

THEORETICAL INVESTIGATION OF CO₂ ADSORPTION PATHWAY OVER
N-[3-(TRIMETHOXYSILYL)PROPYL] ETHYLENEDIAMINE-MODIFIED
MESOPOROUS SILICA SORBENTS



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İmge Kalkan

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APPROVED BY:

Prof. Dr. Tuğba Davran Candan
(Thesis Supervisor)
(Yeditepe University)

.....

Prof. Dr. Nihan Çelebi Ölçüm
(Yeditepe University)

.....

Assist. Prof. Dr. Burcu Dedeoğlu
(Gebze Teknik University)

.....

DATE OF APPROVAL: / / 2023

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Name, Surname

İmge Kalkan

Signature

.....

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ABSTRACT

THEORETICAL INVESTIGATION OF CO₂ ADSORPTION PATHWAY OVER N-[3-(TRIMETHOXYSILYL)PROPYL] ETHYLENEDIAMINE-MODIFIED MESOPOROUS SILICA SORBENTS

Elucidation of the adsorption pathways of carbon dioxide (CO₂) over mesoporous silica sorbents modified by amines is significant for the development of high-performance sorbents that would meet the future challenges regarding the emissions. This study aims to investigate the CO₂ adsorption pathway over N-[3-(trimethoxysilyl)propyl] ethylenediamine (AEAPS)-modified mesoporous silica sorbents by using DFT modeling to reveal whether the intra-molecular CO₂ capture is possible and which amine groups (primary or secondary) are more reactive in this process. Our calculations showed that CO₂ was captured in the forms of carbamate and carbamic acid; and hydrogen bonding interactions (both amine-amine and amine-surface) were critical for the thermodynamic and kinetic feasibility of the adsorption pathways. Intra-molecular capture was possible, but the long chain length of the molecule seemed to restrict the amine-amine interactions within the molecule. Both primary and secondary amine groups contributed to the adsorption of the CO₂, meaning that amine functionality was less deterministic on the process in comparison to the hydrogen bonding interactions.

ÖZET

N-[3-(TRİMETOKSİSİLİL)PROPİL]ETİLENDİAMİN İLE MODİFİYE EDİLMİŞ MEZOPORLU SİLİKA ADSORBANLARI ÜZERİNDE CO₂ TUTUNMA MEKANİZMASININ HESAPLAMALI OLARAK İNCELENMESİ

Karbon dioksitin (CO₂) aminle modifiye edilmiş mezogözenekli silis sorbanlar üzerindeki adsorpsiyon mekanizmasının netleştirilmesi, emisyonlarla ilgili gelecekteki hedefleri karşılayacak yüksek performanslı tutucuların geliştirilmesi için oldukça önemlidir. Bu çalışma, CO₂ tutulma mekanizmalarının N-[3-(trimetoksisilil)propil]etilendiamin (AEAPS) ile modifiye edilmiş mezoporlu silis adsorbanları üzerinde DFT metodu kullanılarak incelenmesini hedeflemektedir. Böylece, molekül içi CO₂ yakalamanın mümkün olup olmadığı ve hangi amin gruplarının (birincil veya ikincil) bu süreçte daha reaktif olduğu ortaya çıkarılacaktır. Hesaplamalarımız, CO₂'nin karbamat ve karbamik asit formlarında tutulduğunu göstermiş ve hidrojen bağı etkileşimlerinin (hem amin-amin hem de amin-yüzey) adsorpsiyon mekanizmalarının termodinamik ve kinetik uygulanabilirliği için oldukça ktitik olduğunu ortaya koymuştur. Molekül içi yakalama mümkün gözükse de, AEAPS molekülün zincir uzunluğunun molekül içindeki amin-amin etkileşimlerini kısıtlıyor olabileceği düşünülmüştür. Hem birincil hem de ikincil amin grupları, CO₂'nin adsorpsiyonuna katkıda bulunmuş, böylece amin işlevselliğinin tutulma üzerinde hidrojen bağı etkileşimlerine göre daha az belirleyici olduğu saptanmıştır.

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LIST OF SYMBOLS/ABBREVIATIONS

APTMS	3-aminopropyl-trimethoxysilane
B3LYP	Becke's three parameter hybrid functional
CCS	Carbon capture and storage
DFT	Density functional theory
E	Electronic Energy
E_j	Exchange Energy
E_T	Kinetic Energy
E_v	Potential Energy
E_{xc}	Exchange-correlation functionals
FTIR	Fourier transform infrared spectrophotometer
GGA	Generalized gradient approximation
$\hat{H}$	Hamiltonian Operator
LDA	Local density approximation
MAPS	N-(methylaminopropyl)-trimethoxysilane
MCM-41	Mobile composition matter no 41
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MOF	Metal organic frameworks
NMR	Nuclear magnetic resonance
PEI	Polyethyleneimine
SBA-15	Santa Barbara Amorphous type material
TEPA	Tetraethylenepentamine
TS	Transition state
Ψ	Wave function

1. INTRODUCTION

Carbon dioxide (CO₂) emissions have increased dramatically since the beginning of the industrial revolution, causing climate change and global warming. For the mitigation of the severe effects of global warming, immediate action that would diminish the emission of the gas significantly should be taken. Carbon capture and sequestration (CCS) that involves the capture of the gas from giant point sources and long-term storage of it in suitable geological formations is one of the most promising near-future solutions proposed for the solution of the problem [1].

CO₂ absorption using aqueous amine solutions is the most conventional way of capturing the gas in the post-combustion capture technologies [2]. Although these solutions absorb CO₂ in large amounts with fast reaction kinetics, aqueous amine scrubbing cannot be used in large scale due to the high regeneration costs, corrosion problems and amine degradation associated with the method [3]. Hence, it is critical to develop alternative technologies that would overcome these problems and help us reach the emission goals objected for the next century.

Among these alternatives, adsorption of CO₂ using post-synthetically modified amine-based solid sorbents has emerged as a viable method benefiting from the low regeneration costs of the solid sorbents and the high CO₂ affinity of the amine structures at the same time [4]. There has been extensive research in the field since the discovery of these sorbents, most of them focusing on the measurement of the adsorption capacities as well as the optimization of the sorbent properties to maximize this capacity [74,75,76,77,78]. Although a clear understanding of the CO₂ interaction pathway with the adsorbents is critical for the development and rational design of high-performance CO₂ adsorbents, mechanistic studies are still very few.

This study aims to examine the CO₂ adsorption pathways over N-[3-(trimethoxysilyl)propyl] ethylenediamine (AEAPS)-modified mesoporous silica by using DFT modeling with the purpose of clarifying the benefits of using multi-amines as well as the role of hydrogen bonding interactions on the capture pathways. Two different models involving one (5_5-single-AEAPS) and two AEAPS molecules (5_5-double-AEAPS) were employed to determine whether intramolecular adsorption was possible or not.

Chapter 2 involves theoretical background and the corresponding literature survey on CO₂ capture over amine-based adsorbents. In Chapter 3, information about computational details (namely computational models, parameters, and the methodology) employed in the study is given. In Chapter 4, our results obtained from the calculations performed are summarized with the corresponding discussions. Finally, Chapter 5 presents the major conclusions and recommendations for the future studies.



2. THEORETICAL BACKGROUND

2.1 CARBON DIOXIDE CAPTURE

Carbon dioxide (CO₂) is the main anthropogenic greenhouse gas, the atmospheric concentration of which has reached to ~ 421 ppm by June 2022 as declared by the Scripps Institution of Oceanography and National Oceanic and Atmospheric Administration (NOAA), corresponding to a 50 % increase in comparison to the pre-industrial levels [7]. This dramatic increase was reported to be the main reason for global warming, which is indeed forecasted as the top challenge of the next decade [8]. According to the sixth assessment report of Intergovernmental Panel on Climate Change (IPCC), global warming give rise to the long-term climate change and in turn to fires, tropical cyclones, agricultural and ecological droughts, desertification, extreme sea levels, and land degradation [9]. Projected level of atmospheric CO₂ reaches to ~ 450 ppm by 2100 even if the emissions are reduced by 40-70 % by 2050 (in comparison to the current levels) and 100 % by 2100, corresponding to a 2°C-increment in the global surface temperature [10].

CO₂ is produced in consequence of the fossil fuels combustion. According to the breakdown of emissions by sector provided by Climate Watch and World Resources Institute, 73.2 % of all emissions were energy-related, main contributors being the industrial production (24.2 %), transportation (16.2 %), and buildings (17.5%) [11].Correspondingly, global energy demand of countries, which depends on many socioeconomic factors such as their population, economic and technological development as well as industrialization, is the main factor determining the amount of emissions. Various efforts such as enhancing the efficiency of the current processes or employing innovative energy conversion devices and cost-effective alternative energy resources like solar, wind, or biomass have been realized with the purpose of minimizing the emissions [12]. However, the consequences of these efforts are limited, and energy sector is expected to be dependent on the fossil fuels in the near future as well, which in turn indicates the necessity for taking immediate and effective actions to cut down the CO₂ discharges [13].

