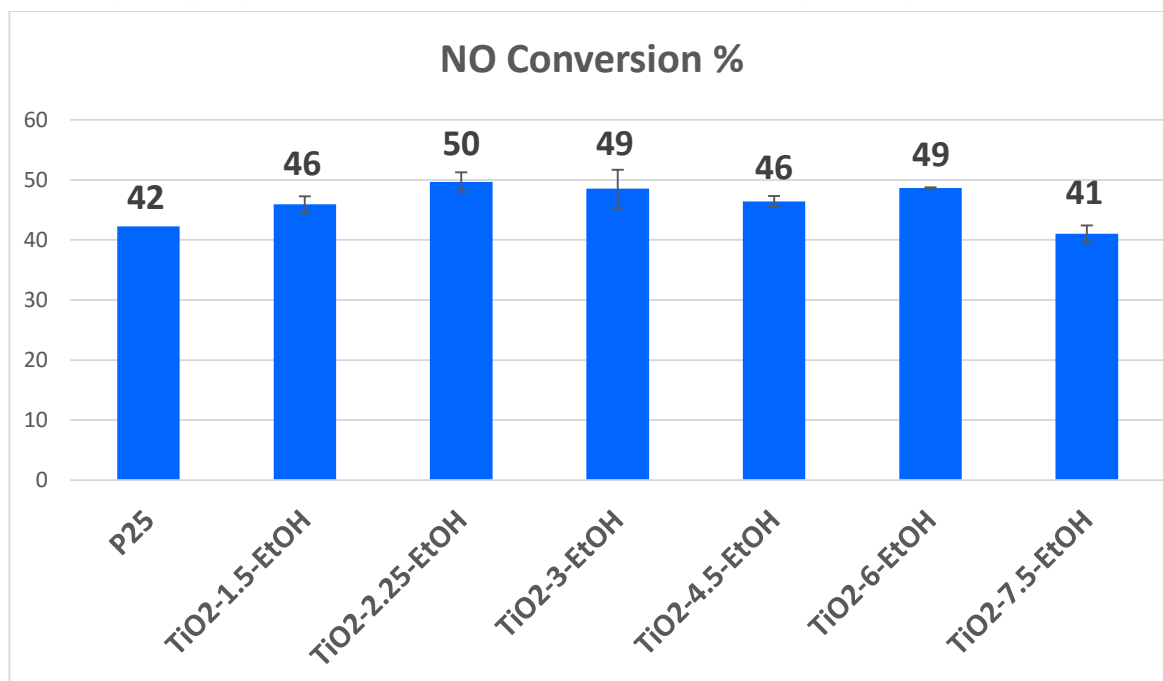


Figure 3.4: NO Conversion % for TiO₂ samples loaded with different amounts of ethanol.

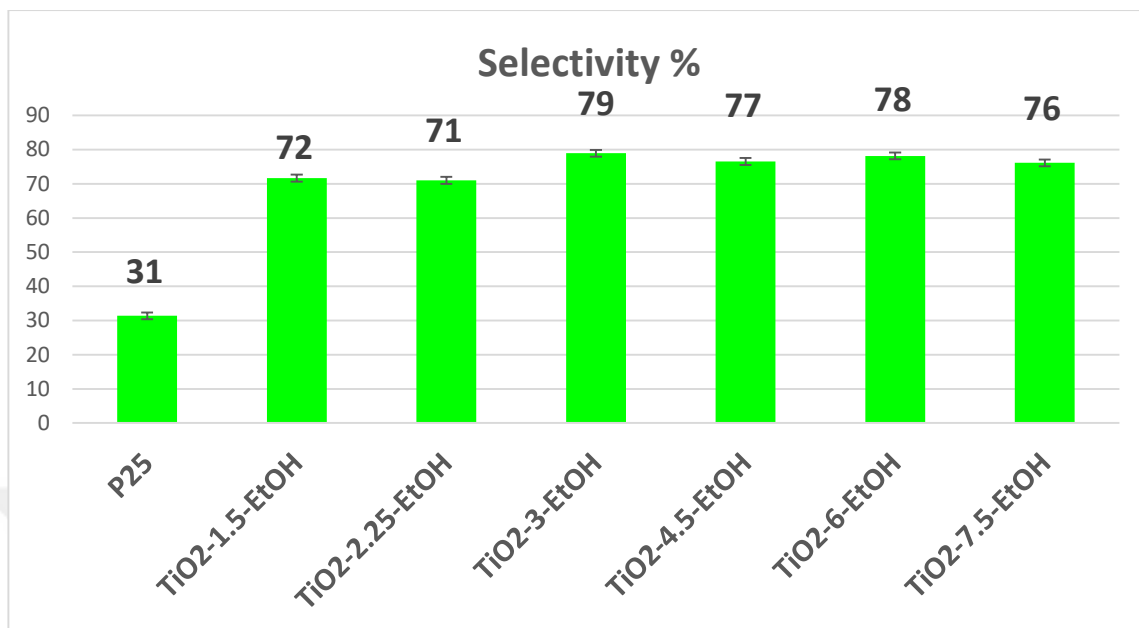


Figure 3.5: Selectivity % for TiO₂ samples loaded with different amounts of ethanol.

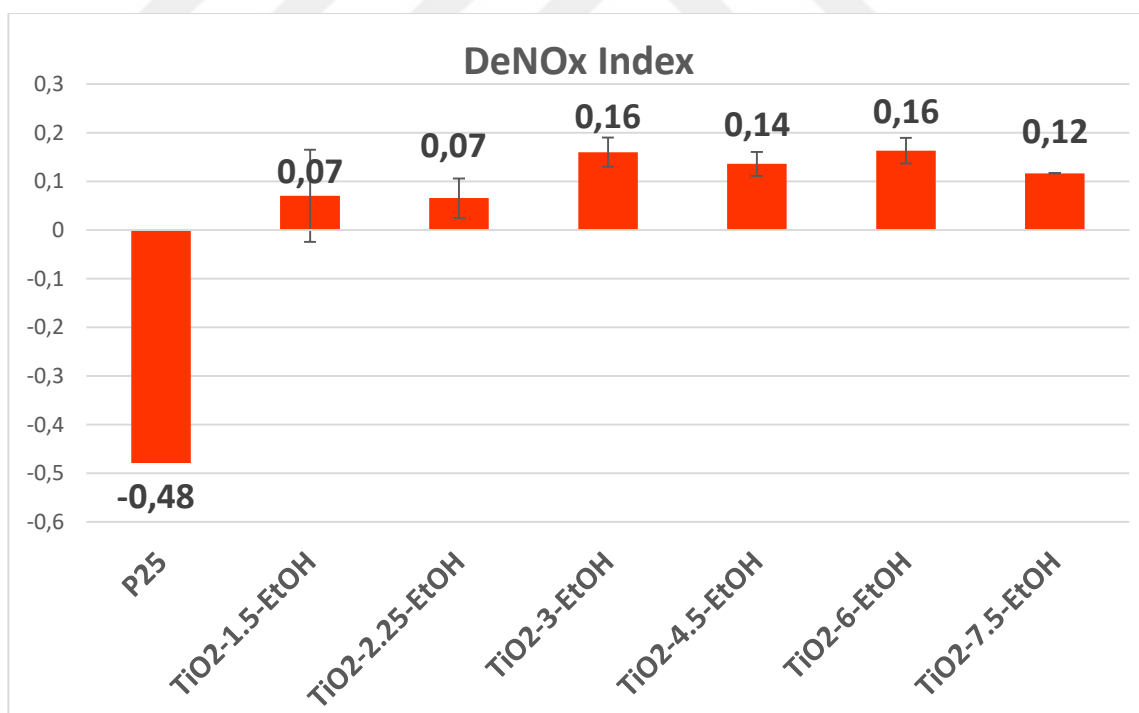


Figure 3.6: DeNOx Index values for TiO₂ samples loaded with different amounts of ethanol.

From Figure 3.4, it can be inferred that there is a notable increase (about 9%-19%) in the NO Conversion% for five of the six ethanol loaded TiO₂ samples compared to that of P25. The NO Conversion% values of the samples, except TiO₂-7.5-EtOH, were obtained ranging from 46% to 50% in which the highest percentage belonged to TiO₂-2.25-EtOH. A significant improvement was observed for the Selectivity % of the ethanol loaded TiO₂ samples ranging from 71% to 79% compared to that of P25 (31%) (Figure 3.5). TiO₂-3-EtOH showed the highest Selectivity% among six ethanol loaded TiO₂ samples.

DeNO_x Indexes of all of the ethanol loaded TiO₂ samples had greater and positive values compared to that of P25 with a negative DeNO_x Index of -0.48 (Figure 3.6). Thus, it is clear that ethanol treatment enhances PHONOS performance of P25. The highest DeNO_x Index values obtained for TiO₂-3-EtOH, TiO₂-4.5-EtOH, and TiO₂-6-EtOH were 0.16, 0.14 and 0.16, respectively.

In conclusion; based on the NO Conversion%, Selectivity%, and DeNO_x Index values for ethanol treated P25 samples, the most promising catalyst for PHONOS was determined to be TiO₂-3-EtOH which had 49% NO Conversion %, 79% Selectivity %, and +0.16 DeNO_x Index value compared to those of P25 (42%, 31% and -0.48, respectively).

3.2.3 Photocatalytic Performance of TiO₂-EtOH Samples After

Different Thermal Treatment Temperatures

After the ethanol loading optimization of TiO₂ (P25), seven different calcination temperatures from 100 °C to 500 °C were selected to find optimum calcination temperature for the best photocatalytic performance. Different calcination temperatures yielded

different colored catalysts as shown in Figure 3.1 and after 1-h performance tests, the data for the photocatalytic activities of the calcined TiO_2 samples showed that photocatalytic performance cannot be directly linked to the color of the sample. NO Conversion%, Selectivity%, and DeNOx Index values of TiO_2 samples calcined at different temperatures are given in Figures 3.7, 3.8 and 3.9.

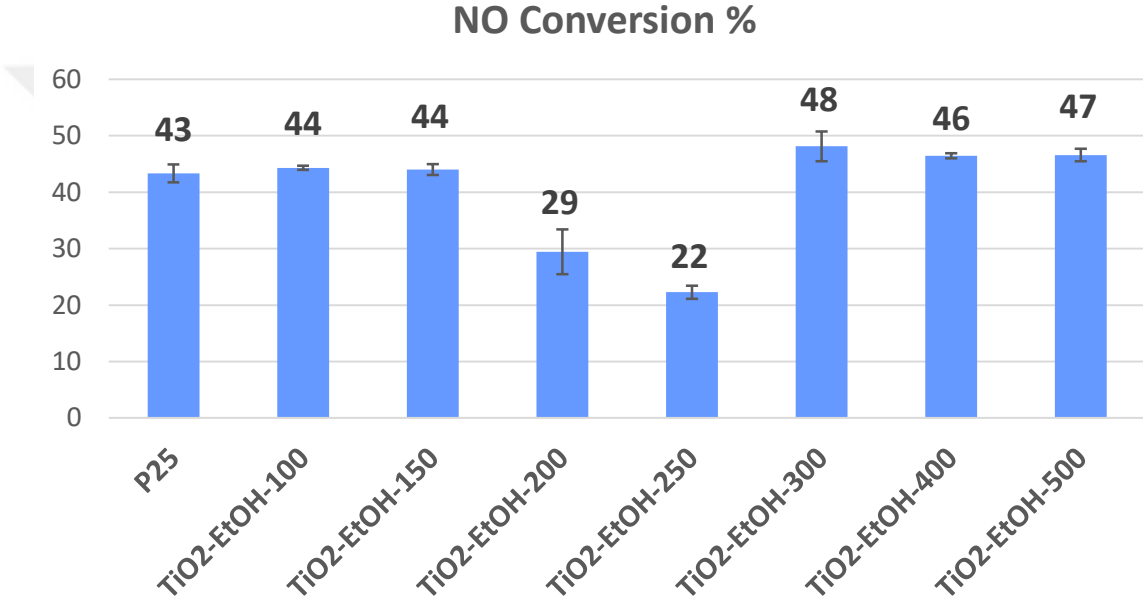


Figure 3.7: NO Conversion % data for different calcination temperatures of ethanol treated TiO_2 .

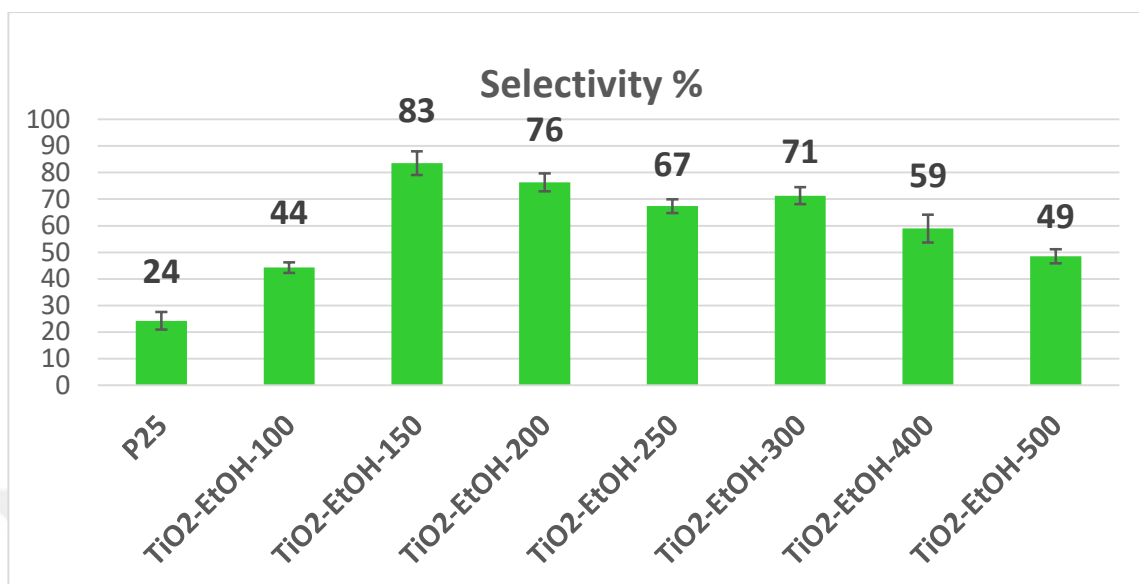


Figure 3.8: Selectivity % data for different calcination temperatures of ethanol treated TiO₂.

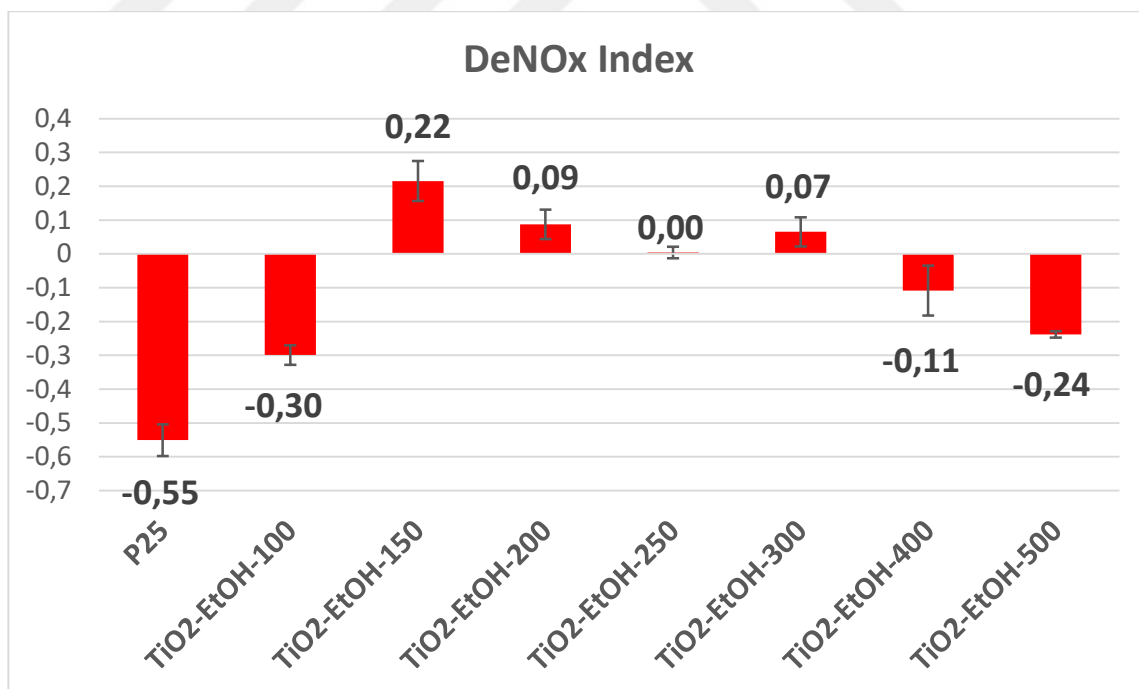


Figure 3.9: DeNOx Index data for different calcination temperatures of ethanol treated TiO₂.

By comparing the color trend (Figure 3.1) and NO Conversion % (Figure 3.7) of the calcined TiO₂ samples, it can be said that NO Conversion% did not increase as the color of the catalyst changed towards brown, in contrast the brown colored TiO₂-EtOH-200 and TiO₂-EtOH-250 showed the lowest NO Conversion % values, even lower than that of P25. Other than these two calcined TiO₂ catalysts, remaining samples had similar NO Conversion% values (44%-48%) to that of P25 (43%). It appears that both ethanol treatment and variation of calcination temperature did not cause much improvement on the NO Conversion% of TiO₂.