Carbon capture and storage (CCS) has emerged as a promising strategy for meeting the targeted emission values declared by the IPCC [14]. CCS is a three-step process composing of the separation of CO₂ from the flue gas streams at large point sources (like cement plants,

coal-based power plants, or refineries); the transportation of the captured gas to the proper geological formations where it will be stored; and long-term sequestration [15]. Of the three steps involved in CCS, capture step is the most challenging one requiring more effective carbon dioxide separation from the flue gas. There are three principal approaches in use, namely pre-combustion, post-combustion, and oxy-fuel combustion to capture CO_2 . Pre-combustion approach contains the partial oxidation of the fuel using air or oxygen steams to obtain the synthesis gas (syngas) that is mainly consisted of CO and H_2 . CO then reacts with H_2O producing CO_2 and H_2 via the catalytic water-gas shift reaction. The resulting gas stream involves mainly CO_2 and H_2 ; CO_2 is finally isolated from the H_2 stream [16]. In oxy-fuel combustion process, an air separator is involved, and combustion of the hydrocarbon fuel is achieved under a pure oxygen stream, resulting in a mixture of highly concentrated CO_2 and water vapor [17]. Finally, post-combustion process includes the separation of CO_2 from exhaust gases (flue gas) that is composed mainly of N_2 , CO_2 , and H_2O . Opposite to the previous 2 approaches, carbon dioxide concentration in the flue gas is quite low ($\sim 12\text{-}15\%$) making the separation much harder. However, due to the easily integrated nature of post-combustion approach to the existing systems as well as the high costs of the air separation and gasification units included respectively in the pre-combustion and oxy-fuel combustion processes, post-combustion capture is the generally-used approach [18]. Schematic representation of these three approaches is demonstrated in Figure 2.1.

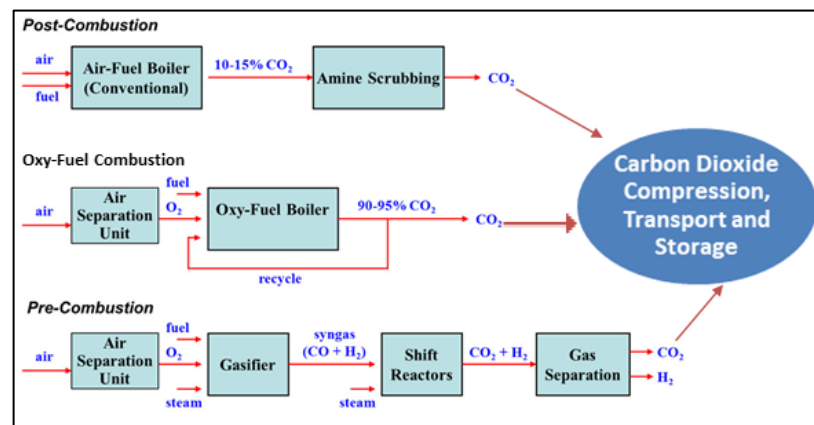


Figure 2.1. Flow chart of post combustion, oxy-fuel combustion and precombustion [19]

2.2. CARBON DIOXIDE ABSORPTION

Absorption is a process in which one substance enters into the bulk phase of another substance and it takes place in two different ways, i.e. physical and chemical. In physical absorption, absorbent and absorbate develop weak van der Waals forces between each other. In the chemical process, on the other hand, there is a chemical reaction between the absorbent and absorbate [20].

Chemical absorption of CO₂ by aqueous amine solutions is the most conventional way of capturing the gas that is employed in the post-combustion process. A classical amine absorption process is shown in Figure 2.2. As can be seen in the provided schema, flue gas stream meets the solvent (aqueous amine solution) in the absorber, where a chemical reaction between CO₂ and the amine takes place. CO₂-rich solution is then dispatched to the desorber, where CO₂ is separated from the solvent (amine solution) by heating. In absorption processes, the selection of a proper solvent is quite determining on the efficiency of the absorption and desorption columns. Accordingly, selected solvent should have a high carbon dioxide bearing capacity with fast absorption kinetics and low reaction enthalpy [21].

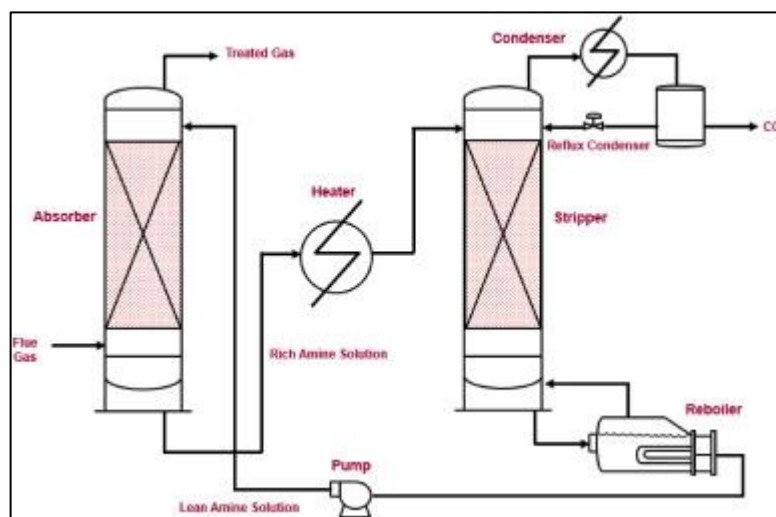


Figure 2.2. Representative amine scrubbing process [21]

Aqueous amine solutions have frequently been under investigation for this purpose due to the strong interactions of amines with CO₂. Among the amine structures considered, monoethanolamine (MEA) is by far the most widely studied one and serves as a benchmark in the field. It is a primary amine, and it can absorb high quantities of CO₂ with a fast reaction

kinetics [22]. However, owing to the strong interaction between MEA and CO₂, obtained product is very stable and the regeneration step is very energy-intensive (so very costly). Besides, there are problems associated with corrosion and solvent degradation [23]. All these issues prevent the use of MEA-based CO₂ capturing systems in large scale to achieve the targeted emission numbers at the end of the century.

Hence, alternative amine solutions that would eliminate the drawbacks associated with MEA systems were sought. DEA (diethanolamine) and MDEA (N-methyldiethanolamine) are the two most-frequently studied ones involving secondary and tertiary amine groups, respectively; due to their less volatile and less corrosive nature in comparison to the MEA [24]. MEA and DEA were reported to capture CO₂ with a reaction stoichiometry of CO₂: N = 1:2 in the forms of ammonium carbamate, whereas the CO₂/N was 1 in case of MDEA solutions, the end product being ammonium bicarbonate. Accordingly, MDEA seemed to absorb more CO₂ than MEA and DEA did. However, experiments reported that the absorption capacities of MEA and DEA were close to each other and much higher than that of the MDEA since the absorption kinetics was extremely slow for MDEA solutions [25]. Product stabilities, on the other hand, decreased in the order MEA > DEA > MDEA. Since the stability of the product was proportional to the regeneration energy, MDEA was the most promising amine in terms of regeneration energy. Nevertheless, all of the amines considered for CO₂ absorption had their own advantages and disadvantages; no single amine structure being superior to MEA in all aspects [26].

Sterically hindered amines, especially AMP (2-amino-2-methyl-1 propanol), were also investigated widely with the purpose of finding an alternative to MEA. They were shown to capture CO₂ in forms of bicarbonate (like tertiary amines) resulting in a reaction stoichiometry of CO₂:N = 1:1. Consequently, they were expected to have higher CO₂ absorption capacities and lower regeneration energies in comparison to MEA due to the diminished product stability of the bicarbonates [27,28]. However, considerably slower absorption kinetics observed in case of sterically hindered amines prevented these structures to be used as MEA substituents [29].

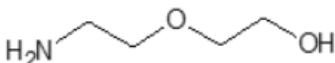
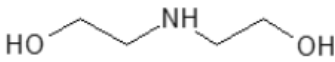
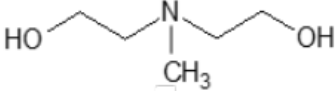
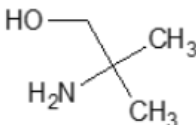
PRIMARY	Monoethanolamine [MEA]	
	Diglycolamine [DGA]/ aminoethoxy ethanol [AEE]	
SECONDARY	Diethanolamine [DEA]	
TERTIARY	Methyldiethanolamine [MDEA]	
HINDERED	2-Amino-2-methyl-1-propanol (AMP)	

Figure 2.3. Most-frequently used amine structures for CO₂ absorption [30]

Amine blends that would combine the advantages of both types (primary/secondary and tertiary/sterically hindered amines) were the next group of investigated structures. By blending a tertiary alkanolamine solution with a primary or a secondary one, the mixture could benefit from the fast reaction kinetics of the primary amine and the lower product stability and lower corrosivity of the tertiary amine. Accordingly, MDEA blends were formed and examined for CO₂ absorption. It was demonstrated MEA+ MDEA and DEA + MDEA blends enhanced energy savings in absorption systems and offered lower regeneration costs [31]. Besides, addition of MEA or DEA to MDEA solutions were observed to accelerate the absorption rates [32]. The equilibrium solubility of CO₂ in aqueous MDEA+MEA solutions were higher than that of the MDEA+DEA blends at high temperature [33] but increasing the concentration of MEA too much resulted in a decline of CO₂ solubility [34].

Blending primary or secondary amines with the sterically hindered ones was also popular due to the improved absorption capacity of these blends. AMP, having a much faster reaction kinetics and lower regeneration energy than MDEA, has frequently been used for this purpose [35]. Addition of a small amount of MEA or DEA into aqueous AMP was shown to enhance the absorption rate significantly [36,37], this effect being more pronounced in AMP blends compared to the MDEA [38,39]. In terms of absorption capacity, on the other hand, DEA+AMP blend were found to be inferior to the MEA+AMP solution [40].

Cyclic amines, due to their fast reaction kinetics and high CO₂ absorption capacities, were used as activators in aqueous amine solutions, so the use of blends involving these structures was also very common [41]. Its lower water solubility, however, decreased its potential to be used for CO₂ capture in large scale [42].

Finally, alkyl amines with multiple amino groups such as 2-(2-aminoethylamino) ethanol (AEEA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) were also considered frequently due to their potential to enhance the CO₂ uptake. These structures had much better CO₂ absorption capacities in comparison to the primary and secondary monoamines due to the much higher number of amine sites available in these molecules [43,44]. Much higher absorption capacities of CO₂ were generally reported for AEEA, DETA, TETA, and TEPA relative to MEA [45], but high viscosities associated with the larger ones (like TETA and TEPA) were reported to cause diffusional barriers for CO₂ under some conditions [46]. Molecular models of the piperazine and commonly used alkyl amines with multiple amino groups were demonstrated in Figure 2.4.

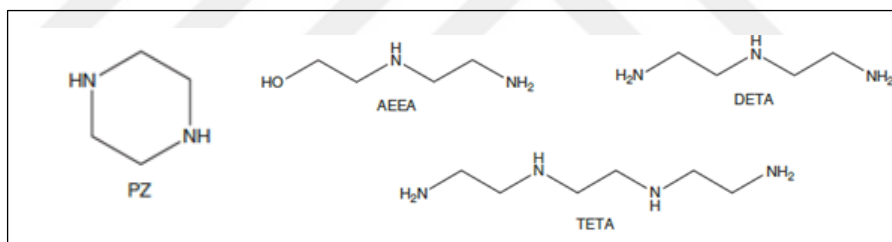


Figure 2.4. Commonly used cyclic amine and alkyl amines with multi amino groups structures [47, 48]

As it is clear from the above discussion, despite of the extensive research performed in the field of CO₂ absorption with various amine structures and blends, no amine solutions with superior performance in comparison to the MEA systems could be identified. Hence, other possibilities such as using solid adsorbents for CO₂ capture have emerged.

2.3. CARBON DIOXIDE ADSORPTION

As may be remembered from the above discussion, regeneration of MEA-based systems is quite costly. The factors that increase the regeneration costs (or energy requirements) are the high stability of the end product (ammonium carbamates) as well as the large amounts of energy required for heating and evaporating the water in the solution. Correspondingly, use

of solid adsorbents for CO₂ capture has appeared to be a potential solution to overcome the cost-related problems of the MEA systems. Both physical and chemical adsorbents have been considered as capture materials for CO₂.

2.3.1. Physical Adsorbents

Early studies concentrated on the assessment of CO₂ adsorption performances of some common physisorbents like zeolites, carbonaceous materials, and metal organic frameworks (MOFs).

Zeolites are well ordered microporous minerals that are composed of crystalline aluminosilicates [49]. In case of CO₂ adsorption over zeolites, the uptake was shown to escalate with increasing partial pressure of CO₂ and decreasing temperature. At 25°C, Santosh K et al. reported the adsorption capacity of the zeolite 13X as 6.2 mmol CO₂/g and 6.5 mmol CO₂/g at 1 bar and 8 bar, respectively. If the temperature was increased to 35°C at 8 bar, however, CO₂ uptake declined 6.2 mmol CO₂/g [50, 51]. Besides, impurities such as SO_x, NO_x and H₂O were needed to be removed prior to adsorption in order to restrict their competitive adsorption with CO₂ [52].

Activated carbons are the most widely investigated class of carbonaceous materials for CO₂ adsorption. They can be obtained from substances like coal or industrial byproducts, so they have low raw material cost [53]. CO₂ uptake of the activated carbon fibres were shown to decline from 2.74 mmol CO₂/g to 2.33 mmol CO₂/g, as the temperature increased from 25°C to 40 °C. Further increase of the temperature up to 55°C resulted in an adsorption capacity of 1.61 mmol CO₂/g at 1 atm [54]. Pressure, however, had an inverse effect on the capacity. Tahvildari et al. measured the CO₂ adsorption capacity of the activated carbon as 21.5 mg CO₂/g at 4 bar and 38.8 mg CO₂/ g at 8 bar at 35°C [55]. Finally, addition of water vapor into the CO₂ stream was reported to decrease the adsorbed amount from 0.38 mmol CO₂/ g to 0.32 mmol CO₂/ g [56].

MOFs are microporous crystalline structures comprised of centered cations attached by organic binders to obtain a 3D structure. Their tunable pore characteristics makes them quite attractive for physisorption purposes [57]. At 0.6 bar, CO₂ uptake of a MOF was reported to decrease from 108.8 mg CO₂/ g at 25°C to 68.97 mg CO₂/ g at 55°C. If the pressure was

increased to 3.1 bar at 25°C, on the other hand, measured capacity was 119.05 mg CO₂/ g [58]. Similar to the cases of zeolites and activated carbon, CO₂ uptake was shown to decrease from 12 mmol CO₂ /g to 10 mmol CO₂ /g upon the introduction of humidity over Mg-MOF-74 [59,60]. Besides, water vapor was reported to cause structural deformities in the crystalline lattice of MOFs [61].

In conclusion, although these materials showed good CO₂ adsorption performances at high pressures and low temperatures in the absence of humidity; they were demonstrated to lose their ability to adsorb CO₂ under flue gas conditions (75°C, ~0.1 bar of CO₂ partial pressure, and humidity).

2.3.2. Chemical Adsorbents

The origin of the poor adsorption performances of the physisorbents under flue gas conditions was the weak interactions between CO₂ and the adsorbents. This underlined the necessity of much stronger interactions for selective adsorption of CO₂ and led to the idea of using physisorbents whose surfaces are modified with various amine structures for more effective CO₂ capture. In this way, amine-based solid sorbents have emerged and have extensively been investigated for their CO₂ capture performances.

Amine-based solid sorbents comprise amine groups immobilized onto physisorbents like mesoporous silica, zeolites, carbonaceous materials, and etc. Mesoporous silica structures are more frequently employed due to their large surface areas, large pore volumes and easily tunable pore sizes [62]. These structures are synthesized via the polycondensation reaction of silica around the quaternary ammonium surfactants that are used as templates (Figure 2.5). These templates are then eliminated by calcination or extraction leading to the formation of mesopores within the silica structure.

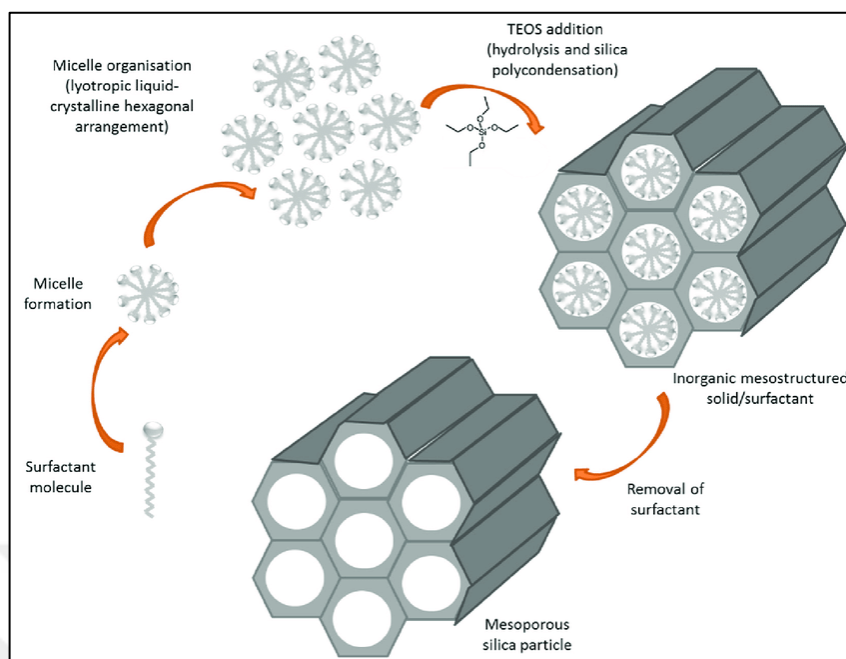


Figure 2.5. Diagrammatic representation of the synthesis of mesoporous silica [63]

MCM-41 (Mobile Composite of Material 41) and SBA-15 (Santa Barbara Amorphous-15) are the two most common types of mesoporous silica that are used for amine functionalization. Both possess amorphous pore walls and two-dimensional hexagonal arrangements of pores, pore sizes ranging from 2 nm to 10 nm for MCM-41 and 5 nm to 30 nm for SBA-15 [64]. Figure 2.6. demonstrates the molecular structure of MCM-41.

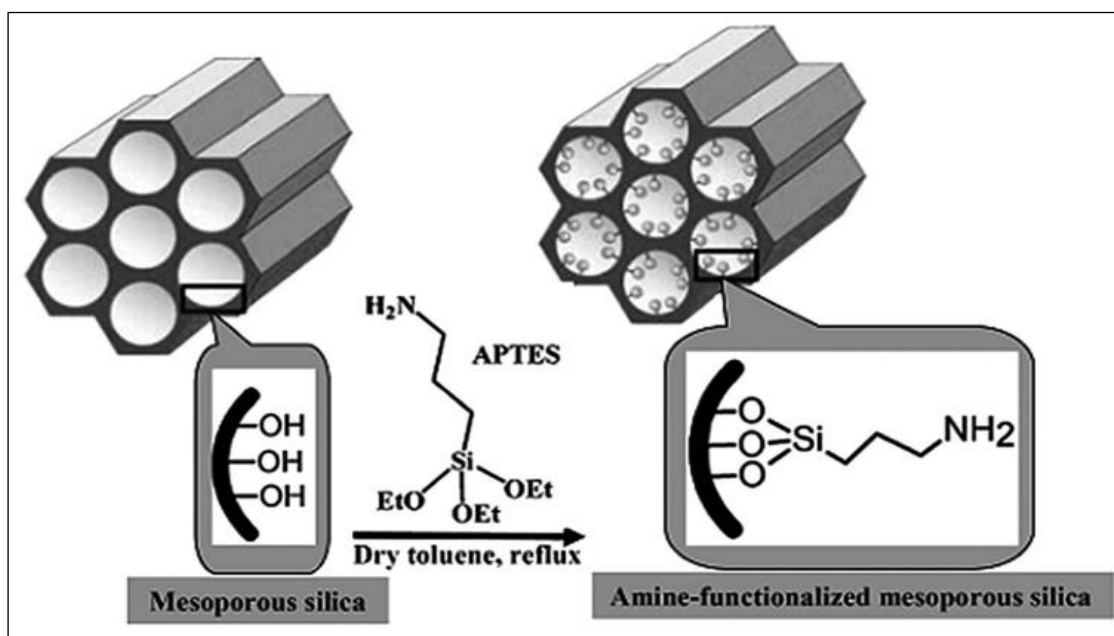


Figure 2.6. Molecular structure of MCM-41 and amine based mesoporous silica [65]

Amine modification of the mesoporous silica surfaces is generally accomplished in two different ways, namely impregnation and grafting. In the impregnation method, amino containing species are physically attached to the silica surface with the help of weak van der Waals interactions. This process results in high amine loadings and in turn high CO₂ uptakes. However, amine efficiencies (C/N) are usually low due to the diffusional restrictions of CO₂ to the active sites [66]. In the grafting method, on the other hand, amino groups are covalently attached on the support surface. This occurs via a condensation reaction between the -OCH₃ of the organosilane and the 3 surface -OH of the mesoporous silica support [67]. Amine loading is determined by the number of hydroxyl groups available at the support surface, so the amount of loading was usually much lower than that of the impregnated samples resulting much lower uptake but higher amine efficiencies [68]. Figure 2.7. demonstrates the two methods used for amine functionalization.