Introduction or formation of defects (specifically V_{os}) on TiO₂ is said to enhance its both UV and visible-light photocatalytic activity and it was reported that photogenerated electrons can be trapped below the CB resulting in the lifetime of charge carriers is reduced [82,83,84]. It is also reported that the defects in high extent on TiO₂ act as recombination centers which hinders the lifetime of photogenerated charge carriers [85, 86, 87, 88]. As any photocatalytic process is initiated by these charge carriers, the concentration of defects cannot be correlated directly with photocatalytic activity but rather there seems a limit for the optimum number of defects for high photocatalytic activity which may explain the decline in NO Conversion % of TiO₂-EtOH-200, TiO₂-EtOH-250 samples in this study (Figure 3.7) [65]. As their colors suggest that these two samples were thought to have the highest concentration of defects, therefore decrease in NO Conversion% can be linked to the aforementioned reasons. The increase in NO Conversion% of TiO₂-EtOH-300 can be also explained with this thought where there may be enough defects that enhance NO oxidation, consequently making TiO₂-EtOH-300 to have a higher NO Conversion % than P25.

Another intriguing result was observed for Selectivity% of the calcined TiO₂ catalysts (Figure 3.8). Despite of an observed volcano plot for Selectivity %, such a trend cannot be correlated with color change, where the maximum Selectivity % (83%) was achieved with TiO₂-EtOH-150 catalyst which had a darker color. Other “colored” catalysts TiO₂-EtOH-200, TiO₂-EtOH-250, and TiO₂-EtOH-300 had also significantly good Selectivity% (76, 67, and 71% respectively), but these values were considerably lower than that of TiO₂-EtOH-150 (83%). Nevertheless, all of these catalysts had much better Selectivity % in comparison to P25 (24%), even the Selectivity% of the “white” catalysts TiO₂-EtOH-100, TiO₂-EtOH-400, and TiO₂-EtOH-500 were 44, 59, and 49%, respectively. The overall increase in selectivity for each catalyst was speculated to be caused by the introduced defects and newly formed carbonaceous species on the surface of the catalyst after ethanol treatment and calcination of P25 which will be addressed in the upcoming sections.

In light of the NO Conversion % and Selectivity% values, the best photocatalytic performance was achieved with TiO₂-EtOH-150 which had a DeNO_x Index of +0.22 (Figure 3.9). When this value is compared to that of P25 (-0.55) (Figure 3.3), it can be said that simple ethanol treatment and relatively low calcination temperature on TiO₂ can result with a TiO₂ catalyst that can detoxify the air efficiently in NO_x oxidation.

TiO₂-EtOH-200, TiO₂-EtOH-250, and TiO₂-EtOH-300 catalysts also showed positive DeNO_x Index values-of which can be attributed to their high Selectivity% (Figure 3.9). Despite having positive DeNO_x Index values, TiO₂-EtOH-200 and TiO₂-EtOH-250 had evidently low NO Conversion Percentages (29% and 22%) than P25 (44%) rendering these catalysts not ideal for PHONOS (Figure 3.7). The last catalyst with a positive a DeNO_x Index value was TiO₂-EtOH-300 (+0.07), but it is obvious that TiO₂-EtOH-150

outperforms this catalyst (+0.22). The “white” colored ethanol treated and calcined catalysts TiO₂-EtOH-100, TiO₂-EtOH-400, and TiO₂-EtOH-500 had enhanced Selectivity % but their DeNO_x Index values, though not as bad as that of P25, were negative (Figure 3.9).

To conclude this section, mild-brown colored TiO₂-EtOH-150 was found the best-performing catalyst in 1-h PHONOS performance tests. Hence, further 15-h long run PHONOS measurement were performed with only TiO₂-EtOH-150 photocatalyst.

3.2.4 Photocatalytic Performance of TiO₂-EtOH-150 in Long Run Measurements

To test the long-run performance of the best-performing catalyst for NO_x removal, a 15-h experiment was conducted with TiO₂-EtOH-150. As all of its performance parameter (NO Conversion %, Selectivity %, and DeNO_x Index) values were compared with those of the benchmark catalyst P25, a separate 15-hour experiment was also conducted with P25. All performance parameters were calculated for the first and every third hour interval. NO Conversion%, Selectivity% and DeNO_x Index values of P25 and TiO₂-EtOH-150 were plotted side by side in Figures 3.10, 3.11, and 3.12.

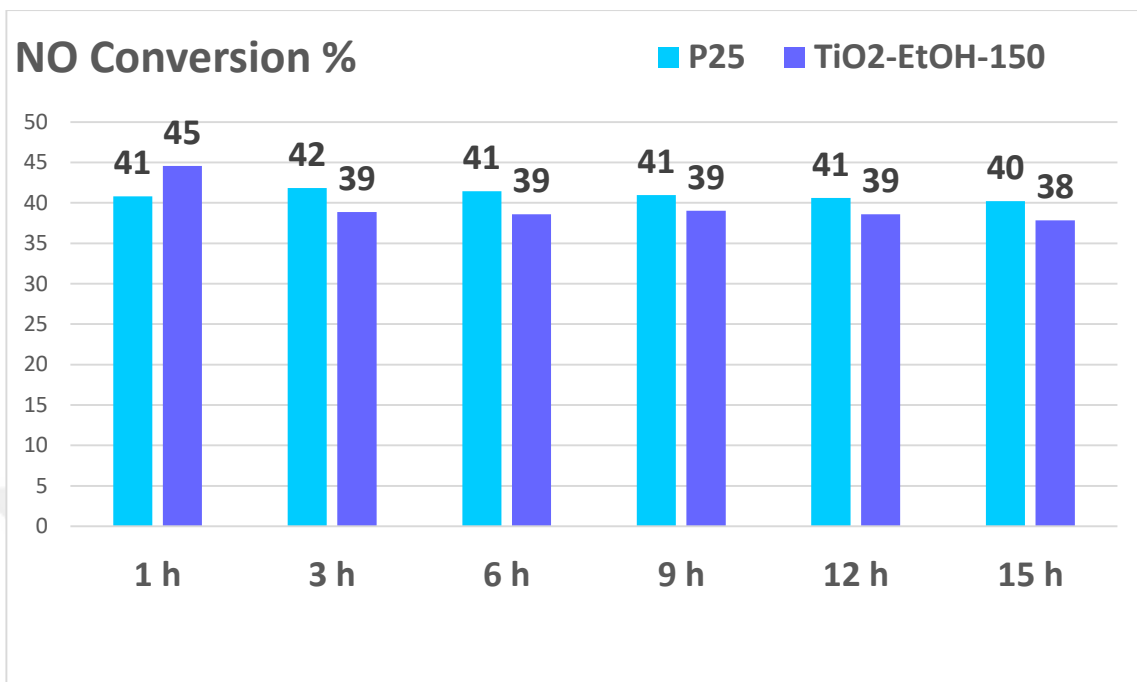


Figure 3.10: NO Conversion % of P25 and TiO₂-EtOH-150 on 1st, 3rd, 6th, 9th, 12th and 15th hour marks.

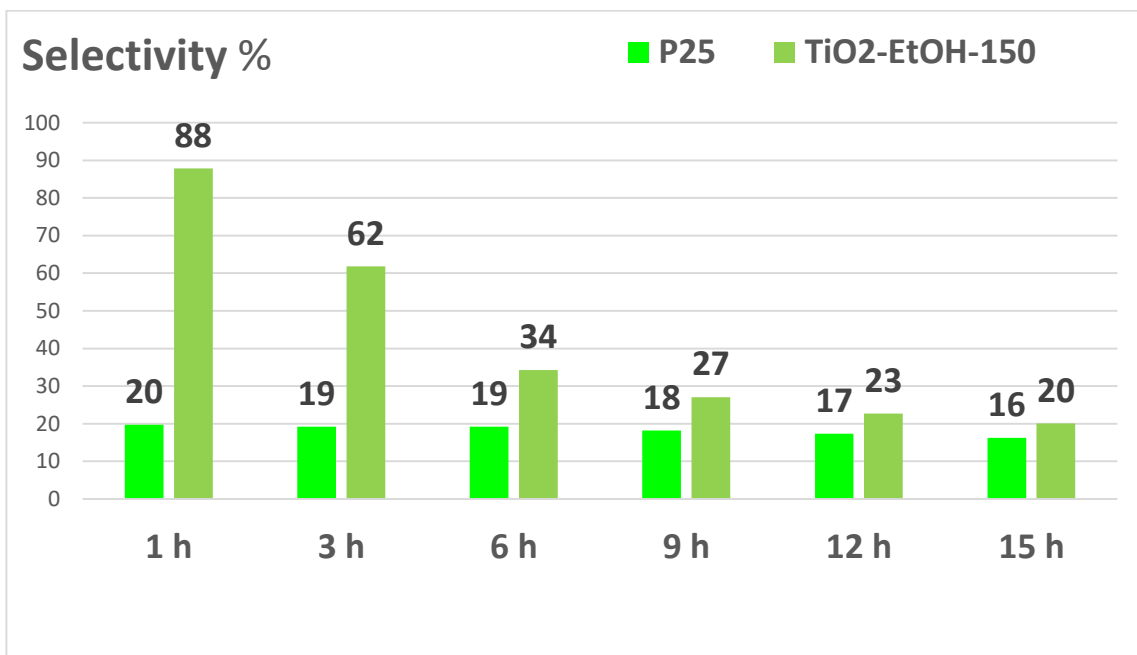


Figure 3.11: Selectivity % of P25 and TiO₂-EtOH-150 on 1st, 3rd, 6th, 9th, 12th and 15th hour marks.

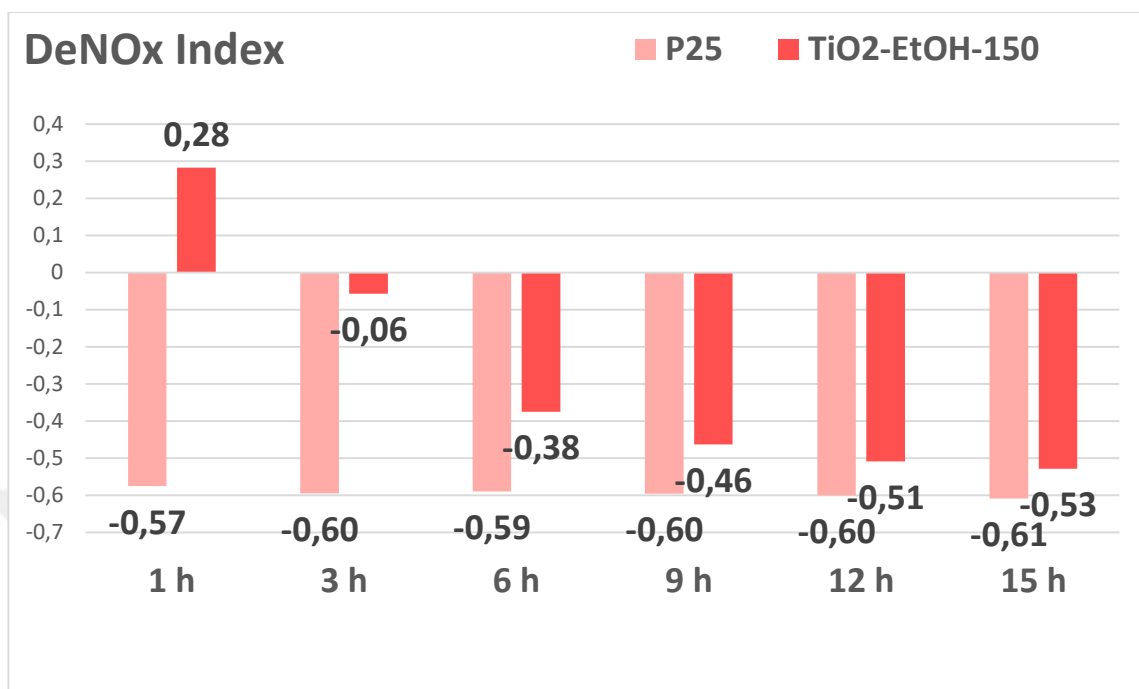


Figure 3.12: DeNO_x Index of P25 and TiO₂-EtOH-150 on 1st, 3rd, 6th, 9th, 12th and 15th hour marks.

While NO Conversion% of TiO₂-EtOH-150 had a slight decrease after the 3rd hour, the value stayed close to that of P25 over 15-h span (Figure 3.10). This indicates that both catalysts are able to oxidize similar amounts of NO (around 40%) into other NO_x species even in the long run. Therefore, NO Conversion% did not have a detrimental effect on the photocatalytic performances of the catalysts in long run experiments.

A critical observation is made from Selectivity% changes over time for the TiO₂-EtOH-150 catalyst (Figure 3.11). As mentioned in the previous part, TiO₂-EtOH-150 had the best Selectivity% of 83% while P25 had only 24% selectivity (Figure 3.8). The main reason for positive DeNO_x Index value for TiO₂-EtOH-150 was due to its high Selectivity%. For the TiO₂-EtOH-150 catalyst over the course of time, a substantial drop in its selectivity was observed which eventually converged with the selectivity of P25 around the end of

the 12th hour (Figure 3.11). Thus, the DeNO_x Index values of TiO₂-EtOH-150 also converged to the DeNO_x Index values of P25 which occurred around 12th hour (Figure 3.12).

The decay in selectivity of TiO₂-EtOH-150 over time may be speculated by the fact that the carbonaceous species introduced by ethanol have either transformed into other carbonaceous species that are unable to enhance NO_x oxidation and storage or undergo photo decay over time which will be investigated further in the upcoming sections.

3.2.5 Photocatalytic Performance of CaO added TiO₂-EtOH-150

As the drop in Selectivity% has a detrimental effect on photocatalytic performance of TiO₂-EtOH-150 in the long run, CaO was utilized to increase the NO_x storage uptake and hence the long-run efficiency of the catalyst. The addition of alkaline earth oxides was first introduced for NO_x Storage Reduction (NSR) catalysts to increase NO_x uptake [89,90,91]. Here CaO was used mainly due to its basic nature which is thought to keep the produced NO₂ on the surface of the catalyst [92].

After physically mixing TiO₂-EtOH-150 and CaO (20%, w/w), a long-run catalytic test was conducted. To see the effect of the addition of CaO on long-run efficiency in the photocatalysis, the performance parameter (NO Conversion %, Selectivity %, and DeNO_x Index) values of TiO₂-EtOH-150-CaO mixture was compared with those TiO₂-EtOH-150 in Figures 3.13, 3.14, and 3.15.

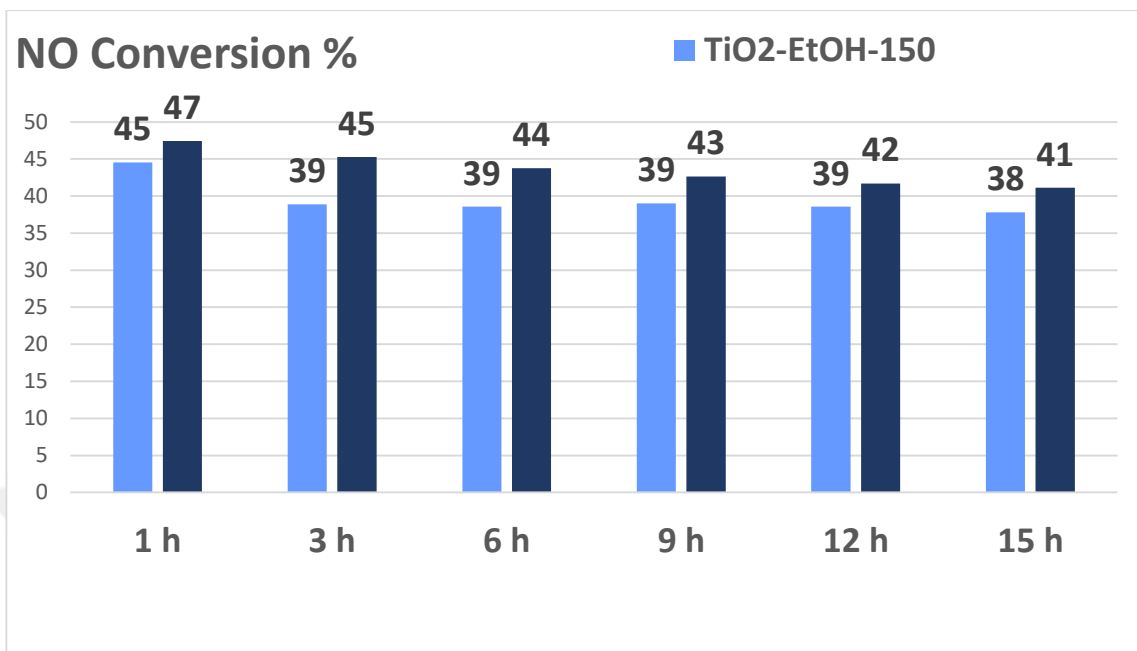


Figure 3.13: NO Conversion % of TiO₂-EtOH-150 and TiO₂-EtOH-150-CaO on 1st, 3rd, 6th, 9th, 12th and 15th hour marks.

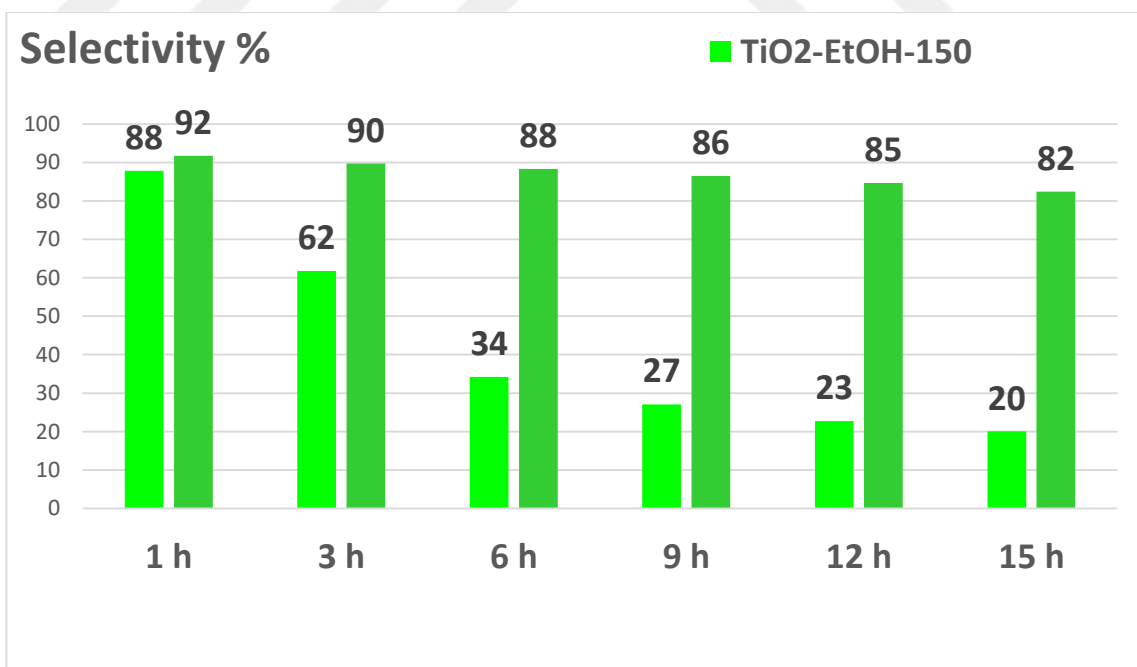


Figure 3.14: Selectivity% of TiO₂-EtOH-150 and TiO₂-EtOH-150-CaO on 1st, 3rd, 6th, 9th, 12th and 15th hour marks.