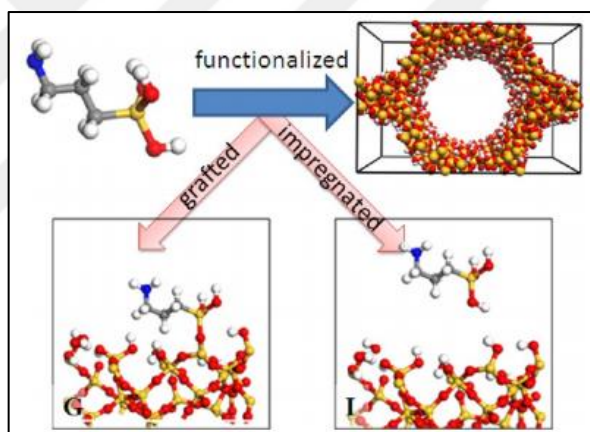


Figure 2.7. Molecular models of grafted and impregnated APTMS on MCM-41 [69]

Amine-based silica sorbents are usually classified into two main groups according to the preparation method. Samples prepared by impregnation are known as Class 1 sorbents, while the ones synthesized by grafting are called Class 2. Figures 2.8 and 2.9 present the most common amine structures that are employed for impregnation and grafting.

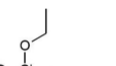
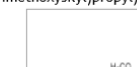
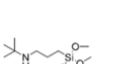
3-aminopropyltrimethoxysilane (APTES) 	N-(3-(trimethoxysilyl)propyl)ethylenediamine(AEAPS) 	3-aminopropyltrimethoxysiloxane (APS) 3-(methylamino)propyltrimethoxysiloxane (MAPS) 3-(phenylamino)propyltrimethoxysiloxane (PAPS) 
N-(3-trimethoxysilylpropyl) diethylenetriamine (TRI) 	[Trimethoxy[3-(methylamino)propyl]silane(TMMAAP) (N,N-dimethyl-3-aminopropyltrimethoxysilane (DMAPS) 	(3-amino-3-methylbutyl)trimethoxysilane (AMBS) (N-cyclohexylaminopropyl) trimethoxysilane (CHAPS) (tert-butylaminopropyl)trimethoxysilane (TBAPS) 

Figure 2.9. The most common amine structures used for the synthesis of class 2 adsorbents [71]

2.3.3. CO₂ Adsorption over Amine-Based Mesoporous Silica

Amine-based mesoporous silica sorbents have attracted great attention in the last two decades due to their potential to eliminate the serious problems associated with the wet scrubbing methods. The extensive research in the field has started with the pioneering work of Xu et al. [72]. In their study, they prepared PEI impregnated MCM-41 by using wet impregnation method. The maximum CO₂ adsorption capacity (215 mg CO₂/g sorbent) at 75 °C and 1 atm was obtained for 50 wt % PEI loading into MCM-41 adsorbent and it was 24 times higher than that of the bare-MCM-41.

TEPA (tetraethylenepentamine), involving more than one amino group, has been widely examined for CO₂ adsorption. Wang et. al. investigated the effect of the pore size on the adsorption performance of TEPA-based mesoporous silica by employing two distinct mesoporous silica with different pore sizes. CO₂ uptake was found to be much larger over the sample with larger pore size (7.6 nm) compared to the one with smaller pores (5.6 nm). Maximum capacities were reported as 3.48 mmol CO₂/g and 4.28 mmol/g under dry and humid conditions, respectively [73]. Chen et al. compared the adsorption capacity of TEPA-impregnated samples to that of the PEI (polyethyleneimine)-containing ones and reported that the CO₂ uptake over the first one (239 mg CO₂/g at 75 °C and 225 mg CO₂/g at 60 °C) was much higher than that of the second (210 mg CO₂/g at 75 °C and 171 mg CO₂/g at 60 °C) [74]. Similar findings were observed by Qi et al. as well [75].

Mukherjee et al. studied the effect of amine type on the CO₂ adsorption capacities employing monoethanolamine (MEA), N-(2-aminoethyl)ethanolamine (AEEA) and benzylamine (BZA) for the impregnation of MCM-41. The adsorption capacities of the AEEA, BZA and MEA-based sorbents were measured as 2.34 mmol CO₂/g, 0.908 mmol CO₂/g, and 1.47 mmolCO₂/g, respectively at 25°C and 1 bar. Higher CO₂ uptake in case of AEEA was attributed to the presence of more (two) amine sites present in the AEEA structure [76]. Investigation of the effect of chain length of various multi-amines on their adsorption performances was the subject of another study. Adsorption capacities (at 35°C) of 1.19 mmol CO₂/g, 1.43 mmol CO₂/g, 1.96 mmol CO₂ /g and 2.34 mmol CO₂/g, respectively for the ethylenediamine (EDA), diethylenetriamine (DETA), tetraethylenepentamine (TEPA) and pentaethylenhexamine (PEHA)-impregnated MCM-41 samples were reported. Their findings implied a direct proportionality between the chain length and adsorption capacity,

longer chain length meaning more amine sites [77]. Karademir et al. performed a similar study with DETA, TETA (tetraethylenetetramine) and PEI-impregnated MCM-41 and SBA-15 at 75°C and 1 bar. Adsorption capacities were 1.24 mmol CO₂/g for DETA, 1.64 mmol CO₂/g for TETA, and 2.06 mmol CO₂/g for PEI over MCM-41, while they were 0.96 mmol CO₂/g, 2.17 mmol CO₂/g, and 3.01 mmol CO₂/g, respectively for DETA, TETA, and PEI over SBA-15 [78]. In this manner, their observations were in perfect agreement with the previous finding.

Leal et al. grafted 3-aminopropyltriethoxysilane (APTMS) on to the silica gel and studied the CO₂ adsorption over this sorbent under both dry and humid conditions. Introduction of the water vapor into the reaction stream increased the CO₂ uptake from 9.10±0.05 cm³ CO₂/g to 20.80 ±0.05 cm³ CO₂/g at 100 °C and 1 atm. This was attributed to the transformation of the surface bound carbamates (observed under dry conditions) into bicarbonate structures with the introduction of the humidity [79].

To see the effect of additional amino groups on the adsorption capacity, CO₂ capture performances of the APTMS and AEAPS (N-[3-(trimethoxysilyl)propyl]ethylenediamine, multi-amine)-grafted MCM-41 and SBA-15 were compared. For both mesoporous silica, adsorption capacities of the AEAPS-grafted samples (2.20 mmol CO₂/g for MCM-41 and 1.27 mmol CO₂/g for SBA-15) were found to be higher than their counterparts of the APTMS-grafted samples (1.16 mmol CO₂/g for MCM-41 and 0.96 mmol CO₂/g for SBA-15) [80]. Delaney et al. performed a similar study with APTMS, AEAPS, and N-(3-trimethoxysilylpropyl)diethylenetriamine (DAEAPTS)-modified hexagonal mesoporous silica (HMS) and obtained much higher capacities for CO₂ adsorption over [81]. Another examination held by using the same amine structures were published by Chaffee et. al. They reported that DAEAPTS-grafted samples had the highest adsorption capacities among the others under dry conditions and this was suggested to be originating from the high amine content (15.8 wt%) of the sample [82].

Pore expansion was a usually applied treatment to the mesoporous silica structures with the purpose of enhancing the CO₂ adsorption capacities. Harlick and Sayari based the pore-expanded MCM-41 (PE-MCM41) with DAEAPTS and announced a CO₂ uptake of 2.65 mmol CO₂/g at 25°C and 1 atm under dry conditions that was much higher than the value obtained with ordinary MCM-41 [83].

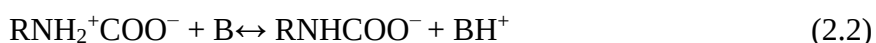
Hiyoshi et al. grafted APTMS, AEAPS and DAEAPS on to SBA-15 and measured the adsorption capacities of these sorbents at 333K and 15 kPa of CO₂ partial pressure in the absence and presence of water vapor. Adsorption capacities were reported as 0.66 mmol CO₂/g, 1.36 mmol CO₂/g, and 1.58 mmol CO₂/g, respectively for the APTMS, AEAPS, and DAEAPS under dry conditions that were proportional to the amine content of the samples as well as the surface amine density [84]. In the same study adsorption performances of the APTMS, N-methylaminopropyltrimethoxysilane (MAPS), and N,N-dimethyl-3-aminopropyl)trimethoxysilane (DMAPS)-grafted samples were also measured with the purpose of determining the effect of amine functionality on the adsorption performance. The adsorption capacity of DMAPS in the absence and presence of water vapor was very low (0.05 mmol CO₂/g) showing that tertiary amines were not useful for CO₂ capture process. APTMS (primary), on the other hand, could achieve a higher CO₂ uptake (0.52 mmol CO₂/g under dry conditions) compared to the MAPS (secondary, 0.25 mmol CO₂/g under dry conditions). The adsorption capacity (0.87 mmol CO₂/g under dry conditions) of AEAPS was higher than those of both APTMS and MAPS [84]. Similar observations that multi-amines could achieve a higher CO₂ uptake was reported by others as well [85].

Double functionalization is a relatively new method for the preparation of the amine based solid sorbents. This method, by involving both impregnation and grafting, aims to combine the advantages of both [86]. Sanz et al. were the first to use this method with the purpose of obtaining high-nitrogen-content adsorbents. Accordingly, they grafted the surface of the SBA-15 with APTMS or TA that was followed by the impregnation of these grafted samples by TEPA or PEI. In this way, they could achieve very high amine loadings on the surface of the samples and measured the adsorption capacities of these at 75 °C and 100 kPa. The adsorption capacity of the double-functionalized sample with APTMS and TEPA was reported as 5.31 mmol CO₂ /g that was much higher than the values obtained for APTMS-grafted or TEPA-impregnated SBA-15 [87]. A similar study was performed over MCM-41 as well resulting in complementary findings [88]. Many other studies involved this double functionalization method and reported that the amine efficiencies as well as the adsorption capacities were much higher compared to the sample prepared by single functionalization due to the high nitrogen content of these samples [70,86].

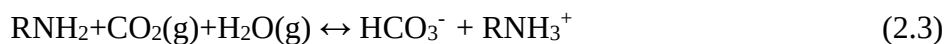
2.4. CARBON DIOXIDE CAPTURE PATHWAY

An effective adsorbent for CO₂ capture that would meet the 2100 targets should possess high adsorption capacity, high selectivity, fast reaction kinetics, mild regeneration conditions and high stability under flue gas conditions [1]. Development of such a sorbent requires rational design and a clear understanding of the CO₂ adsorption pathways over amine-based mesoporous silica is indispensable for this design.

In the early days of research, CO₂ adsorption pathway was believed to be identical to that of absorption. According to the findings reported by comprehensive kinetic and theoretical investigations, primary and secondary amines absorb CO₂ in the forms of ammonium carbamates. This reaction takes place in two steps and is known as the zwitterion pathway [89]. In the first step, the lone pair on the nitrogen atom interacts with the carbon dioxide molecule to form a zwitterionic intermediate (equation 2.1). In the second step, this intermediate is deprotonated by a base molecule that could be water, hydroxide or another amine molecule (equation 2.2). As it is clear from the observed reaction stoichiometry, two amine molecules are required for the absorption of one CO₂ molecule.



Tertiary amines do not have any hydrogen atoms that may be transferred to the adjacent amine as it was the case in the two-step zwitterion pathway. Hence, absorption of CO₂ by aqueous tertiary amine solutions take place in a different way. Although various pathways were reported by different groups, the most prevailing pathway is the one-step base-catalyzed hydration pathway, in which CO₂ is absorbed in the forms of bicarbonates [90]. This pathway involves a reaction between carbon dioxide, amine and water that result in the formation of an ammonium bicarbonate structure (equation 2.3). The reaction stoichiometry indicates that, different from the previous case, one amine molecule is required for absorbing one CO₂ molecule which in turn means that CO₂ absorption capacities of tertiary amines should be higher. However, this was hardly reported by the previous studies due to the slow reaction kinetics of tertiary amines [91]. Sterically hindered amines were shown to react with CO₂ also via the base-catalyzed hydration pathway as long as the amine groups can access the water molecules [92].



Due to the early assumption that CO₂ absorption and adsorption took place in the same way, most of the mechanistic studies performed in the field of CO₂ adsorption over amine-based silica sorbents concentrated on the specification of adsorption products. For this, initially IR, later NMR (sometimes in conjunction with DFT) analysis was used. Very recently, more systematic DFT analysis were also published in the field focusing on the determination of the adsorption pathways over primary and secondary amine-modified silica sorbents.

2.4.1. IR Analysis of CO₂ Chemisorption over Amine-Based Silica

Leal et al. examined the adsorption species of CO₂ over APTMS-grafted silica gel under dry and humid conditions by using FTIR. The bands identified at 1411 cm⁻¹ and 1385 cm⁻¹ were assigned to a carbamate and bicarbonate structures, respectively. Formation of the bicarbonates was suggested to take place via a conversion from carbamates upon the introduction of water [79]. In their study performed over APTMS-grafted MCM-48 under dry and humid medium, Huang et al. reported vibrational peaks at 1382 cm⁻¹, 1432 cm⁻¹ and 1485 cm⁻¹ corresponding to the bicarbonate and carbamate structures [93]. Bidentate carbonates (1543 and 1363 cm⁻¹) and monodentate bicarbonates (1472 and 1428 cm⁻¹) were later identified over APTMS-SBA-15 by Khatri, using isotopic shifts to understand the role of water [94]. A similar study reported the presence of bidentate bicarbonates (1634 cm⁻¹), bidentate carbonates (1575 cm⁻¹ and 1390 cm⁻¹), monodentate bicarbonates (1493 cm⁻¹ and 1432 cm⁻¹), monodentate carbonates (1337 cm⁻¹), and carbamic acid (1595 cm⁻¹, 1440 cm⁻¹, and 1330 cm⁻¹) over APTMS-grafted SBA-15 in the presence of water [95].

Richner and Puxty obtained the IR spectra of aqueous MEA, DEA and AMP during carbon dioxide absorption and the peaks at 1360 cm⁻¹ and 1350 cm⁻¹ were attributed to bicarbonates. Accordingly, they assigned the peak at 1350 cm⁻¹ that was observed over APTMS-SBA-15 under humid conditions to bicarbonate [96]. Identification of bicarbonate peaks at 1616 cm⁻¹ and 1358 cm⁻¹ over APTMS and DMAPS-modified SBA-15 were reported by others as well [97].

Unlike the previous studies, Danon and Bacsik did not report the formation of any bicarbonates and carbonates over APTMS-based SBA-15. They attributed the band at 1714

cm^{-1} to C=O stretching of the surface bound carbamate and the peak at 1564 cm^{-1} to the symmetric deformation of NH_3^+ (ammonium carbamate). When benzylamine spacer was utilized to produce isolated amine groups, formation of only the silylpropylcarbamates (surface-bound carbamates) were observed that were produced via the interactions between the intermediate carbamic acid and hydroxyl groups [98]. In a subsequent study of the same group that was performed over APTMS and ((3-aminopropyl)methyldiethoxysilane) APMDES-modified MCM-48 under high vacuum conditions, formation of ammonium carbamate ion pairs as well as carbamic acids were reported under both humid and dry conditions based on the vibrational peaks identified at 1715 cm^{-1} and 1518 cm^{-1} , respectively [99]. Other studies attributed the peak at 1680 cm^{-1} to carbamic acid [100], the peaks at 1430 cm^{-1} and 1571 cm^{-1} to ammonium carbamate ion pairs and the ones at 1490 cm^{-1} , 1637 cm^{-1} and 2150 cm^{-1} to NH_3^+ groups found in ammonium carbamate ion pairs over APTMS [101]. The band at 1700 cm^{-1} was, on the other hand, assigned to the overlapping bands of silylpropylcarbamate and carbamic acid [101].

In-situ IR analysis carried out over different types of amines (APTMS, MAPS, AEAPS and TA (3-trimethoxysilylpropyl)diethylenetriamine)) grafted on SBA-15 under dry conditions suggested the formation of alkylammonium carbamates. The peaks that were assigned to N–H stretch of carbamate ($\sim 3439 \text{ cm}^{-1}$) were observed in case of APTMS, AEAPS, and TA but not MAPS [84]. Similar bands identified around 3300 cm^{-1} and 3370 cm^{-1} were reported by others too and assigned to the N-H stretch of alkylammonium carbamate over APTMS-modified sorbents [102]. Another examination performed over APTMS (mono amine), AEAPS (di amine) and TA (tri amine)-grafted SBA-15 prepared by ethanol extraction reported vibrational frequencies at 3445 cm^{-1} , 3052 cm^{-1} and 1626 cm^{-1} which were attributed to nitrogen-hydrogen stretching in RNHCOO^- , nitrogen-hydrogen stretching in RNH_2^+ and nitrogen-hydrogen deformation in RNH_3^+ , respectively. The sharp peaks identified at 1562 cm^{-1} and 1436 cm^{-1} were, on the other hand, assigned to the oxygen-carbon-oxygen asymmetric and symmetric stretching of COO^- in the alkyl carbamate anion. Accordingly, formation of alkylammonium carbamate was suggested over APTMS, AEAPS and TA [103].

Comparison of the IR spectra of CO_2 adsorption over APTMS and MAPS grafted SBA-15 demonstrated the evolution of monomeric carbamic acid was (1690 cm^{-1}) in case of APTMS; monomeric (1686 cm^{-1}) and dimeric (1658 cm^{-1}) carbamic acids in case of MAPS.

Monomeric carbamic acid structures were stabilized via the interaction with surface silanols, while adjacent amine interactions were required for the stabilization of the dimeric carbamic acid [104]. Observation of these paired carbamic acids were also reported over TEPA and polyethylene glycol (PEG)-based silica, the peak identified at 1696 cm^{-1} being attributed to these structures [105].