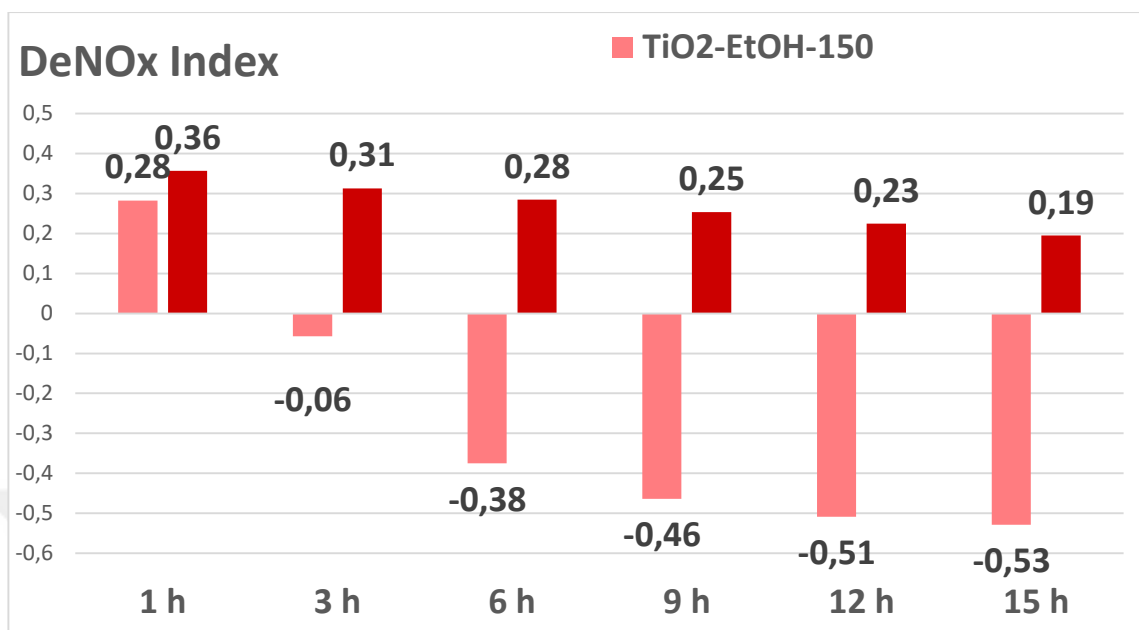


Figure 3.15: DeNO_x Index of TiO₂-EtOH-150 and TiO₂-EtOH-150-CaO on 1st, 3rd, 6th, 9th, 12th and 15th hour marks.

For NO Conversion% on the samples of TiO₂-EtOH-150 and the CaO mixed analogue (Figure 3.13), there seems to be a slight increase in NO Conversion %, this may be attributed to CaO domains on the surface being able to facilitate diffusion of NO_x species away from the active sites towards themselves which result in a slight positive effect on NO Conversion % [92].

The intended outcome for the CaO addition was clearly seen in Figure 3.14, where Selectivity% improved slightly, from 88% to 92%, though the major influence of CaO was seen on the minimal decline of Selectivity % over the hours. At the end of 15th hour, attained Selectivity% value was 82% for the TiO₂-EtOH-150-CaO mixture which was only outperformed by the first hour of the TiO₂-EtOH-150 catalyst, no CaO added analogue.

The increase in Selectivity % consequently had positive effects on DeNO_x Index (Figure 3.15), where the TiO₂-EtOH-150-CaO mixture had better DeNO_x Index values at all hour marks. TiO₂-EtOH-150-CaO mixture even had a +0.19 DeNO_x Index value even after the 15th hour which is nearly on par with the first hour of TiO₂-EtOH-150 when error margins are considered (Figure 3.9). Therefore, it can be concluded that TiO₂-EtOH-150-CaO mixture is an efficient PHONOS catalyst with a long lifetime. To further understand about the effects of the calcination temperature on the photocatalytic performances of ethanol treated and calcined TiO₂ catalysts, their characterizations were carried out.

3.3 Characterization of the Samples

3.3.1 Analysis of Crystallographic Structure via XRD

For analyzing the crystallographic structures of P25 and calcined TiO₂-EtOH catalysts, XRD measurements were conducted. The expected phases for P25-based materials are anatase and rutile, therefore the cards for XRD diffraction patterns of anatase and rutile were supplied from ICDD (No: 00-021-1272 for anatase, No: 00-021-1276 for rutile) and they were plotted at the bottom of the graph with the XRD diffraction patterns of P25 and calcined TiO₂-EtOH catalysts in Figure 3.16.

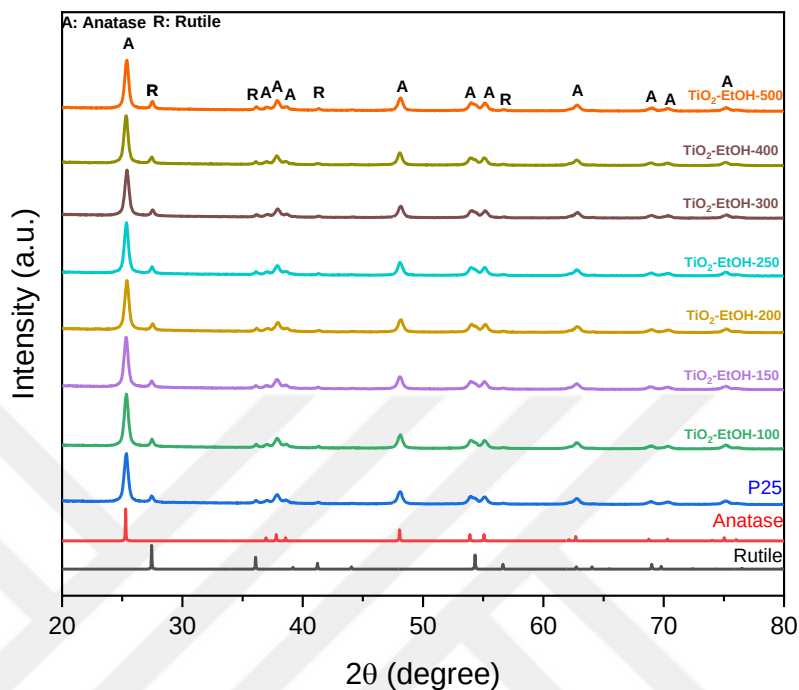


Figure 3.16: XRD diffraction patterns of rutile, anatase, P25, and the calcined TiO_2 -EtOH catalysts.

As mentioned in Section 1.2.1, P25 is a mixture of anatase and rutile, in which anatase phase is dominant (roughly 5:1) [39]. All of the calcined TiO_2 -EtOH catalysts gave the same diffraction peaks with nearly the same peak intensities and widths as P25, which was expected, since anatase to rutile transformation is reported to occur at around 600 °C in the presence of ethanol [93].

XRD analysis of the calcined TiO_2 -EtOH catalysts revealed that they all have the same crystallographic structure as P25. In other words, no “bulk” crystallographic structural changes occurred due to different calcination temperatures. It should be mentioned that XRD analysis is not a surface sensitive method, therefore changes in the surface may have

been missed. Similar results for other reduced titania papers also support this claim [59, 94, 95, 96, 97].

3.3.2 Examination of Surface Disorders by Raman Spectroscopy

To further complement structural characterization made by XRD, Raman spectroscopy was used for the determination of disordered structures in the calcined TiO_2 -EtOH catalysts as this method is surface sensitive. Raman spectra of the samples are given in Figure 3.17.

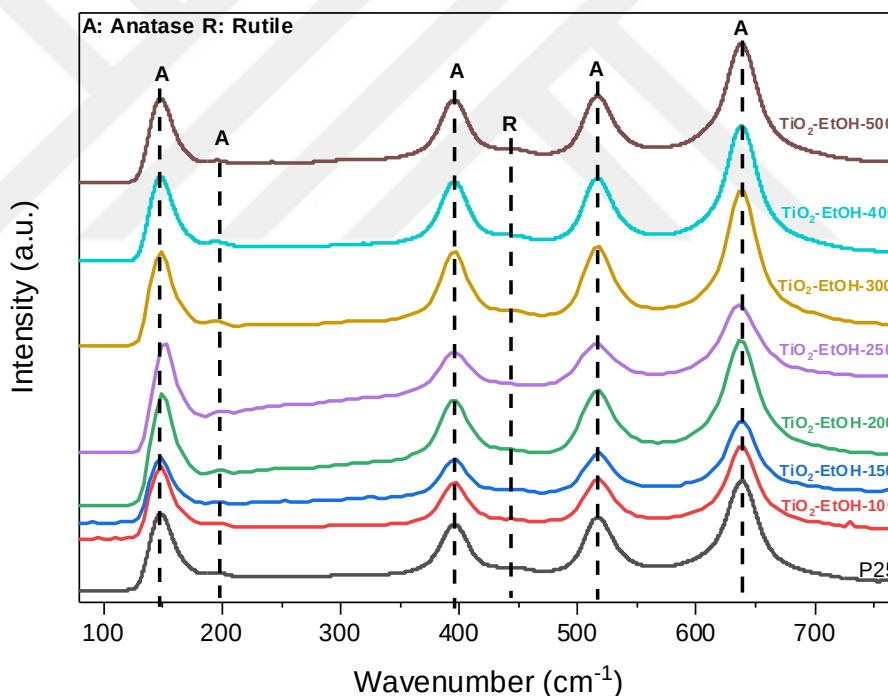


Figure 3.17: Raman spectra of P25 and all calcined TiO_2 -EtOH-3 catalysts.

In accordance with XRD diffraction patterns, characteristic peaks of anatase (E_{1g} peaks of 144, 197, 639 cm^{-1} ; B_{1g} peaks of 399, 519 cm^{-1} ; A_{1g} peak of 513 cm^{-1}) were dominant for all samples with a slight hint of rutile peak at around 447 cm^{-1} assigned to rutile (E_g). The

remaining characteristic peaks of rutile were either obscured by anatase peaks such as 143 cm^{-1} (B_{1g}) and 612 cm^{-1} (A_{1g}) or had very little intensity 826 cm^{-1} (B_{2g}) which was not assigned in Figure 3.17 [98, 99]. One noticeable feature of Figure 3.17 was, brown colored samples of $\text{TiO}_2\text{-EtOH-200}$ and $\text{TiO}_2\text{-EtOH-250}$ (Figure 3.1), had a baseline tilt which was associated with fluorescence caused by carbonaceous surface species on these catalysts.

Since XRD peaks of all of the analyzed samples had nearly the same FWHM, it can be assumed that all calcined $\text{TiO}_2\text{-EtOH}$ catalysts have similar bulk crystal sizes as P25 (ca. 21 nm) [100], hence there should be no confinement effects caused by the finite size of the grains ($< 10\text{ nm}$) [101]. With this in mind, one common analysis for reduced TiO_2 with Raman spectroscopy is to check the difference in the 144 cm^{-1} (E_{1g}) peak, broadening or a redshift in this peak could indicate lattice disorders [102, 103]. After doing a baseline correction for $\text{TiO}_2\text{-EtOH-200}$ and $\text{TiO}_2\text{-EtOH-250}$, 144 cm^{-1} peak was plotted again.

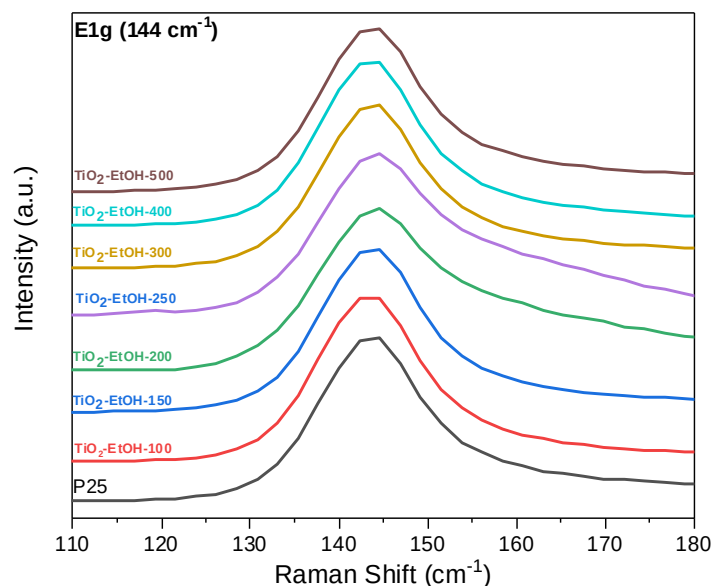


Figure 3.18: E_{1g} peak (144 cm^{-1}) of P25 and all calcined $\text{TiO}_2\text{-EtOH}$ catalysts (Baseline corrected for $\text{TiO}_2\text{-EtOH-200}$ and $\text{TiO}_2\text{-EtOH-250}$ samples).

Because of instrumental restrictions (maximum wavenumber resolution being $<4.5\text{ cm}^{-1}$ at 614 cm^{-1}), a comment regarding peak position shift is not credible therefore the FWHM of each sample was calculated and the following trend was achieved (Figure 3.19),

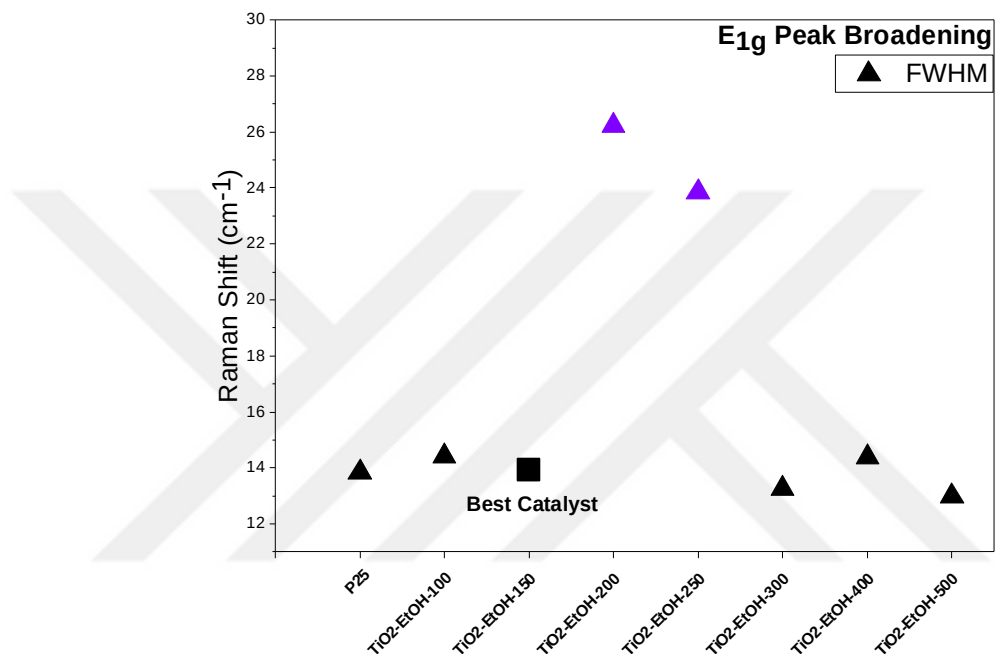


Figure 3.19: E_{1g} peak (144 cm^{-1}) of P25 and all calcined TiO_2 -EtOH catalysts. (TiO_2 -EtOH-150 was represented with square, TiO_2 -EtOH-200 and TiO_2 -EtOH-250 were represented with blue colored triangles)

As seen in Figure 3.19, it is clear that the brown-colored catalysts of TiO_2 -EtOH-200 and TiO_2 -EtOH-250 (Figure 3.19, blue colored triangles) have noticeable peak broadening therefore the interpretation of lattice disorders facilitated by non-stoichiometry caused by the introduction of defects can be made [102, 104, 105, 106]. Moreover, since Raman spectroscopy is a rather surface-sensitive method one can speculate that these defects could be associated with oxygen vacancies (V_{O} s) on the catalyst surface [94, 107].

Here the question is why mild brown-colored catalysts, $\text{TiO}_2\text{-EtOH-150}$ (Figure 3-19, square) and $\text{TiO}_2\text{-EtOH-300}$, which are assumed to have a noticeable concentration of defects, have similar FWHM to white colored catalysts and P25. The reason for this is thought to be caused due to lack of resolution on the instrument that Raman Spectra was taken, had there been an instrument with a better resolution, $\text{TiO}_2\text{-EtOH-150}$ and $\text{TiO}_2\text{-EtOH-300}$ samples would have had a broader 144 cm^{-1} peak, thus a volcano plot for the FWHM would have been achieved like in the case of color change.

In light of our XRD and Raman analyses, it can be proposed that calcined $\text{TiO}_2\text{-EtOH}$ catalysts have bulk structure just as P25 has, while on the surface and subsurface regions it can be speculated that TiO_2 is in a reduced form (TiO_{2-x}) containing oxygen vacancies (V_{Os}) and there are also carbonaceous species adsorbed on the surface (Figure 3.20).

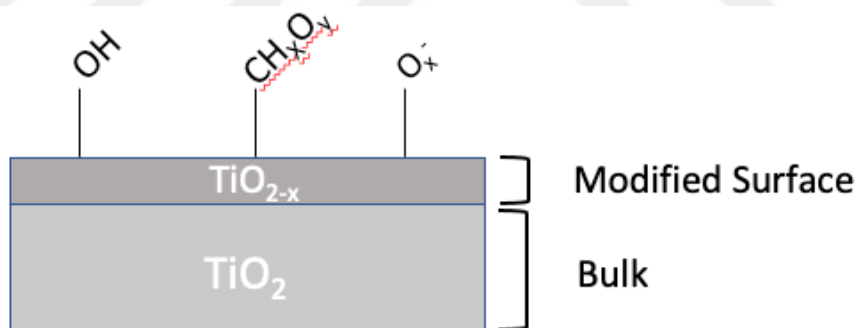


Figure 3.20: Illustration of hypothesized structure of calcined $\text{TiO}_2\text{-EtOH}$ catalysts (Note: P25 is known to have defects therefore assignment of bulk as TiO_2 is an oversimplification).

3.3.3 Bandgap Analysis by DR-UV-vis Spectroscopy

Since color changes of calcined TiO_2 -EtOH catalysts indicate differences in their light absorption, it is necessary to compare UV-vis spectra of all catalysts. Accordingly, DR-UV-vis spectroscopy was utilized and bandgap energy values were also determined. Acquired optical absorption spectra are given in Figure 3.21.

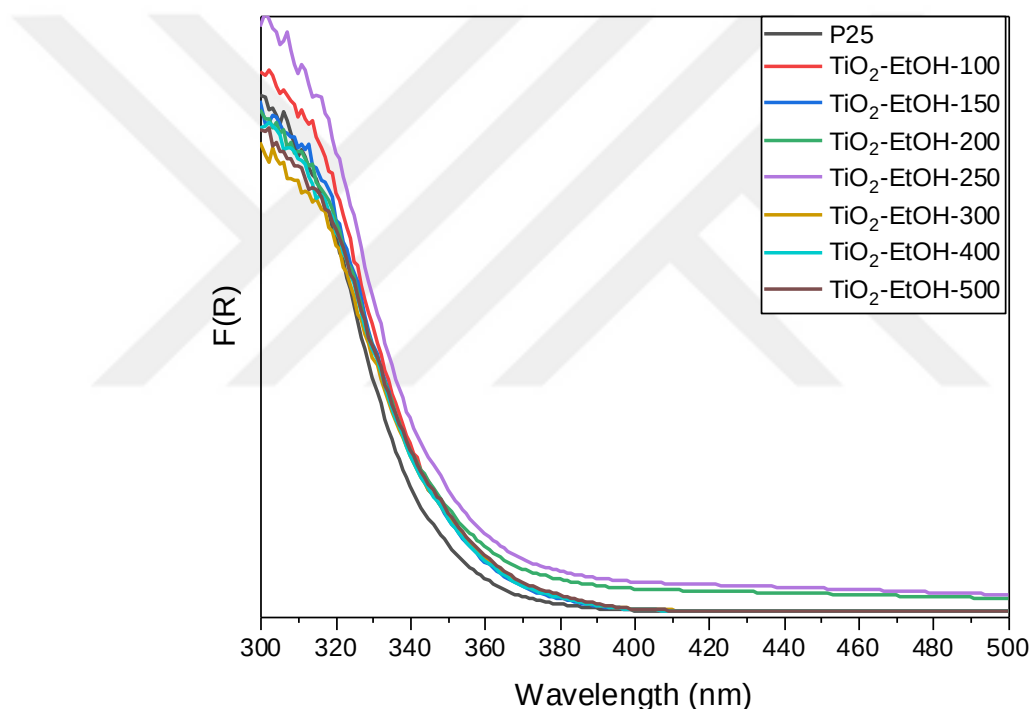


Figure 3.21: Optical absorption spectra of P25 and calcined TiO_2 -EtOH catalysts.

From 3.21, it is clearly seen that all calcined TiO_2 -EtOH catalysts had better light absorption above the wavelengths of ~ 330 nm compared to P25. Other than TiO_2 -EtOH-200 and TiO_2 -EtOH-250, light absorption of each catalyst goes to zero around ~ 410 nm. Therefore, the color change observed in the catalysts (Figure 3.1), can be linked with light

absorbance, also ethanol treatment on TiO₂ can be said to enhance the UV-light absorption as the absorbance of P25 which is not treated with ethanol can be clearly distinguished from the other absorbances as it is the lowest.

Although the UV-light absorption enhances for all ethanol-treated TiO₂, even TiO₂-EtOH-200 and TiO₂-EtOH-250 samples still absorb light at 500 nm, it should be noted that light absorption cannot be directly correlated with photocatalytic activity [103].

After optical light absorption analysis, the bandgap energy variance of all samples was examined. The Tauc method was implemented (Eq-3-1) [108, 109, 110] using the following relationship:

$$(\alpha \cdot h\nu)^{1/\gamma} = B (h\nu - E_g) \quad (\text{Eq 3-1})$$

where, α is the energy-dependent absorption coefficient, h is the Planck constant, ν is the frequency of photon, B is a constant and E_g is the band gap energy of the sample. The factor of γ is dependent on the electron transfer between valence band and conduction band, if the transition is direct γ takes $1/2$, and if its indirect γ takes the value of 2. This value depends on the characteristic behavior of a semiconductor.

Tauc method was further implemented with Kubelka and Munk's theory [111] in which Obtained Kubelka-Munk function ($F(R_\infty)$), from measured reflectance was substituted for α term in Eq 3-1,

$$F(R_\infty) = \frac{K}{S} = \frac{(1-R_\infty)^2}{2R_\infty} \quad (\text{Eq 3-2})$$

K is the absorption and S is the scattering coefficient where R_∞ corresponds to the reflectance of an infinitely thick specimen. After the substitution of $F(R_\infty)$ into Eq 3-1, the following equation was obtained,

$$(F(R_\infty) \cdot h\nu)^{1/\gamma} = B (h\nu - E_g) \quad (\text{Eq 3-3})$$

Although one can estimate the bandgap of the catalyst from this equation it should be noted that P25 contains phases of anatase and rutile, which have indirect and direct bandgaps. Moreover, bandgaps of anatase and rutile are known to not align therefore only a rough estimation can be done. Since anatase is the dominant phase in all catalysts for this study, γ was taken as 2, and the following Tauc plot was obtained (Figure 3.22),

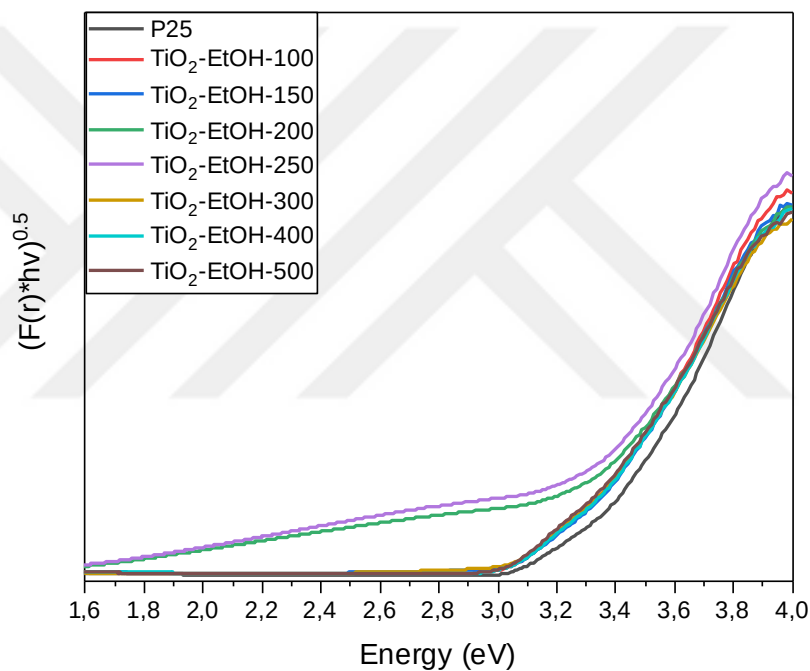


Figure 3.22: Tauc plot of P25 and all calcined TiO₂-EtOH catalysts.

To estimate bandgap, the common implementation to the Tauc plot is to extrapolate the region where steep increase starts to occur. One thing to keep in mind with this method is that this application is known to be only appropriate when the spectrum belongs to a bare semiconductor. As the catalysts in this study, the samples are known to have defects and surface complexes, hence application of Tauc method is not ideal. Since the bandgap should not change as the bulk material remains the same, a modified version of Tauc

method, with a baseline approach was used in this study [112], where a baseline was drawn below the fundamental absorption, which corresponds to the semiconductor band edge, and slope of fundamental absorption was extrapolated to that baseline, in which bandgap estimation was done (Figure 3.23).

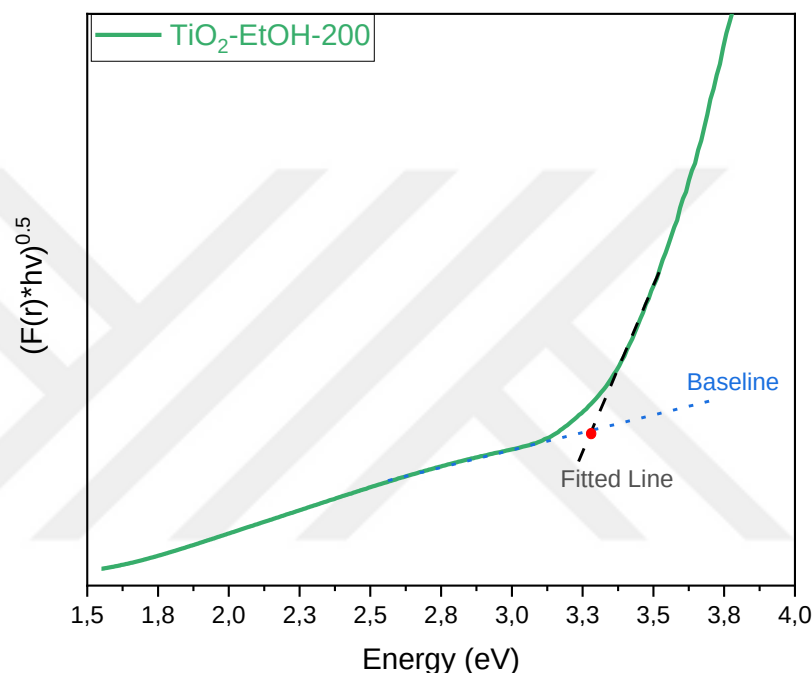


Figure 3.23: Bandgap determination by using baseline analysis for TiO₂-EtOH-200.

As this method only estimates bandgap, it was thought that exact values estimated for each catalyst should not be reported, but all of the estimated bandgaps were close to ~3.2 eV. Since there is not a significant shift in the position of the band edge as it is present for some works involving doping of TiO₂ [113 , 114, 115, 116], it can be concluded that ethanol treatment of TiO₂ does not change the bandgap significantly.

The observed light absorption at higher wavelengths and the tails observed toward in lower energies in the Tauc plot thus is attributed to the interband states as these states are

due to surface modifications, such results were also reported for reduced titania works [96, 102, 117, 118]. Therefore, it can be argued that ethanol treatment of TiO_2 induces interband states mainly for the samples of $\text{TiO}_2\text{-EtOH-200}$ and $\text{TiO}_2\text{-EtOH-250}$, thus the presence of interband states can be correlated with the introduced defects.

3.3.4 Surface Analysis via XPS

To further elucidate the variance in the core level and valence band among ethanol treated and calcined TiO_2 catalysts, XPS was utilized. Since there can be major errors when improper B.E. referencing methods are used especially in the valence band, first an initial overview of this topic will be discussed.

P25 is a semiconductor, also it is known that various amounts of different carbonaceous species are present on its surface due to manufacturing process. In addition, the samples used in this study are in powder form, therefore it is certain that there will be charging issues to overcome thus it is important to have a proper charge neutralization methodology. To achieve this, all of the samples were isolated from the ground by using insulating tape which is known to minimize differential charging as much as possible [119], following that, the flood gun with the lowest voltage and current was utilized to further eliminate differential charging with minimum sample damage (Section 3.2.4.1).

After the differential charging topic is elaborated, referencing was discussed. Rather than using a reference point such as C1s or an internal reference, which is using one characteristic peak in the sample as a reference and then shifting each peak with respect to the reference peak, Ti^{4+} peak of $\text{Ti } 2p_{3/2}$ of P25 was adjusted to a $\text{Ti } 2p_{3/2}$ value in a reference paper [120] with the electron flood gun. Thus, no B.E. reference was used and

no B.E. shifts were made throughout any point in this study. Flood gun values were kept the same all throughout the study.

C1s referencing or the utilization of adventitious carbon as a reference is thought to be not correct, firstly due to C1s peak do not have an exact value (since it is known to range from 284.7 to 285.2 eV) [121], which can lead to serious differences for valence band region. Adventitious carbon is known to have varying binding energies on different metals [122]. Therefore, adventitious carbon may have different binding energies for the currently investigated samples. Despite all of these downsides, C1s can still be used as a reference though not the binding energy of C1s which is with respect to Fermi Level, but rather the vacuum level of C1s which is known to be constant (289.5 eV) [122]. As vacuum level is the summation of C1s relative to Fermi level and work function, one needs to determine the work function of each sample. To achieve that Ultraviolet Photoelectron Spectroscopy (UPS) measurements are required which was not possible in our case due to unavailability of the instrument.

Moreover, since Ti^{4+} peak can have a redshift depending on its chemical environment (as the catalysts in this study are known to have defects, the shifts in Ti^{4+} peak can differ from sample to sample), internal reference is not ideal for referencing. For the case of oxygen, it is known that there are lattice oxygens and oxygenates on the surface after ethanol treatment, and there can be peaks from Ti-OH's and all of these peaks are convoluted in O1s region and can vary depending on the sample, thus O1s was not also ideal for an internal reference.

As mentioned, C1s and O1s peaks are expected to be convoluted with many different species therefore no comments will be made about these regions (despite this data were

acquired) (Appendix A) . Rather, only Ti 2p core level and valence band regions will be discussed here.

3.3.4.1 Charge Neutralization on P25

As mentioned above, Ti 2p_{3/2} peak in [120] was taken as reference, with a value of 459.06 eV for Ti⁴⁺ peak obtained for polycrystalline anatase samples, which is thought to be a good mimic of P25. For getting a similar peak value, different electron flood gun parameters were explored (Figure 3.24 (a)), and an acceptable spectrum with respect to [120] was obtained with 0.8 eV and 16.8 μ A electron flood gun settings (Figure 3.24 (b)).

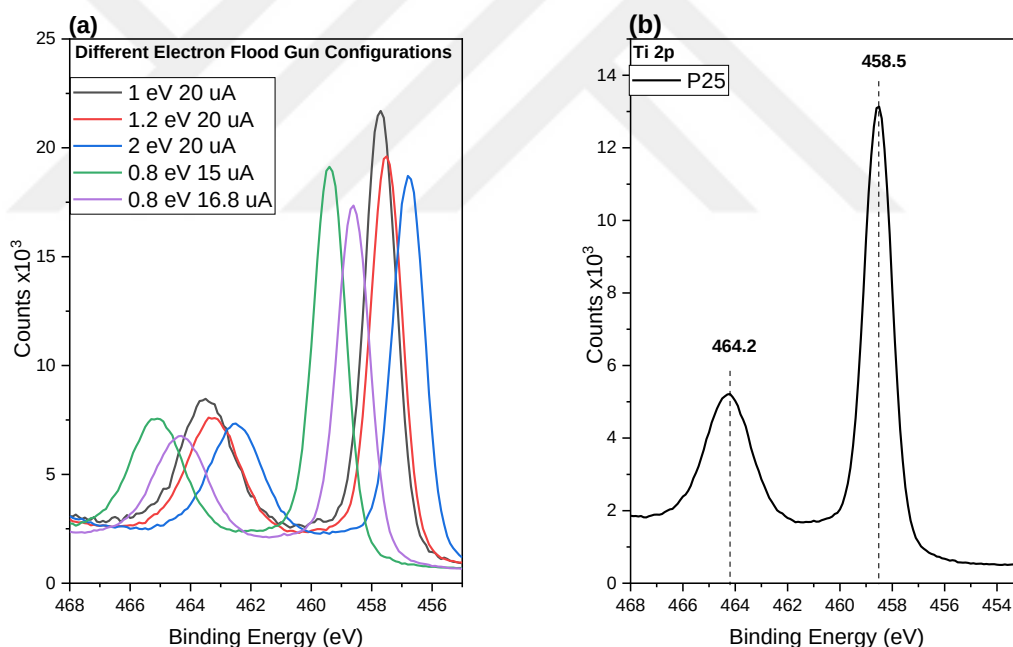


Figure 3.24: Ti 2p XP Spectrum of P25, (a) Different electron flood gun configurations, (b) Obtained Ti 2p spectrum of P25 with 0.8 eV and 16.8 μ A electron flood gun configuration.

As seen from the spectrum (Figure 3.24 (b)), there is no sign of differential charging (evident by the observed FWHM values and the lack of additional Ti2p spectral artifacts) and an acceptable Ti2p_{3/2} B.E. value for Ti⁴⁺ peak (485.5 eV). All of the following experiments were conducted with this particular set of electron flood gun parameters. Therefore, unless there is differential charging and insufficient charge compensation, it should be possible to compare different catalysts under these circumstances.