IR spectra of DETA, TEPA and PEI-modified SBA-15 proposed the formation of ammonium carbamate and carbamic acid formations under dry conditions; bicarbonate formation under humid conditions [106]. Yu et al. performed a similar study over TEPA in the presence of water vapor and reported the formation of both carbamic acid (2535 cm^{-1}) and ammonium carbamate (1313 cm^{-1} 2996 cm^{-1}). Besides, CO_2 was suggested to adsorb on the primary amino groups, while water preferred the secondary ones. [107]. In another study carried out by Jie Yu over TEPA-based sorbents, CO_2 was argued to adsorb on the primary amino groups in the form of ammonium carbamates and on the secondary amino groups as carbamic acid based on the peaks identified at 1326 cm^{-1} (carbamate) and 1681 cm^{-1} (carbamic acid) [108]. Formation of zwitterions was also reported based on the peaks identified at 1411 cm^{-1} and 1313 cm^{-1} that were attributed to the NCOO bending observed in these structures [21].

2.4.2. NMR Analysis of CO_2 Chemisorption over Amine-Based Silica

As it is quite clear from the above summary, there is a huge discussion about the CO_2 adsorption species observed over amine-based mesoporous silica sorbents. Correct assignment of the IR peaks is indeed quite challenging owing to the low intensity of the bands as well as the strong overlap between them. Accordingly, NMR -which is known to be capable of not only discriminating between different adsorption species but also the various conformers of those species- has emerged as an alternative tool for the analysis of CO_2 adsorption.

Pinto et al. were the first who employed ^{13}C NMR with the purpose of determination of the CO_2 adsorption species over amine-based mesoporous silica sorbents. Their NMR spectra of APTMS demonstrated 2 resonances at 125 ppm and 164 ppm. The first one was assigned to the physically adsorbed CO_2 , while the second was deconvoluted into two different resonances at 160 ppm and 164 ppm which were attributed to the presence of carbamic acid

and carbamate structures, respectively [109]. Similar peaks (between 150 ppm and 170 ppm) that were ascribed to the formation of these two species were reported for various amine-grafted-SBA-15 by other groups as well. For example, Foo et. al. examined the CO₂ adsorption over APTMS, MAPS and DMAPS; and observed peaks at 160.8 ppm (carbamic acid) and 164.6 ppm (ammonium carbamate) in case of APTMS and MAPS. It was suggested that the carbonyl groups were strongly hydrogen-bonded to either the adjacent amines or the surface silanols; carbamic acid was formed via the interplay of CO₂ with an amine group whereas ammonium carbamate production took place with the involvement of the adjacent amine. In the case of DMAPS (tertiary), on the other hand, only bicarbonate formation was observed at a resonance of 161 ppm [104]. Similar ¹³CNMR resonances at 162.2 ppm (over DMAPS) and 162.4 ppm (over TEPA) were reported by others too [97,106].

The 164-ppm resonance was indeed controversial. Although almost all the groups ascribed this resonance to an alkyl ammonium carbamate structure, formation of an ionic ammonium carbamate could not be verified by DFT calculations, but the assignment was based on ¹³CNMR chemical shift anisotropy tensor analysis [6]. Other groups reported similar resonances at 163 ppm over APTMS and 156.9 ppm over MAPS; and attributed these to the formation of ammonium carbamates via intermolecular interactions [110]. In case of AEAPS, on the other hand, primary carbamates were observed at 156.8 ppm, while the secondary ones were at 162.6 ppm [110]. The resonance obtained at 162 ppm over AEAPS was, in another study, ascribed to a surface-bound carbamate structure [111].

NMR analysis of CO₂ adsorption over APTMS samples with various surface amine densities (2.8 mmol/g, 0.9 mmol/g and 0.5 mmol/g) reported peaks at 164 ppm, 160 ppm and 154 ppm. The first peak (being dominant in case of high surface amine density) was considered as an ammonium carbamate species, while the remaining ones were attributed to the presence of two different carbamic acid species. The first carbamic acid (160 ppm) was observed when the amine density was high and was proposed to be a carbamic acid that was strongly hydrogen bonded to the adjacent amine. The second one (154 ppm), on the other hand, was dominant when the amine density was low and thought to be an isolated carbamic acid that had no interactions with the adjacent amines [112]. Significance of the surface amine density on the CO₂ adsorption performance of the sorbents was underlined in other studies too [113]. ¹H resonance detected at 11.8 ppm over MAPS and AEAPS was also

attributed to carbamic acid and was reported to be absent in case of APTMS [6]. Based on this, it was argued that the carbamic formation was dominant in secondary amines [6].

Finally, ^{13}C NMR analysis performed over hyperbranched amino silica (HAS) polymers (which involved primary, secondary, and tertiary amines together) declared the formation of carbamate, carbamic acid and bicarbonate based on the resonances identified at 164 ppm, 160.3 ppm and 163 ppm, respectively [114].

2.4.3. DFT Analysis of CO₂ Chemisorption over Amine-Based Silica

DFT (Density Functional Theory) analysis was initially used for the verification of the predicted species by NMR or FTIR. For this, various molecular models of the anticipated carbamate and carbamic acid species were formed and DFT-optimized. Following this, NMR shifts as well as the vibrational frequencies were calculated via the DFT method and estimated values were compared to those obtained experimentally [115].

Accordingly, DFT-calculated NMR shifts for primary and secondary amines were reported to be in perfect agreement with those obtained experimentally under both dry and humid conditions. Carbamic acid was the dominating product in case of dry medium whereas carbamate could be stabilized with complex hydrogen bonding networks under humid conditions independent of the functionality of the amine involved. DFT-estimated IR frequencies were also shown to be in good agreement with the experimentally observed ones [116].

Much recently, DFT has been used to perform a thorough reaction pathway analysis of the CO₂ adsorption over silica sorbents grafted with APTMS and MAPS [117,118]. Cho et al. investigated the adsorption pathway of APTMS-based mesoporous silica by using DFT calculations. Two different molecular models, i.e. one without the SiO₂ molecules, and the other with the SiO₂ molecules, were employed to elucidate the effect of surface silanols on the reaction pathway. The reaction taking place over the model without the SiO₂ surface was shown to be thermodynamically and kinetically less feasible compared to the other one. Surface silanols played an active role in the formation of adsorption species (carbamic acid and carbamate) in case of the model with SiO₂ surface [117]. The omission of the SiO₂

surface in the first model might, yet, have resulted in the neglect of potential impact of the surface interactions on the stabilization of the reaction species.

For this reason, our group has recently performed an investigation of the CO₂ adsorption pathways over APTMS and MAPS-based mesoporous silica by using DFT analysis. Ammonium carbamate and carbamic acid were shown to be the main adsorption species; various carbamic acid structures (differing from one another in the hydrogen bonding network that they had) were observed. Hydrogen bonding interactions (both amine-surface and amine-amine) rather than the amine functionality were shown to be critical on the capture performance. Surface silanols were shown to not only affect the reaction thermodynamics and kinetics via stabilization of the adsorption species, but also took an active role in the required proton transfers. Various reaction pathways were identified suggesting the formation of carbamic acid and ammonium carbamate structures over paired amines [118].

2.5. MOLECULAR MODELING

Molecular modeling is the scientific approach used to represent molecular models numerically and replicate their behavior by using quantum and classical physics equations in the chemical reaction engineering, polymer chemistry, drug design, etc. [119].

Molecular mechanics and molecular dynamics are the two main important methods in modern computational physics. Molecular mechanics (MM) is a simple and fast method to evaluate molecular systems. This approach is dependent on potential functionals and is applied to examine small molecules in addition to large molecules involving many thousands of atoms ignoring breaking or formation of bonds absolutely. In this system, each of the atoms is described as charged particle which are connected by springs forming the molecules. The potential energy of a molecule is composed of individual functions accounting for bond stretching, angle bending, torsional energy and non-bonding interplays. These functions are obtained by experiments and are known as force fields [120]. Molecular dynamics (MD), on the other hand, is a procedure involving the calculation of motion of molecules in a certain period of time via the solution of equations of motion by assuming a potential energy function [121].

Quantum mechanical approach provides the electronic attitude of molecules via the solution of quantum mechanical equations that are based on the Schrödinger equation [122]. This mathematical equation represents the position of the electrons and the energy of the electrons in time and space regarding to the wave nature of an atom. The accurate analytical solution of this equation can be just for one-electron systems while approximate solutions involving the orbital approximation and variational principle are obtainable for larger atoms and molecules. The time-independent Schrödinger equation of the systems containing multi electrons is expressed in equation 2.4

$$\hat{H}\Psi=E\Psi \quad (2.4)$$

The wave function Ψ is representing the electron's movement, $\hat{H}$ is energy operator which is Hamiltonian operator and the energy eigenvalue is E [123].

$$\hat{H} = -\frac{1}{2}\sum_i^{electrons} \nabla_i^2 - \frac{1}{2} \sum_A^{nuclei} \frac{1}{M_A} \nabla_A^2 - \sum_i^{electrons} \sum_A^{nuclei} \frac{Z_A}{r_{i,A}} + \sum_{i<j}^{electrons} \sum \frac{1}{r_{ij}} + \sum_{A<B}^{nuclei} \sum \frac{Z_A Z_B}{R_{AB}} \quad (2.5)$$

The Hamiltonian operator consists of five terms as shown in equation 2.5, such as the nuclei's attraction of electrons and electron's kinetic energies, the internuclear repulsions and interelectronic repulsions, all terms affecting the system's total energy. The approximation of Born-Oppenheimer, that is dependent on the supposition that nuclei is stationary because of the relatively slower motion of nuclei in comparison to the electrons, is usually employed to simplify the equation. Accordingly, the movement of nuclei and electrons is decoupled and the equation is simplified to the form given below:

$$\hat{H}^{el} = -\frac{1}{2}\sum_i^{electrons} \nabla_i^2 - \sum_i^{electrons} \sum_A^{nuclei} \frac{Z_A}{r_{i,A}} + \sum_{i<j}^{electrons} \sum \frac{1}{r_{ij}} \quad (2.6)$$

This equation (equation 2.6) is still hard to solve owing to the interactions among individual electrons. Hence, other approximations which would consider that electron's movement is independent from each other were required. This approximation is known as the Hartree-Fock approximation and results in a number of coupled differential equations, each comprising a single electron's coordinates. The approximation of Linear Combination of Atomic Orbitals was further introduced in order to convert these equations into algebraic ones and simplify the solution to a great extent [124].