3.3.4.2 Ti 2p Core Level Spectra of Ethanol Treated Samples

Upon determining the proper parameters for the charge neutralization of P25, same electron flood gun settings were utilized throughout the rest of the experiments. For convenience, acquired XPS data were normalized (Figure 3.25 (a)), and peak maxima of each spectrum was plotted in a scatter plot (Figure 3.25 (b)),

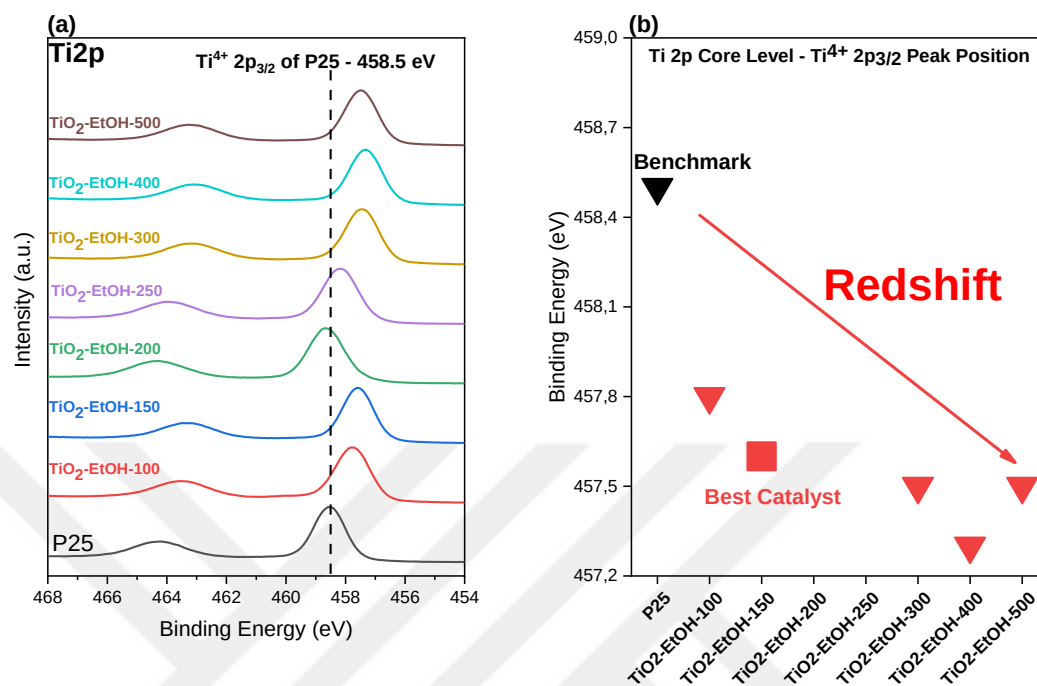


Figure 3.25: XP Spectra of (a) P25 and TiO₂ catalysts on Ti 2p region, (b) Peak maxima of each spectrum (TiO₂-EtOH-150 shown with a red square)

The striking observation in Figure 3.25(a) is that all of the samples had a redshift towards lower binding energies with respect to P25, except TiO₂-EtOH-200 which has a maximum peak at 458.7 eV. As indicated in the previous sections, it is known that TiO₂-EtOH-200 has a modified surface structure due to high concentration of defects, therefore it can be argued that this sample is reduced, thus this blueshift is not due to surface structure of the sample but rather due to insufficient charge compensation. Same is also prevalent for TiO₂-EtOH-250 which also determined to have high surface defects, this catalyst also has a high binding energy compared to other TiO₂-EtOH catalysts. Ti⁴⁺ peak positions of these catalysts can be adjusted to the lower binding energies with changing the electron flood gun configurations, though using different electron flood gun configurations for different

samples would prevent us from comparing them. Thus, the samples TiO₂-EtOH-200 and TiO₂-EtOH-250, which are known to have high amounts of defects, were excluded on making further comments in both Ti 2p core level and in the valence band region.

For the rest of the catalysts (Figure 3.25 (b)), it was observed that all of the Ti⁴⁺ peaks were redshifted compared to Ti⁴⁺ peaks of P25, meaning the Ti⁴⁺ on the catalysts are in an environment more reduced than compared P25. Thus, the initial claim of utilization of ethanol to reduce TiO₂ made in Section (1.4) was proven here. In addition to that the FWHM attained in Raman spectroscopy (Figure 3 18), was unable to give high quality data due to resolution restrictions, which was overcome here and it was seen that the ethanol treated samples were reduced compared to P25.

As there is not a distinct shoulder on Ti 2p peaks, no further fitting was proceeded for the species of Ti³⁺ on the surface, as these species are speculated to be oxidized when exposed to air in literature [94, 107]. Furthermore, it is reported that black titania, a more defect concentrated version, did not have Ti³⁺ signal in conventional XPS [29,45,59, 123], nor in synchrotron X-ray absorption [124] and even not even in EPR measurements [125, 126, 127, 128]. Rather determination of Ti³⁺ ions were done by performing hydrogen thermal treatment [129,130,131,132], chemical reduction [133, 134] and oxidation experiments [134] which were not proceeded in this study. Although it is thought that ethanol treated samples have Ti³⁺ defects alongside with oxygen vacancies (V_os), no conclusion can be drawn from attained XP Spectra.

Further analysis of calculation of energy difference between for doublets due to spin orbit splitting of Ti 2p and FWHM of Ti 2p of each sample were proceeded though not any remarkable comments can be made about them (Appendix B,C).

3.3.4.3 Valence Band Spectra of TiO₂ Samples

In parallel to the acquisition of Ti 2p XP spectra, VB XPS data for each catalyst was also collected using similar instrumental parameters, except that the pass energy was changed from 25 eV to 40 eV and rather than 50 scans, 100 scans were collected and averaged to have a better signal to noise ratio in the VB measurements.

Valence band of titania is reported to have a width around 6 eV, and contains two different low-binding energy states which corresponds to Ti 3d-O 2p π -bonding states and O 2p-Ti 3d σ bonding, with the positions of $\sim$ 5 and 8 eV, respectively. These peaks are heavily dominated by the O 2p character for both rutile and anatase phase, even the lowest binding energy region for anatase was almost completely attributed to O p_{π} states [136, 137, 138], by both theoretical calculations and conclusions drawn from Resonant Photoemission Spectroscopy. Calculated schematic molecular orbital diagram of anatase phase was given in Figure 3.26.

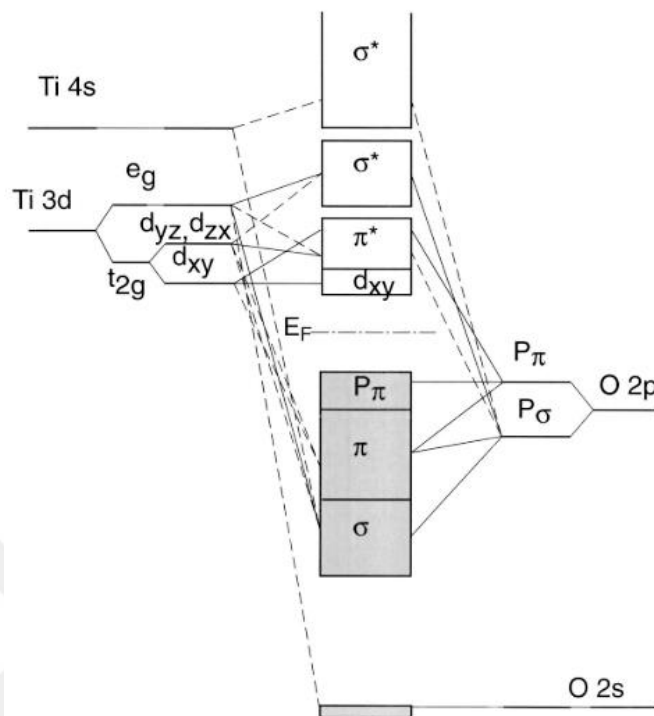


Figure 3.26: Calculated MO diagram for anatase (Taken from Ref[137]).

With these in mind, valence band of P25 was acquired (Figure 3.27). There are two prominent peaks in the valence band region of P25 located at 6.8 eV and 4.9 eV, the bands of σ , π , p_π were assigned conjecturally with the knowledge from Figure 3.26. Since the valence band region is heavily dominated by O 2p, these peaks at 6.8 eV and 4.9 eV will be further denoted as O 2p bonding and O 2p nonbonding herein, as it was done in the literature, respectively [139].

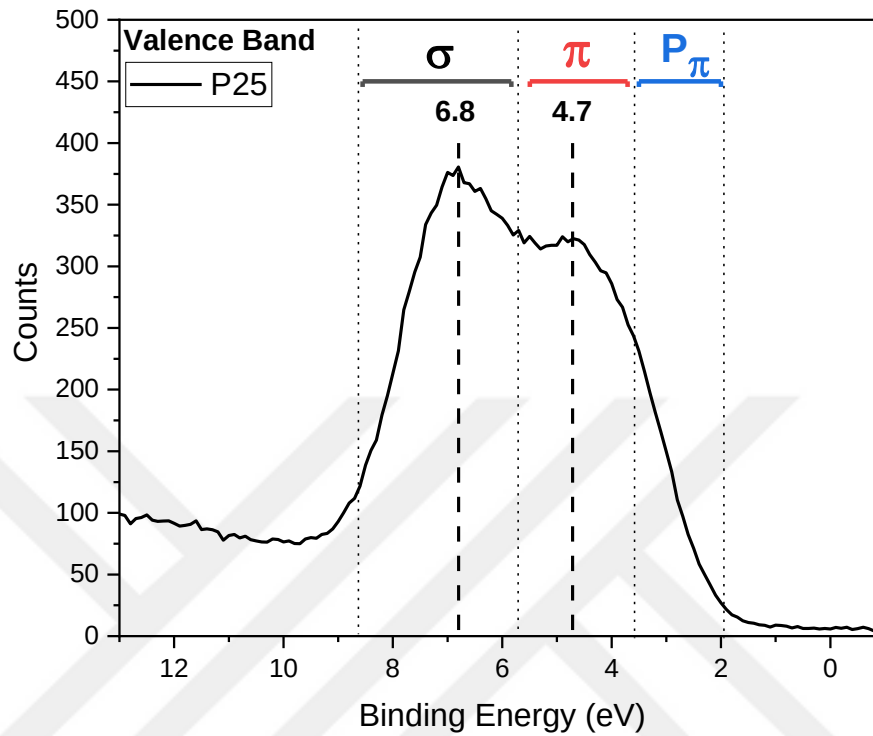


Figure 3.27: Valence band XPS Spectrum of P25.

Moreover, valence band edge of each sample was determined via a linear fitting method. In order to carry out such analysis it was assumed that our samples fulfilled the requirement of VB leading edge being linear, in which resolution of the instrument was thought to be sufficient enough with respect to valence band leading edge from the baseline to provide quality data [140]. Acquired XP spectrum were drawn as scatter plots and the linear method was employed to find the position of valence band edge (Figure 3.28). Reminder that valence band edge is not the bandgap but rather only the difference between Fermi Level (E_F) and the start of the valence band (Figure 3.29).

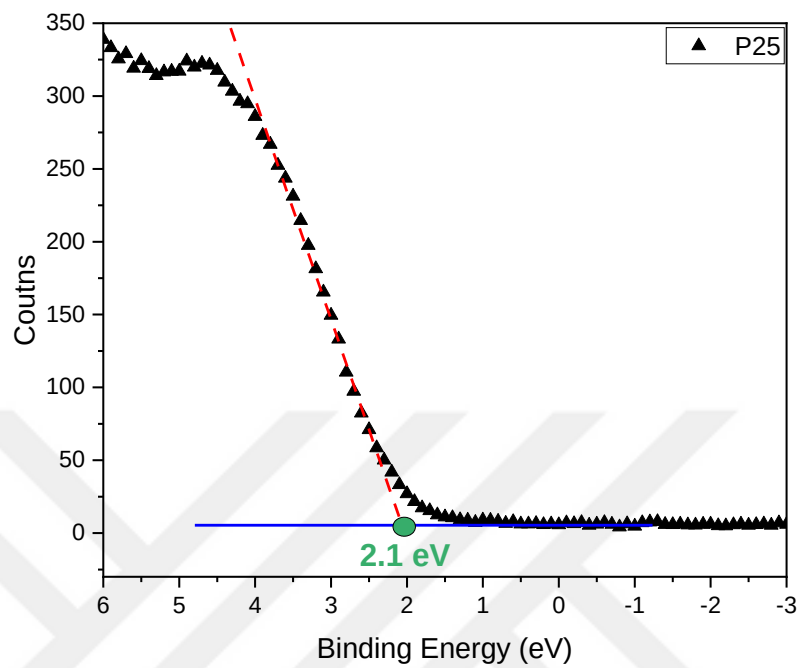


Figure 3.28: Determination of valence band edge with the linear fitting method.

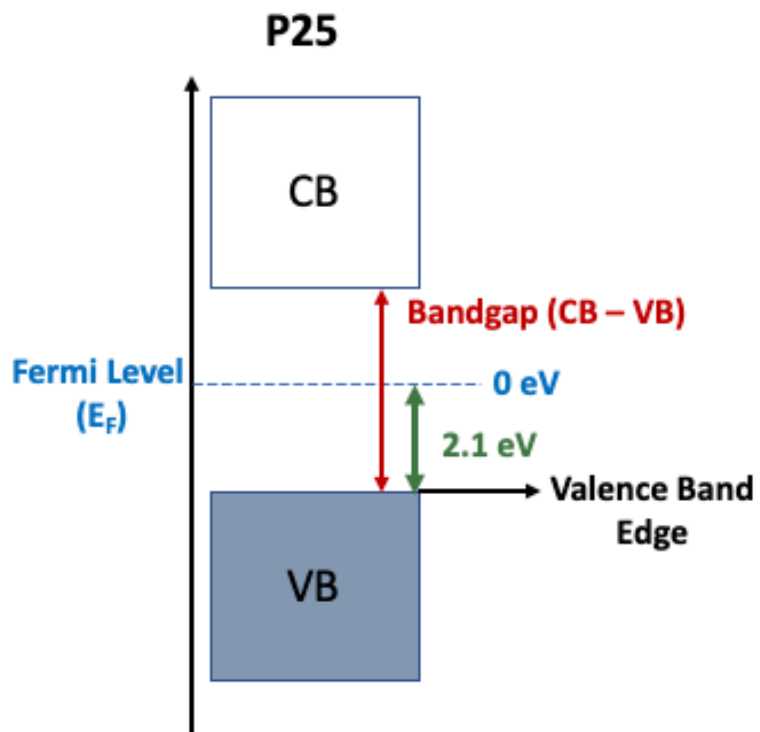


Figure 3.29: Illustration of Bandgap and Valence Band Edge of P25.

Similar analysis was done for each sample (except $\text{TiO}_2\text{-EtOH-200}$ and $\text{TiO}_2\text{-EtOH-250}$ as these samples had insufficient charge neutralization), valence band regions of each sample was plotted in Figure 3.30 (a), and their estimated valence band edges were plotted in a scatter plot in Figure 3.30 (b). For convenience purposes valence band regions were normalized and drawn with respect to y offset.

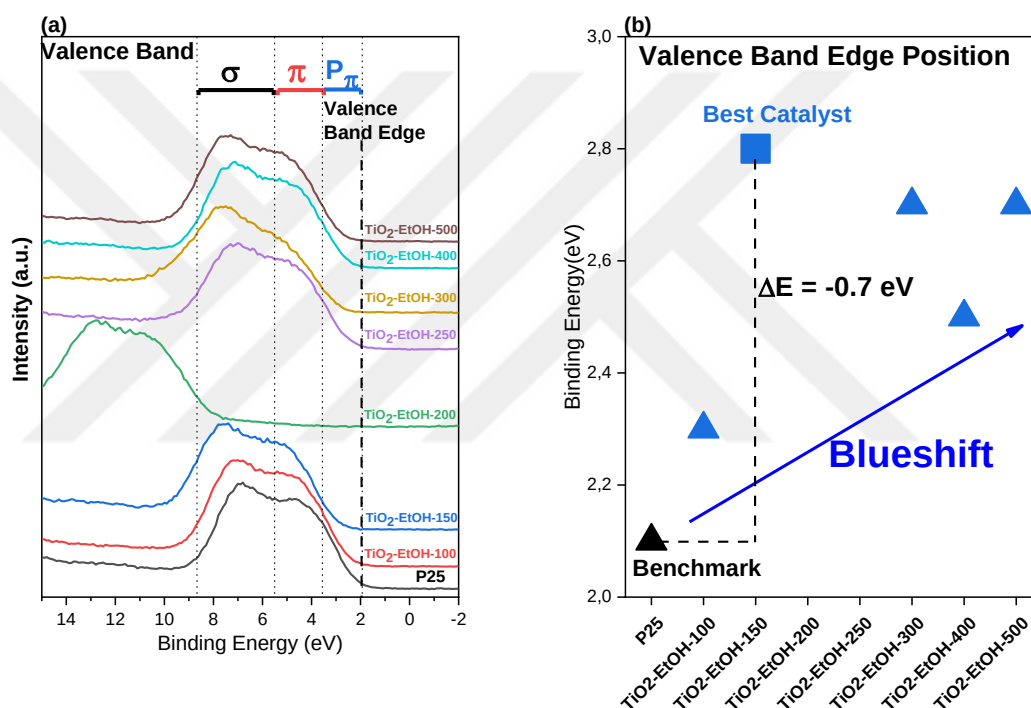


Figure 3.30: Valence band region of all samples (a) A dashed line was drawn from the position of valence band edge of P25 for visual comparison (b) Valence band edges of each sample was estimated and plotted in a scatter plot.

As seen in Figure (3.30 (a)), there is a visible blueshift regarding the valence band edges of the TiO_2 samples compared to P25, which was plotted in Figure 3.30 (b), this was unexpected as most of the reported spectra regarding reduced titania in literature either

had a redshift [59, 102, 141] or did not have any shifts at all in the valence band [96, 117, 126].

For the case of the best catalyst, $\text{TiO}_2\text{-EtOH-150}$, it was seen that valence band edge was blueshifted for about 0.7 eV, which was counterintuitive as change in the valence band edge position may be interpreted as increase in bandgap at first, though it should be stated that no comments can be made about the position of the conduction band, therefore drawing any comments regarding a difference in the bandgap was avoided. An illustration of change of valence band edge positions of P25 and $\text{TiO}_2\text{-EtOH-150}$ was given in Figure 3.31,

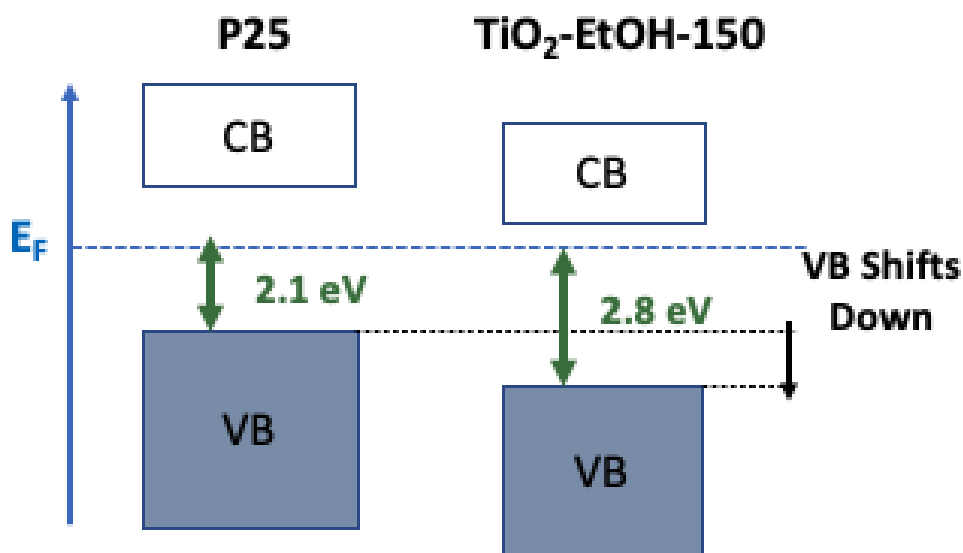


Figure 3.31: Illustration of valence band edge positions of P25 and $\text{TiO}_2\text{-EtOH-150}$.

Same approach that was proceeded for valence band edge (Figure 3.30) was adopted for O 2p bonding peak of valence band and a similar trend was observed, where all samples had a blueshift and the best catalyst, $\text{TiO}_2\text{-EtOH-150}$, had a significant blueshift compared to P25 (Figure 3.32 (a-b)),

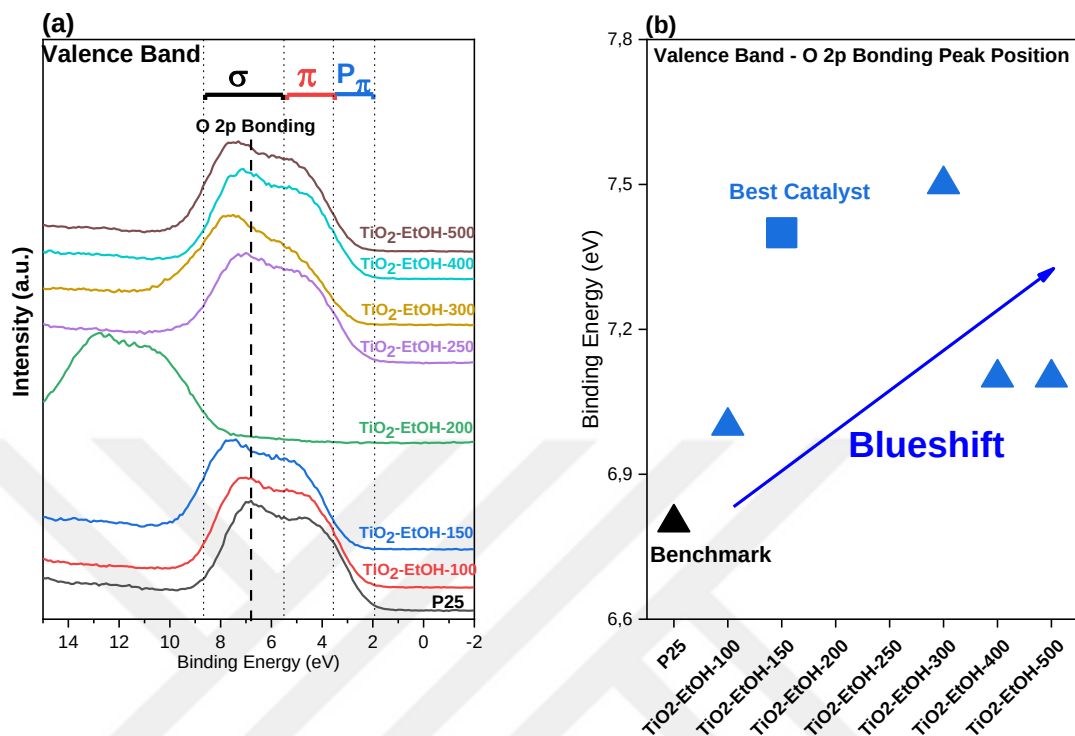


Figure 3.32: (a) Valence band region of all samples (Dashed line was drawn from the position of O 2p bonding peak of P25 for visual comparison) (b) Estimated O 2p bonding peak maxima of each sample was plotted in a scatter plot.

For valence band region, other than a simple blueshift, lineshapes of the samples were also broad and different compared to that of P25 visually. Therefore, rather than a simple blueshift of the valence band region, a change in the valence band states due to ethanol treatment was speculated. In a former study [139], redistribution in the valence band region after H_2 treatment of anatase was investigated by subtracting the H_2 -treated anatase valence band spectrum from that of the anatase before H_2 treatment (Figure 3.33).

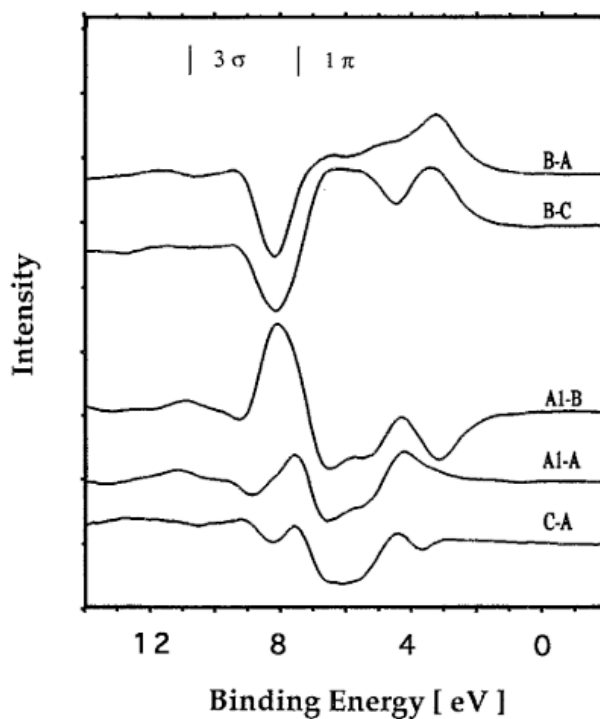


Figure 3.33: Curve A1-B, difference between the spectrum of reduced anatase crystal by H_2 treatment (A1) from oxidized anatase (B) (Taken from [139]).

The Curve A1-B, in Figure 3.33 indicates that there is a growth in intensity of the peak at 8.2 eV whereas a decrease in 3.5 eV region for H_2 -treated anatase sample compared to that of the oxidized anatase. Similar approach was adopted in our study, ethanol treated samples were thought to be reduced whereas P25 was thought to be oxidized version of the catalysts used in this study, therefore all ethanol treated samples were subtracted from P25. As the best working catalyst was TiO_2 -EtOH-150, the difference spectra was highlighted and its change in density of states were compared with other ethanol treated TiO_2 catalysts (Figure 3.34 (a-b)). (Difference spectra of each sample and completely labeled version of Figure 3.34 (b) are in Appendix D)

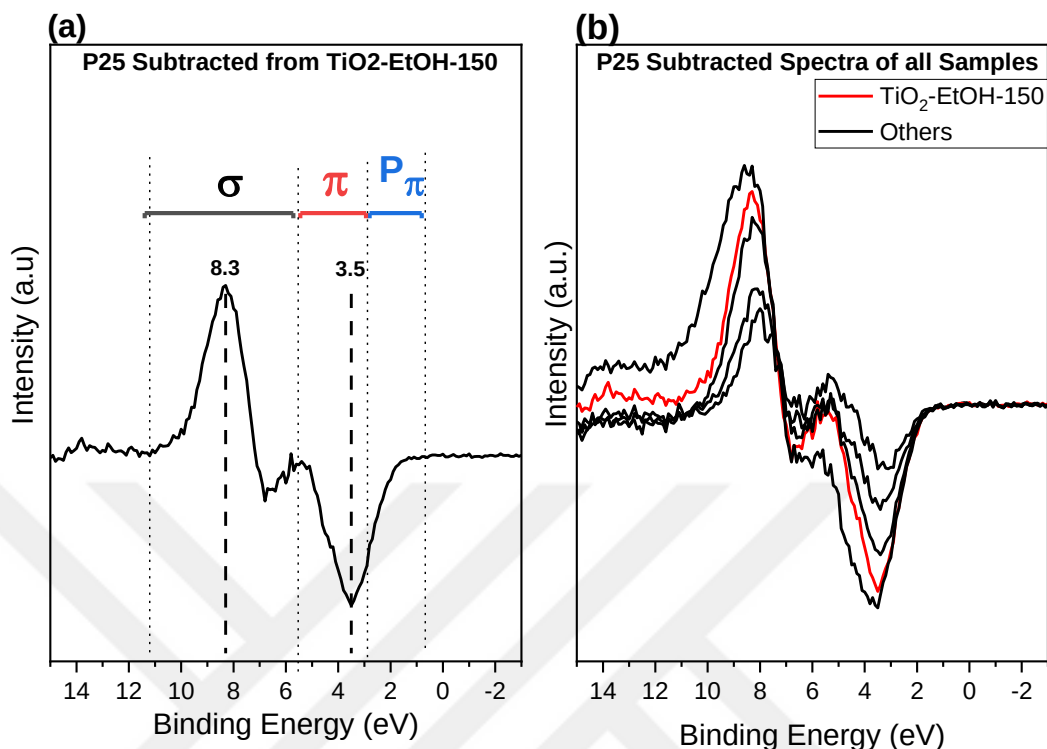


Figure 3.34: a) Subtraction of VB-XPS data of P25 from TiO₂-EtOH-150. b) Subtraction of each VB-XPS data from P25 (TiO₂-EtOH-150 spectrum colored red).

The resulting curves in Figure 3.34 indicate that there are similar trends observed as in the former study (Figure 3.33) [139]. As for TiO₂-EtOH-150 (Figure 3.34 (a)), the peak centered at 8.3 eV was enhanced while the peak at 3.5 eV decreased. The attenuation at 3.5 eV in difference spectrum was attributed to loss of p_{π} band, as this band almost consists solely of O 2p, this depletion meant loss of oxygen on the surface, hence the formation of oxygen vacancies (V_{os}). As for the accentuation at 8.3 eV, as the oxygen contribution depleted after ethanol treatment, the density of states (DOS) redistributed from p_{π} band towards σ band [142]. Similar trends were also seen for other ethanol treated samples (Figure 3.34 (b)), considering the difference in intensity, it was proven that calcination temperature factor in ethanol treatment induces varying concentrations of

defects onto the surface of the catalysts which was not detected by previously done analyses (Reminder that for TiO₂-EtOH-200 and TiO₂-EtOH-250 no further analyses were done in XPS, spectra in Figure 3.34 (b) does not include them). It can be speculated that the unique valence band region of TiO₂-EtOH-150 can be the reason for enhanced photocatalytic activity.

A simple illustration of effect of ethanol treatment on the surface was given in Figure 3.35,

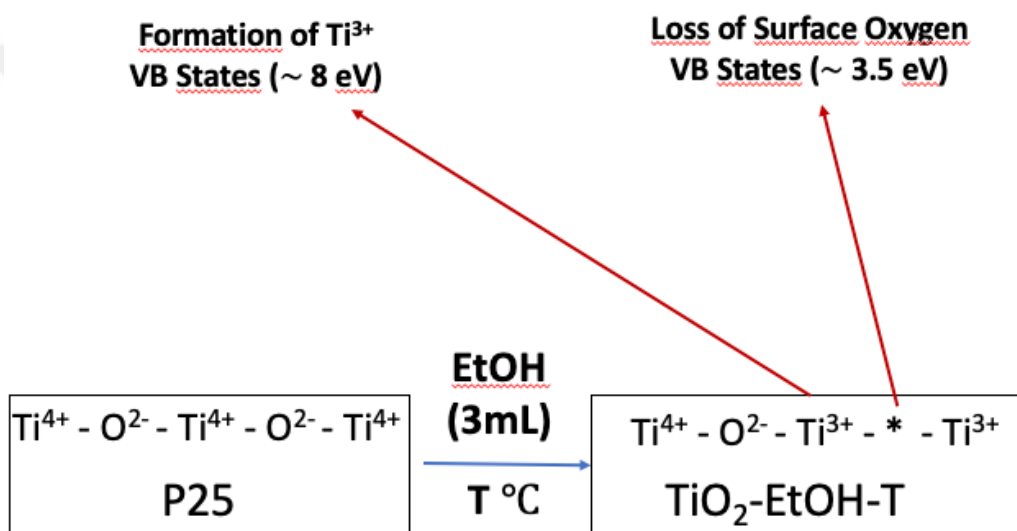


Figure 3.35: An illustration of effect of ethanol treatment on the surface and the origins caused in difference VB Spectra.

Thus, it is seen that ethanol treatment of TiO₂ results in reduction in oxidation state of surface Ti and causes alterations in the electronic density of states in the valence band region.

Lastly to make another comparison regarding the shifts, 2p_{3/2} of Ti⁴⁺ peak of each sample was aligned to 2p_{3/2} of Ti⁴⁺ peak of P25 (458.5 eV) to see the shifts in VB region (Appendix E) and O 2p bonding peak was aligned to O 2p of P25 (6.8 eV) to see the shift in Ti 2p core level (Appendix F)

3.3.5 Analysis of Surface Functionalities by in-situ FTIR Spectroscopy

After a thorough structural analysis had been done to get insights about introduced defects in the previous sections, *in-situ* FTIR spectroscopy method was adapted to determine surface functionalities facilitated by ethanol and calcination processes on P25.

All of the spectra that are presented in this section are difference spectra between the ethanol treated P25 at room temperature and ethanol treated P25 heated in-situ at the given temperatures. The aim here was to gain information about how do carbonaceous species evolve over calcination temperatures.

It is important to note that in-situ FTIR measurements were conducted under vacuum conditions, since annealing of TiO_2 under vacuum is known to generate more defects [143] compared to sample preparation adapted in this study, measured samples here do not completely reflect the samples that performed photocatalytic experiments, but it was assumed that surface functionalities did not change drastically therefore drawing conclusion regarding surface functionalities from these measurements were found to be appropriate. The attained spectra for different temperatures were plotted in Figure 3.36. Ethanol is known to adsorb onto to the TiO_2 surface both by molecularly ($\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}}$) and dissociatively ($\text{CH}_3\text{CH}_2\text{O}_{\text{ads}}$) at room temperature [144].

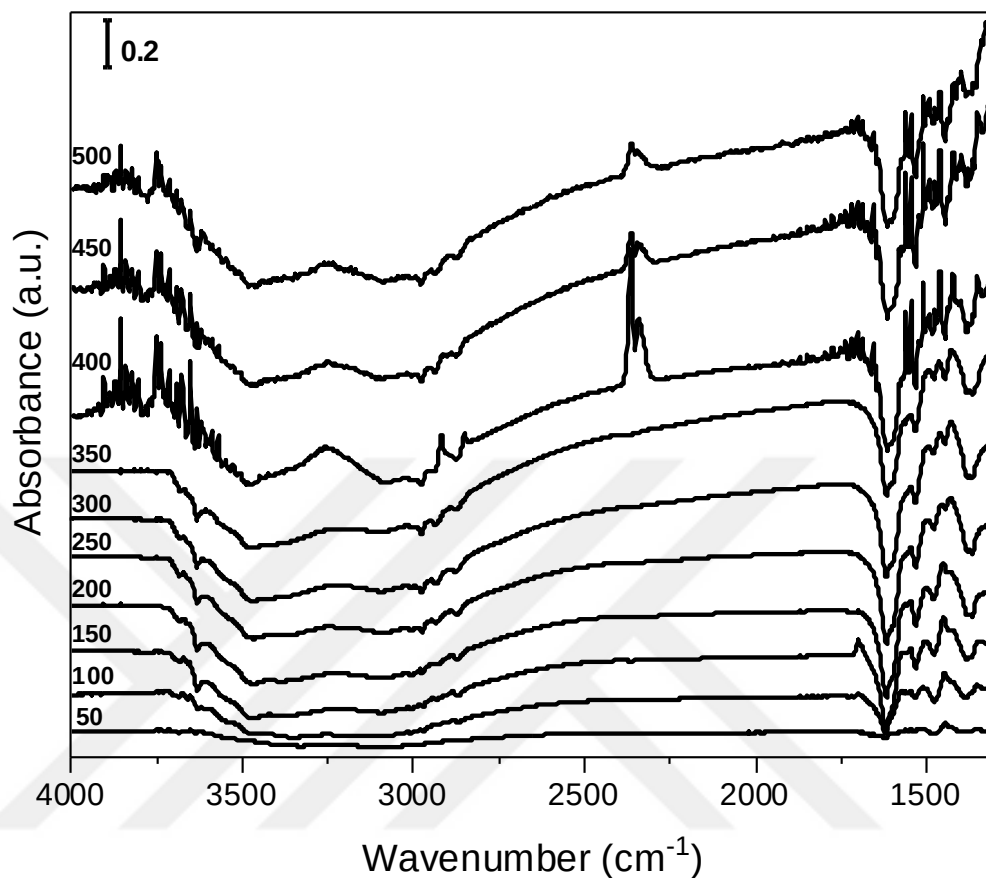


Figure 3.36: Background subtracted in-situ IR spectra of $\text{TiO}_2\text{-EtOH}$ at different temperatures.