On the other hand, in the Hartree-Fock approximation neglecting the interactions among the individual electrons results in an overestimation of the total energy. Therefore, related models such as the Moller-Plesset models, Configuration Interaction and Density Functional Theory have been developed to solve these shortcomings [125].

2.5.1. Density Functional Theory Method

DFT is the main alternative developed to overcome the deficiency of the Hartree-Fock model without being more costly than it. This method achieves the calculation of atoms and molecule's electronic structure by using functionals of electron density. Electronic energy (E) equation of a system of interacting electrons is demonstrated in equation 2.7 [126].

$$E = E_T + E_V + E_J + E_{XC} \quad (2.7)$$

In this equation, the repulsion energy (E_J) is between electrons, the kinetic energy (E_T) resulting from the motion of electron, the interaction energy (E_V) is between nucleus and electron, finally the exchange correlation energy (E_{xc}) involving the last step of the interactions of electron and electron. All the components other than the kinetic energy are associated with the sum of electron density as shown as ρ in equation 2.8.

$$\rho = 2 \sum_i^{orbitals} |\psi_i(r)|^2 \quad (2.8)$$

where ψ_i denotes the Kohn-Sham orbitals. The procedure of finding the orbital coefficients which are unknown that give the minimum electronic energy results from a group of matrix equations and their solutions will provide the ground-state electronic energy of the investigated system [126].

Exchange-correlation term is the only unknown in the electronic energy equation given above and approximations are needed for the calculation of this term. Local density (LDA) and generalized gradient (GGA) are two essential approximations that are in use. LDA assumes that the changes in the density to be slow so the true exchange-correlation energy at each point is approached by the uniform electron gas of the identical density's exchange correlation energy. GGA, besides, considers the spatial variation of the electron density as well [124].

Besides the exchange-correlation functionals involving LDA or GGA approximations, there are also hybrid functionals containing a combination of the Hartree-Fock exchange with LDA or GGA. Determination of the correct functional is very critical for obtaining correct results [127].

2.5.2. Basis Sets

Basis sets are used to simply a group of functions which are linearly combined to reflect the molecular orbitals in a molecule mathematically. These functions are usually atomic orbitals centered on each nucleus and Slater- type orbitals (STO) used to solve the Schrödinger equation for such as hydrogen atoms, were initially employed for constructing the basis set. However, due to the difficulties experienced in the calculation of integrals, Gaussian-type orbitals are used nowadays [128].

STO-3G basis set is the most widespread minimal basis set involving 3 Gaussian primitive functions to demonstrate each orbital. It fails to describe the non-spherical electron distributions in molecules, so it is usually used as a popular starting point for calculations rather than being used to obtain results. [129]. Basis sets of split-valence (SV) and double zeta (DZ) were developed to improve the flexibility to describe the electron distributions. DZ basis set doubles all basis functions, while in SV basis sets the core and valence electrons are treated differently. The valence region is further splitted into two regions as inner and outer [130].

Introduction of polarization and diffuse functions is also common to increase the flexibility of the molecular orbitals. Polarization functions add d-functions for main group elements and p-functions for hydrogen (if the basis set is a double-asterisk one). Polarization functions, on the other hand, add functions that would describe the tail portion of the atomic orbitals more accurately [131].

3. COMPUTATIONAL WORK

3.1. COMPUTATIONAL MODELS

The selection of a molecular model that would successfully represent the studied system without requiring very high computational costs is quite critical for obtaining correct results in molecular modeling. In this study, N-[3-(trimethoxysilyl)propyl] ethylenediamine (AEAPS)-grafted mesoporous silica models were created with the purpose of investigating the CO₂ adsorption pathways over multi-amines. AEAPS involves 2 amine groups in total, one being primary and the other being secondary (Figure 3.1).

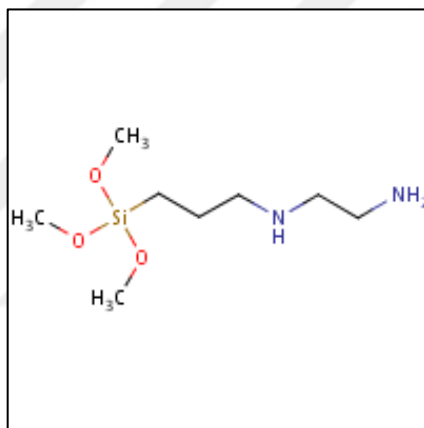


Figure 3.1. AEAPS structure [132]

To understand whether intra-molecular capture is possible and which amine groups (primary or secondary) are more reactive in CO₂ capture, two different molecular models involving one and two AEAPS molecules were created.

Mesoporous silica models, that were compatible with the structure of amorphous silica, were built first, considering the fact that ordered mesoporous silica structures possessed amorphous pore walls. The cluster constructed was named as 5_5 and comprised two connected five-membered rings including 8 SiO₂ groups in total. In the cluster, terminal oxygen atoms were saturated with hydrogen atoms. Obtained cluster was then optimized by the DFT method. The top and side views of the optimized models are represented in Figure 3.2.

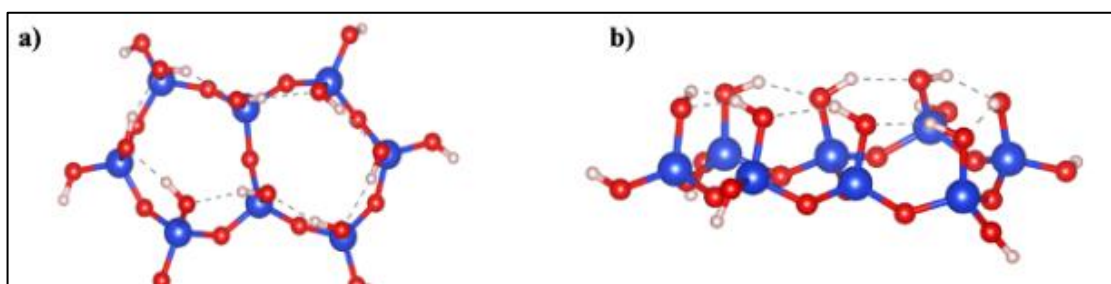


Figure 3.2. Molecular models of (a) top view, (b) side view of the 5_5 cluster Colors represent: red = oxygen, blue = silicon, pink = hydrogen

Next, 5_5 mesoporous silica structures were grafted with one and two AEAPS molecules resulting in 5_5-single-AEAPS and 5_5-double-AEAPS molecular models, respectively. Attachment of each AEAPS molecule on the mesoporous silica surface is accomplished via a condensation reaction taking place between the three -OCH₃ groups of the AEAPS structure and three free surface silanols of the 5_5 cluster. In this way, AEAPS molecules are covalently bonded to the surface of the mesoporous silica. Resulting models are given in Figure 3.3.

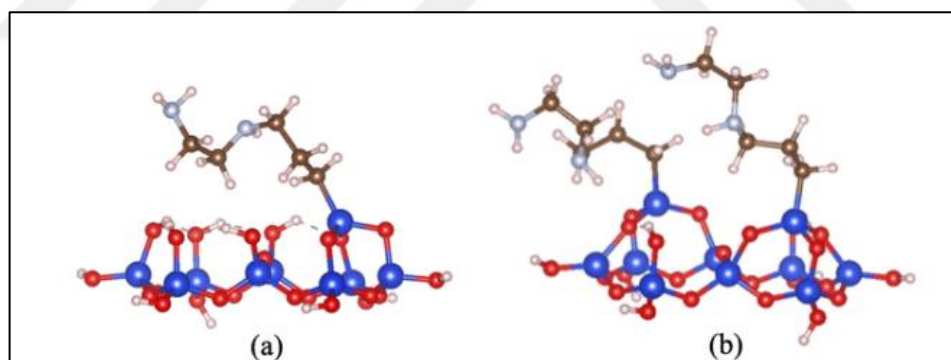


Figure 3.3. Molecular models of (a) 5_5-single-AEAPS, and (b) 5_5-double-AEAPS Colors represent: red = oxygen, blue = silicon, pink = hydrogen, gray = nitrogen, and brown = carbon

Finally, conformational analysis of both models was performed using the Avogadro software. Since the number of conformers obtained for 5_5-double-AEAPS is huge, only the randomly generated 10,000 of them were considered. Of the conformers obtained, the ones that could lead to different CO₂ capture pathways were chosen for reaction pathway analysis.

3.2. COMPUTATIONAL PARAMETERS

Conformational analysis of the obtained models was performed using Molecular Mechanics of the Avogadro 1.2.0 software with the MMFF94 force field [133], while all the calculations required for the reaction pathway analysis were executed by making use of the DFT method of Gaussian 16 [134]. DFT was used with the B3LYP (Becke's three-parameter hybrid functional) exchange-correlation functional [135] and Grimme's D3 dispersion correction [136] was added in order to account for the hydrogen bonding interactions which are critical in this study. The basis set was chosen as the standard 6-31G(d) [137]. This combination of the functional and basis set was shown to produce results that were compatible with the experimental results [118,138].

3.3. COMPUTATIONAL METHODOLOGY

For the study of the CO₂ adsorption over AEAPS-modified MCM-41, molecular models were created first as depicted in the previous section. Determination of the reaction pathways was then achieved via the DFT method, by employing three types of calculations, i.e. geometry optimizations, transition-state searches, and intrinsic reaction coordinate (IRC) calculations.