3.3.5.1 Analysis of 3900-3300, 3200-2600 and 2500-2200 cm^{-1} Regions

As seen in Figure 3.36, there are some changes in the regions of 3900-3300 (O-H Region), 3200-2600 (C-H Region) and 2500-2200 ($\text{CO}_2(\text{g})$ Region) cm^{-1} , detailed versions of these regions are also plotted in Figure 3.37.

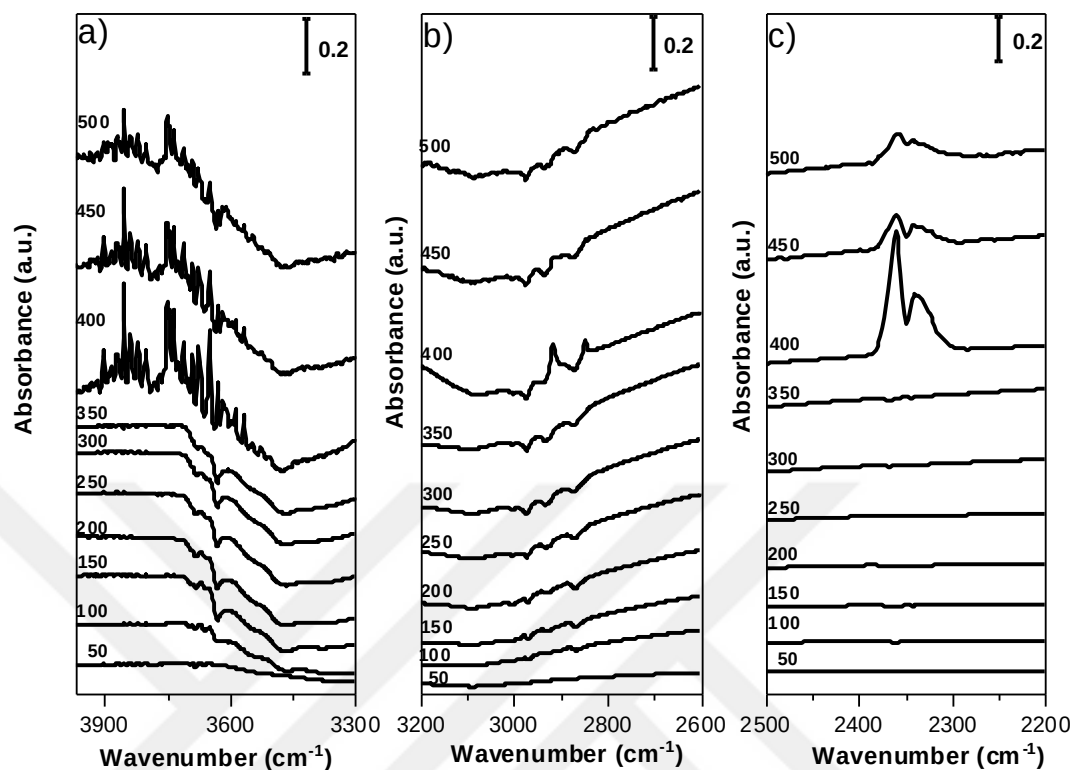


Figure 3.37: Detailed views of a) 3900-3300 cm^{-1} , b) 3200-2600 cm^{-1} and c) 2500-2200 cm^{-1} regions of in-situ IR spectra of TiO_2 -EtOH at different temperatures.

Figure 3.37 (a,c) show that there is $\text{H}_2\text{O}(\text{g})$ and $\text{CO}_2(\text{g})$ evolution for the temperatures above 400 $^\circ\text{C}$. This does not mean all of the carbonaceous species on the surface were eliminated as there is a sharp positive signal observed at 400 $^\circ\text{C}$ in C-H region (Figure 3.37 (b)). It is apparent that there is some degree of total oxidation where ethanol is oxidized to water and carbon dioxide.

It can be seen that there are couple of negative peaks in the O-H region around at $\sim 3700 \text{ cm}^{-1}$ (Figure 3.37 (a)). These were assigned to loss of adsorbed isolated surface OH^- species [145]. Likewise in the C-H region (Figure 3.37 (b)), negative peaks were observed

mainly at 2970, 2930 and 2871 cm^{-1} which was attributed to the loss of adsorbed molecular ethanol ($\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}}$) or adsorbed ethoxide ($\text{CH}_3\text{CH}_2\text{O}_{\text{ads}}$).

Despite oxidation products of ethanol (e.g., $\text{HCOO}^-_{\text{ads}}$, $\text{HCOOH}_{\text{ads}}$, $\text{CH}_3\text{COO}^-_{\text{ads}}$, $\text{CH}_3\text{COOH}_{\text{ads}}$ and $\text{CH}_3\text{CHO}_{\text{ads}}$) do include C-H bonds, the intensity of their signal is lower than ethanol in the region between 3200-2800 cm^{-1} [146, 147]. Therefore it can be argued that adsorbed ethanol is oxidized at temperatures above 100 $^{\circ}\text{C}$.

3.2.5.2 Analysis of 1800-1200 cm^{-1} Region

Following the comments in the previous section, the region between 1800-1200 cm^{-1} was investigated which is thought to be integral to understand the surface properties of the catalysts used in this work, as this part may contain a number of peaks that may correspond to various different oxygenates [148, 149, 150, 151, 152], Due to low A/D count for the temperature above 400 $^{\circ}\text{C}$, no comments were made for $T > 400$ $^{\circ}\text{C}$, remaining temperatures were plotted in Figure 3.34.

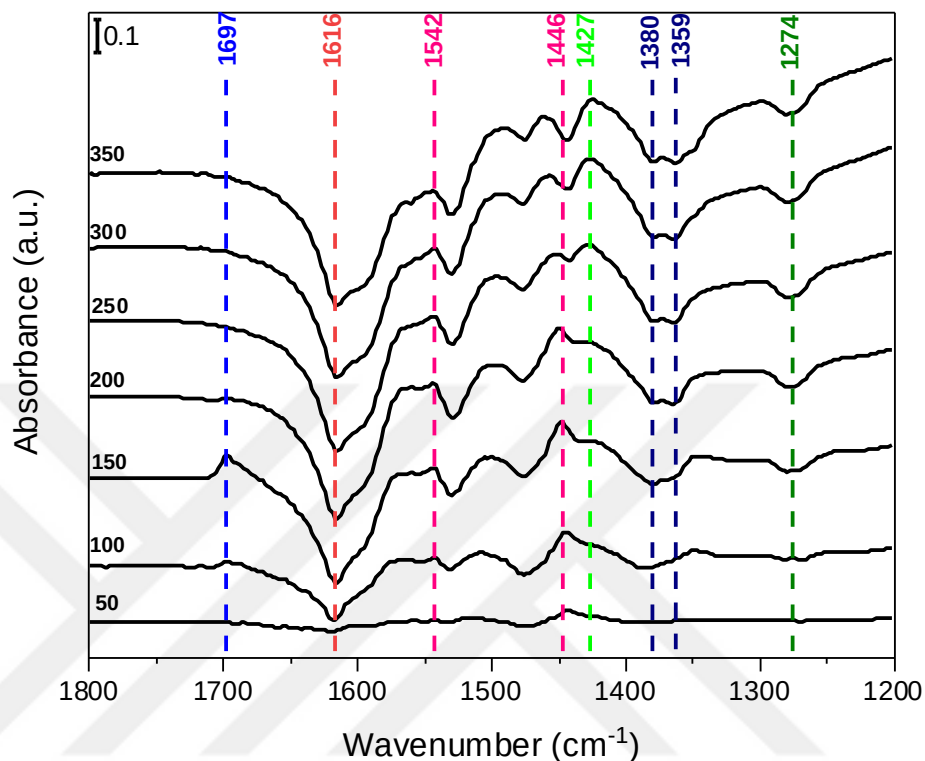


Figure 3.38: 1800-1200 cm^{-1} region of difference in-situ IR data of TiO_2 -EtOH at different temperatures. For convenience, IR peaks of each surface functionality is color-coded: Blue/formic acid, Red/water, Pink/acetate, Green/carbonate, Navy/dissociatively adsorbed ethanol and Dark green/molecularly adsorbed ethanol.

In Figure 3.38, it is seen that there is a sharp increase at 1691 cm^{-1} (blue-dashed line) which reaches its maximum at 150 °C. This signal diminishes as the temperature increases up to 300 °C. This blue-labeled peak was assigned to $\nu(\text{C}=\text{O})$ of adsorbed formic acid on the surface ($\text{HCOOH}_{\text{ads}}$) [144]. Following the peak in 1691 cm^{-1} a broad decrease was observed which had the lowest point at 1616 cm^{-1} , intensity of this peak reached its maximum around 200 °C. This dip was shown with red-dashes in Figure 3.34. Bending

mode of adsorbed water, $\delta(\text{OH})$, was assigned to this dip. Next, the peaks at 1542 and 1446 cm^{-1} (shown with pink-dashed lines) were assigned to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of adsorbed acetate ($\text{CH}_3\text{COO}_{\text{ads}}^-$). Unlike formic acid, the signal of acetate remained rather intact at all temperatures and revealed only a slight blueshift [144]. A rising peak was observed at 1427 cm^{-1} (yellow-dashed line) especially above 250 °C. This peak was assigned to the surface carbonate (CO_3^{2-}) species. Presumably this is one of the products of ethanol total oxidation [153]. Following that two very close dips were observed at 1380 and 1356 cm^{-1} (navy-dashed lines) which were assigned to $\delta_{\text{s}}(\text{CH}_2)$ and CH_2 wagging of dissociatively adsorbed ethanol or ethoxide species ($\text{CH}_3\text{CH}_2\text{O}_{\text{ads}}$). Lastly, a dip was observed at 1274 cm^{-1} (dark green-dashed line) which was assigned to the bending mode ($\delta(\text{OH})$) of molecularly adsorbed ethanol ($\text{CH}_3\text{CH}_2\text{OH}_{\text{ads}}$).

It is apparent that, acetate ($\text{CH}_3\text{COO}_{\text{ads}}^-$) species remain on the surface as temperature varies, though one striking feature that can be correlated with the photocatalytic performance is the intensity of adsorbed formic acid peak at 1697 cm^{-1} (Figure 3.39).

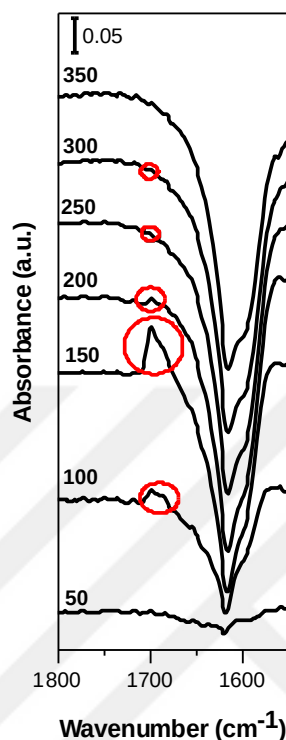


Figure 3.39: 1800-1550 region of difference in-situ IR data of $\text{TiO}_2\text{-EtOH}$ at different temperatures. Sizes of red circles are proportional to the peak intensity of the 1697 cm^{-1} feature.

The peak at 1697 cm^{-1} (assigned to adsorbed formic acid, $\text{HCOOH}_{\text{ads}}$) reaches its maximum at $150\text{ }^{\circ}\text{C}$ and diminishes after $300\text{ }^{\circ}\text{C}$, which can be correlated with the PHONOS Selectivity% (Figure 3.8). Note that Selectivity% reaches its maximum for $\text{TiO}_2\text{-EtOH-150}$ sample (83%) then remains relatively high for samples of $\text{TiO}_2\text{-EtOH-200}$, $\text{TiO}_2\text{-EtOH-250}$ and $\text{TiO}_2\text{-EtOH-300}$ (76%, 67%, 71%, respectively), and then falls below 60% for the calcination temperatures above $300\text{ }^{\circ}\text{C}$, in which no IR signal was observed for adsorbed formic acid ($\text{HCOOH}_{\text{ads}}$) (Figure 3.39).

Thus, the higher PHONOS selectivity of the ethanol treated samples than that of P25, can be linked to the presence of adsorbed acetate ($\text{CH}_3\text{COO}_{\text{ads}}^-$) and adsorbed formic acid ($\text{HCOOH}_{\text{ads}}$) as demonstrated in Figure 3.38. It is likely that these unique oxygenate species may increase the surface residence time of adsorbed NO_2 (and thus facilitate their sorption on the surface) by forming aliphatic nitro organic compounds (e.g., nitro acetate) and/or act as oxidizing agents to oxidize $\text{NO}_2/\text{NO}_2^-$ into surface NO_3^- .



4 Conclusions

In this study in order to attain a high-performance Photocatalytic NO_x Oxidation and Storage (PHONOS) catalyst under UV-A light, a simple monohydric alcohol impregnation protocol was adopted at mild temperature ranges to induce defects and oxygenates derived from ethanol on to the TiO₂ photocatalyst.

Initially optimum ethanol loading was investigated, which was found to be 3 ml ethanol per 250 mg of P25 catalyst. Secondly, optimum calcination temperature was sought to be determined, therefore seven different calcination temperatures were chosen and ethanol induced coloration was observed for samples calcined at the temperatures of 150, 200, 250 and 300 °C, which was correlated with the concentration of defects. Attained samples were tested in 1-h photocatalytic performance tests in which it was seen that color of the catalyst does not directly correlate with the overall photocatalytic performance (i.e., DeNO_x Index). Rather, the TiO₂-EtOH-150 sample had the best combination of NO Conversion% and Selectivity%.

Then, long run photocatalytic activity of best performing catalyst was examined, in which it was observed that catalyst curtailed detoxification process around 3rd hour mark and converged close to P25 values at the end of 15th hour. Accordingly, CaO was introduced to increase and prolong long run Selectivity% of TiO₂-EtOH-150, which was successful, where ~0.2 DeNO_x Index was achieved even after the 15th hour mark.

Next, characterization of the samples were carried out to investigate introduced defects and surface functionalities. XRD results revealed no differences in the bulk crystal structures of the investigated catalysts. Then, Raman Spectroscopy was employed and

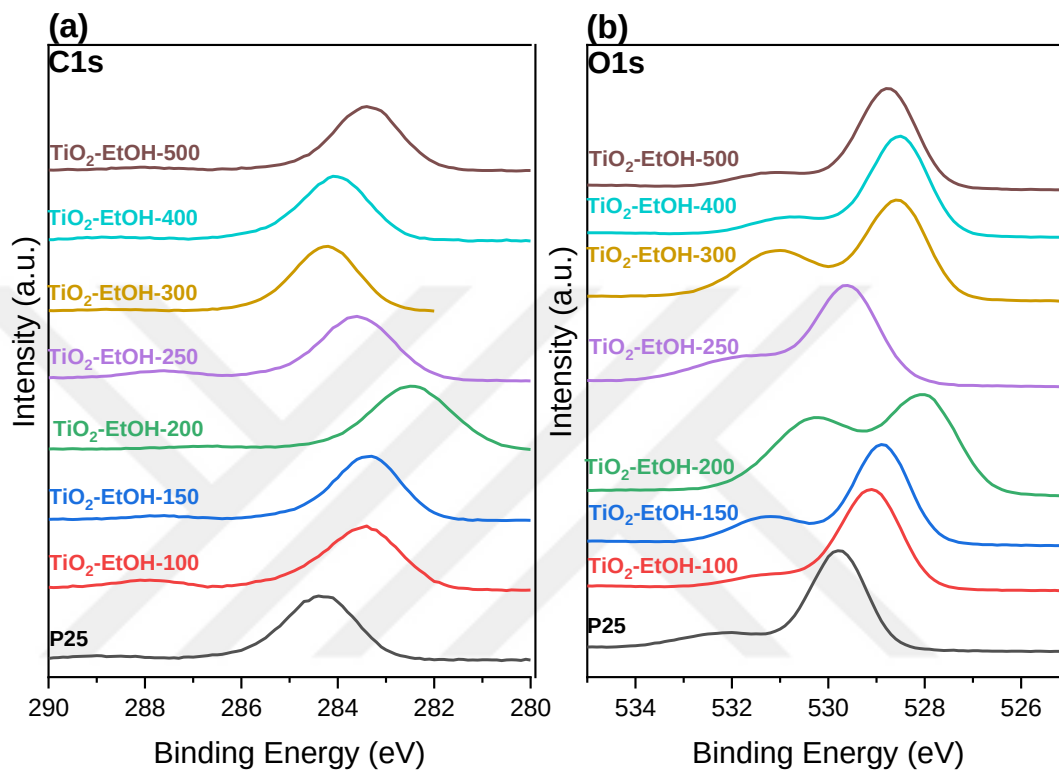
signs of defect presence was observed for TiO₂-EtOH-200 and TiO₂-EtOH-250, but no further comments were made for other samples due to low resolution of the instrument. Moreover, DR-UV-Vis Spectroscopy was adopted where rough estimations of bandgaps of these samples were done, in which it was seen that bandgap stayed relatively the same but there were interband states especially for the samples of TiO₂-EtOH-200 and TiO₂-EtOH-250, also all ethanol treated samples were determined to have higher light absorption in UV-A region than that of P25. XPS measurements revealed that all of the ethanol treated samples had a redshift in Ti 2p core levels compared to P25, which was attributed to the presence of Ti⁴⁺ states with a relatively reduced chemical environment upon ethanol treatment. VB-XPS measurements showed that ethanol treated samples had valence band edges blue shifted compared to P25. More importantly different line shapes of the VB-XPS data of the ethanol treated samples as opposed to P25, was attributed to the redistribution of the valence band states and formation of oxygen vacancies (V_{os}) after ethanol treatment of P25. The unique valence band structure of TiO₂-EtOH-150 was speculated to play a role in enhanced photocatalytic performance of the catalyst. Finally to investigate the surface functionalities, *in-situ* FTIR technique was employed in which surface species originating from ethanol oxidation on TiO₂ were determined. As a result of these measurements, it was observed that ethanol treated samples had adsorbed acetate throughout all temperature ranges and adsorbed formic acid was observed at the temperature ranges between 100-300 °C with a maximum peak intensity at 150 °C. These surface functionalities were correlated with the enhancement of Selectivity% of the ethanol treated TiO₂ samples, in which Selectivity% of the best performing sample, TiO₂-EtOH-150, was attributed to the presence of both of these samples.

In conclusion it by utilization of ethanol on P25, a stable and high performing catalyst for Photocatalytic NO_x Oxidaton and Storage was achieved, where the superior performance of the catalyst was attributed to its unique valence band structure and surface functionalities comprised of adsorbed acetate and formic acid, and also to its characteristic modified VB electronic structure.



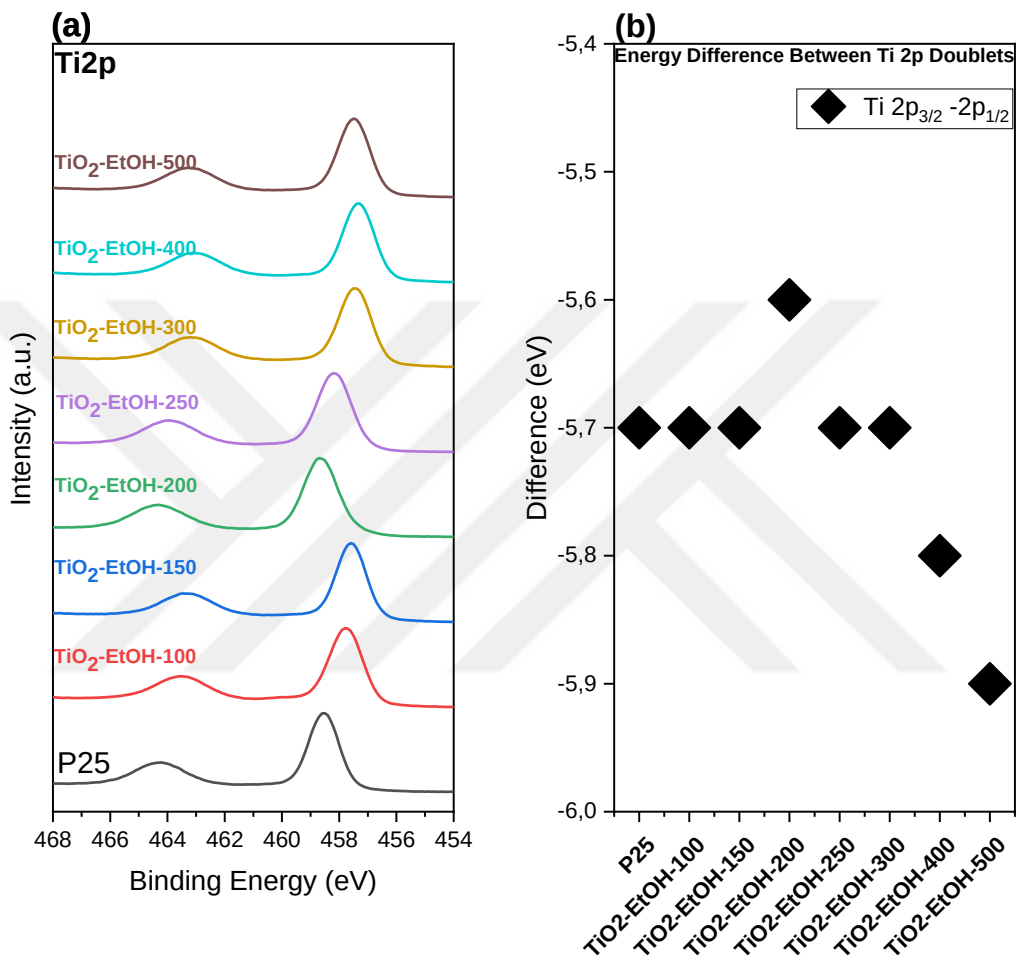
Appendix

Appendix A: Core Level XP Spectra of C1s and O1s



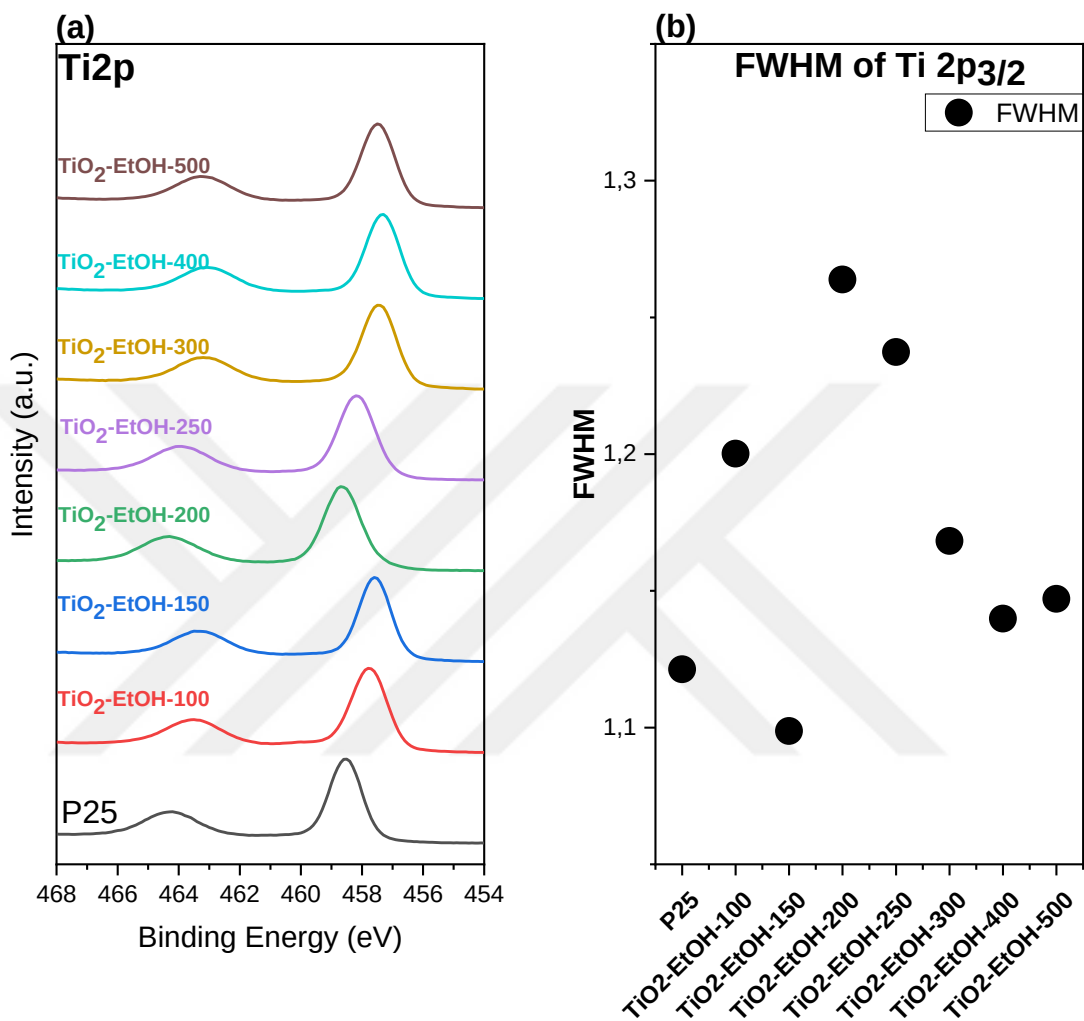
Appendix A.1: (a) O1s core level (b) C1s core level.

Appendix B: Energy Difference of Ti 2p Spin Orbit Splitting for Each Sample



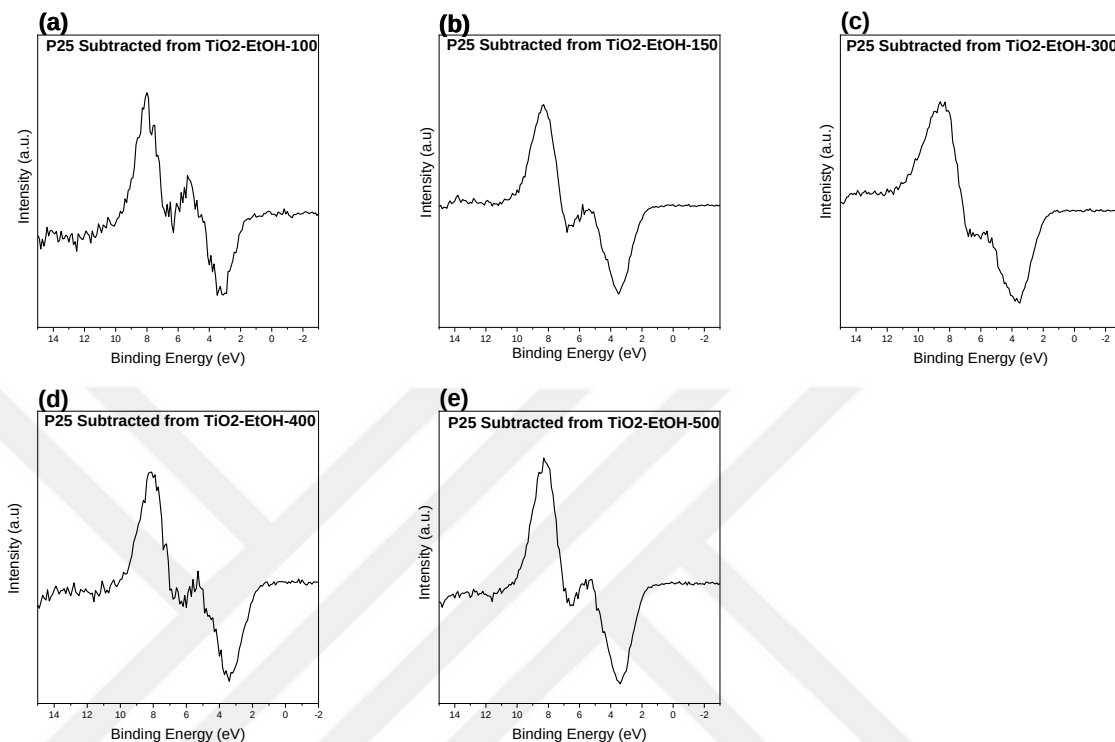
Appendix B.1: Energy difference of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of each sample.

Appendix C: FWHM of Ti 2p_{3/2} of Each Sample

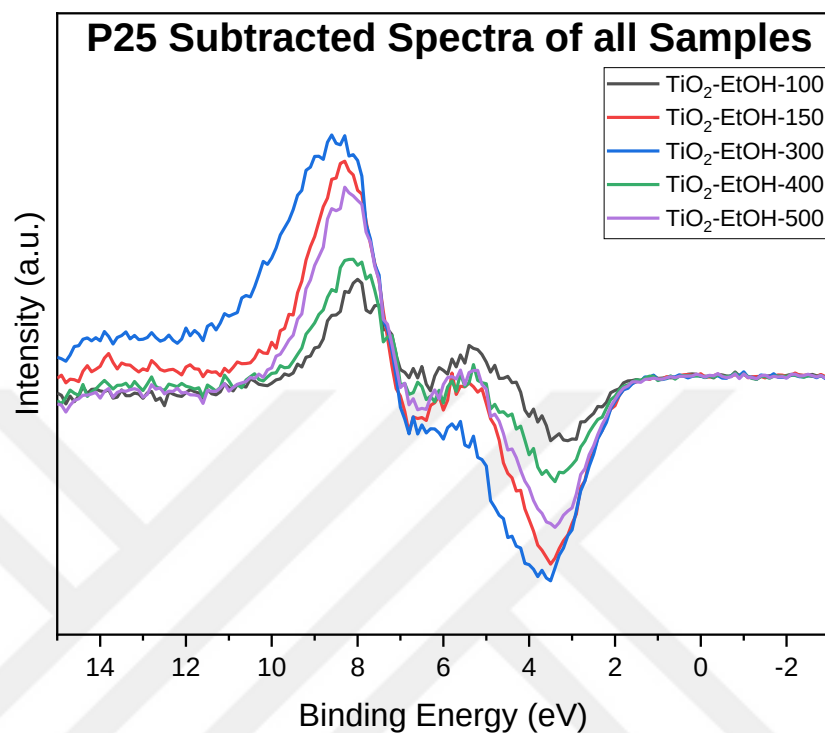


Appendix C.1: FWHM of Ti 2p_{3/2} of each Sample.

Appendix D: Difference Spectra of Each Sample



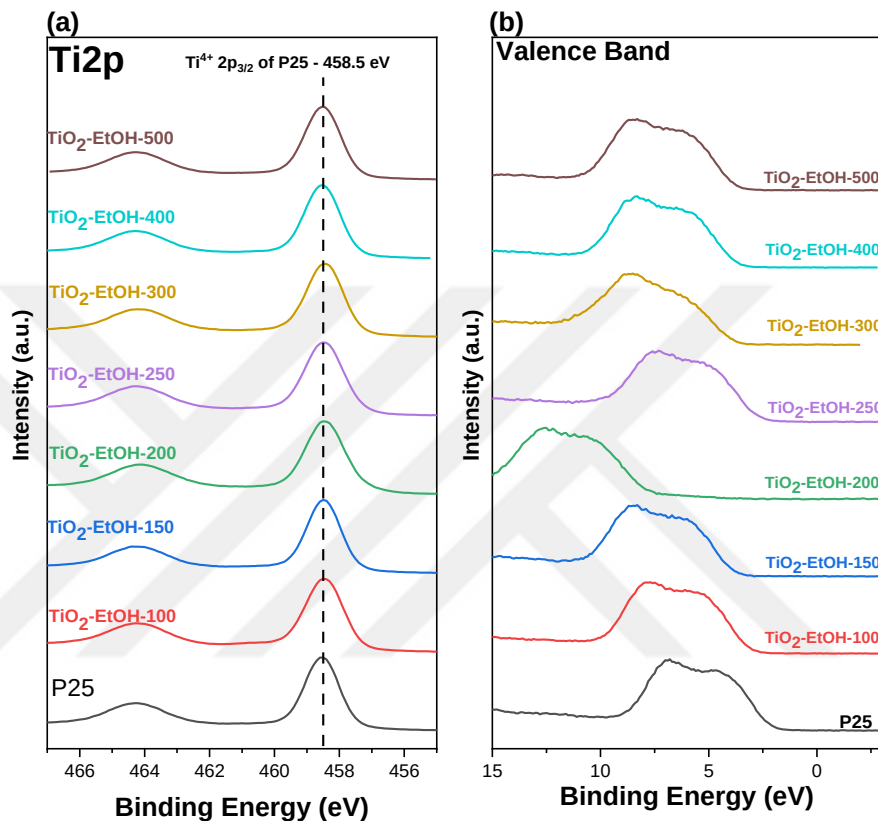
Appendix D.1: Difference spectra of each sample (a) P25 subtracted from TiO₂-EtOH-100, (b) P25 subtracted from TiO₂-EtOH-150, (c) P25 subtracted from TiO₂-EtOH-300, (d) P25 subtracted from TiO₂-EtOH-400, (e) P25 subtracted from TiO₂-EtOH-500.



Appendix D.2: Difference spectra of each sample drawn in single graph for comparison.

Appendix E: Shifts on Valence Band Region when Ti 2p Core Level

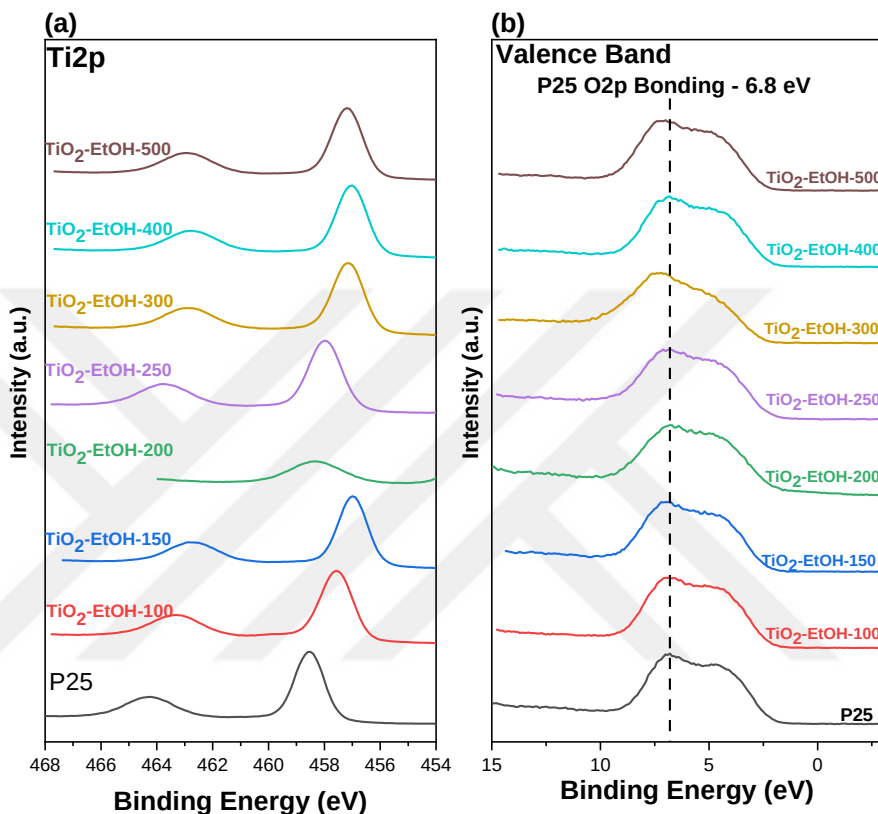
Aligned



Appendix E.1: (a) Ti 2p_{3/2} peak of Ti⁴⁺ of each sample was aligned to Ti 2p_{3/2} of P25 (458.5 eV), (b) Shifts in valence band region due to offset in aligned Ti 2p core level.

Appendix F: Shifts on Ti 2p Core Level when O 2p Bonding Peak

Aligned



Appendix F.1: (a) O 2p bonding peak of each sample was aligned to O 2p bonding peak of P25 (458.5 eV), (b) Shifts in Ti 2p core level due to offset in aligned O 2p bonding peak.

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