Identification of the lowest-energy structures of the reactants, intermediates, and products involved in the reaction pathways as well as the calculation of their energies were accomplished using geometry optimizations. QST2 option of the STQN (Synchronous Transit-Guided Quasi-Newton) procedure of Gaussian 16 was used for finding the transition state structures. Vibrational frequencies were always calculated for confirming the nature of the obtained products (saddle point or global minimum). Finally, IRC calculations were involved to check whether the transition states obtained were the correct ones. All the energies reported in this study are the Gibbs free energies, which were acquired by using the thermochemistry data of Gaussian 16.

In all the calculations, the AEAPS molecule/s, the Si-O-Si bonds attaching this/these molecule/s to the silica surface, the free silanols located at the surface of the 5₅ cluster and the CO₂ molecule (whenever it is involved) were relaxed while the coordinates of all the remaining Si, O, and H atoms were frozen in order to mimic the mechanical fixing

experienced in the real mesoporous silica structures due to the presence of a huge number of SiO_2 units.



4. RESULTS AND DISCUSSION

As explained in the previous section, two different models -involving one and two AEAPS molecules grafted onto the 5_5 mesoporous silica clusters- were created to examine the CO₂ adsorption pathways over multi-amines. Appropriately, our findings regarding the reaction pathway analysis will be discussed in two main sections, each involving the results obtained over one of the created models.

4.1. ANALYSIS OF ADSORPTION MECHANISM OVER 5_5-SINGLE-AEAPS

When one AEAPS molecule is grafted onto the mesoporous silica (5_5) surface, there were 5 free silanols remaining at the surface. Several different conformers were considered for the study of CO₂ adsorption and 8 different pathways were identified. These pathways were direct carbamic acid evolution (DCA), isolated carbamic acid evolution (ICA), zwitterion to carbamic acid evolution (ZCA), surface-assisted carbamic acid evolution (SCA), surface-assisted carbamic acid evolution via an intermediate (SICA), carbamic acid to surface-assisted carbamic acid evolution (CASA), carbamic acid to surface-assisted carbamic acid evolution via an intermediate (CAISA) and surface-assisted carbamate to carbamic acid evolution via the zwitterion (ZSCBA) pathways. Some of these pathways like DCA, ICA, and ZCA have been reported before over APTMS (primary) and/or MAPS (secondary)-grafted mesoporous silica, while the remaining ones have been observed for the first time [118].

Of the 8 pathways observed over 5_5-single-AEAPS, only 2 of them resulted in thermodynamically stable products. The reaction energy diagrams presented in Figure 4.1 involves only the thermodynamically feasible pathways to keep the diagram as simple as possible. The reference point in the diagrams is denoted as REF and has a free energy that is equal to the total energies (free) of the gaseous CO₂ and the matching 5_5-single-AEAPS cluster.

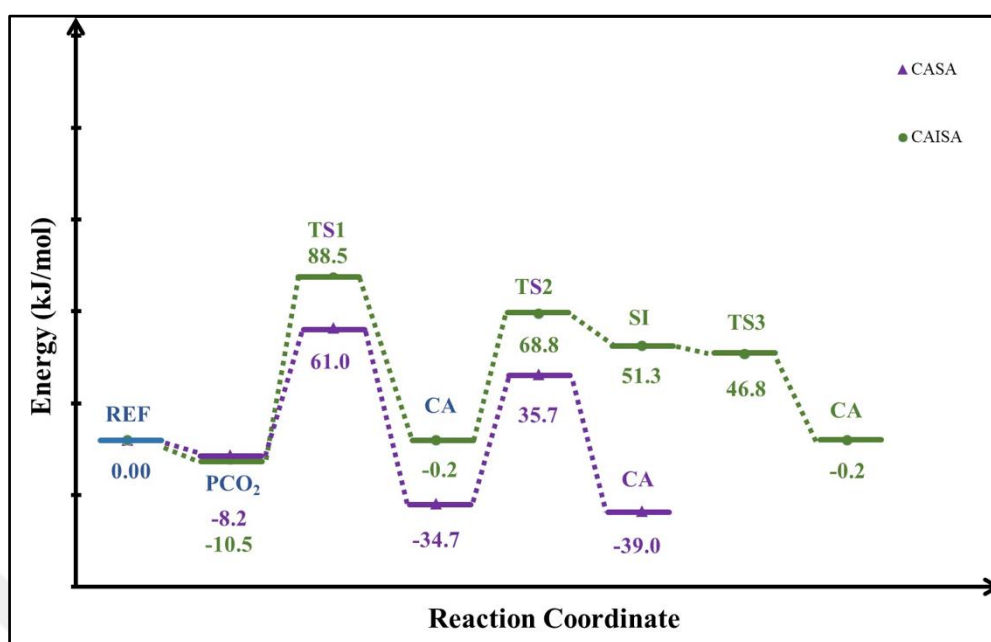


Figure 4.1. Energy diagrams regarding CO₂ Chemisorption over 5_5-single-AEAPS. REF refers Reference point, PCO₂ refers Physisorbed CO₂, TS refers Transition state, SI refers Surface intermediate, CA refers Carbamic Acid

4.1.1. Direct Carbamic Acid Evolution (DCA) Pathway

DCA was one of the pathways that was reported before, over both APTMS (primary) and MAPS (secondary) when the surface interactions of the amine molecules were restricted [117,118,139]. Observation of this pathway here implied that interactions with the surface was somehow restricted indeed, despite of the 5 free surface silanols. According to the pathway identified, physisorbed CO₂ (over one of the amine groups of the AEAPS molecule) was directly converted into a carbamic acid structure via a simultaneous hydrogen transfer from the CO₂-adsorbed amine group to the other one and from this second amino group back to the nearest oxygen of the CO₂ (Figure 4.2). Previous studies demonstrated that various forms of carbamic acid might be detected in the product stream, each differentiating from each other in terms of their stabilities and the hydrogen bonding interactions that they were involved in [6,118]. The carbamic acid obtained here in the DCA pathway was hydrogen bonded to the nearby amine by its -COH group (Figure 4.3(b)) and named as Type I Carbamic Acid in accordance with the previously reported structure [118]. The required activation barrier was calculated as 113.7 kJ/mol, while the relative energy of the product

was +2.3 kJ/mol in comparison to the reference point. Diagrammatic representation of the DCA pathway is given in Figure 4.2.

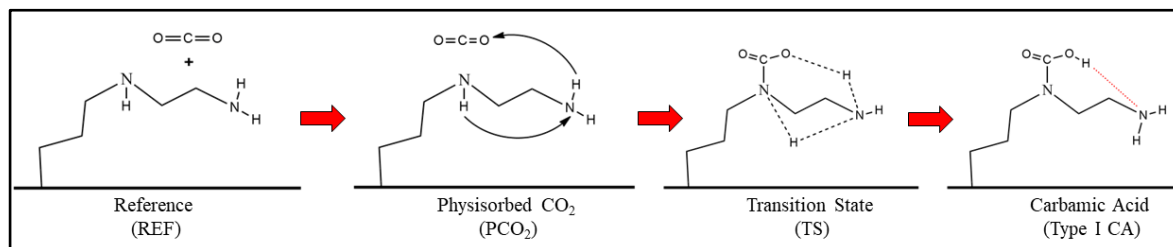


Figure 4.2. Diagrammatic representation of the DCA pathway over 5_5-single-AEAPS

DCA route was identified over both the primary and secondary amino groups of the AEAPS models resulting in comparable product stabilities and reaction barriers. This observation indicated that hydrogen bonding interactions rather than the amine functionality were more deterministic on the adsorption energetics, as reported for APTMS (primary) and MAPS (secondary) before [118]. Figure 4.3 shows the molecular models of the carbamic acid structures being formed over the primary and secondary amines of the AEAPS molecule.

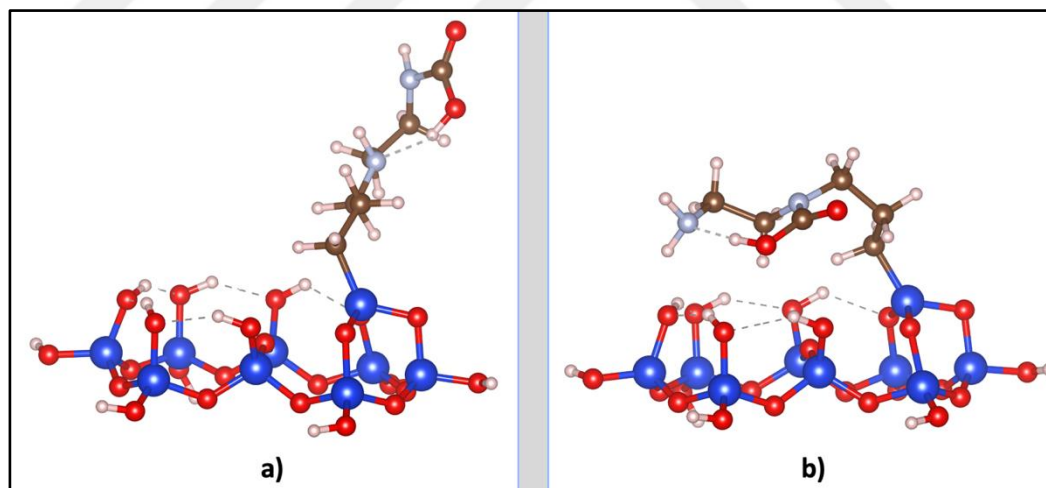


Figure 4.3. Molecular models of the carbamic acid observed along the DCA pathway over (a) primary, (b) secondary amino groups. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.1.2. Isolated Carbamic Acid Evolution (ICA) Pathway

Previous studies reported that formation of a carbamic acid over a single amine group without the requirement of an adjacent amine was possible [118,138,139]. A similar pathway which involved the transfer of a proton from the CO₂-adsorbed amine to the oxygen of the CO₂ was observed over 5_5-single_AEAPS as well and was named as the ICA pathway (Figure 4.4). The end product (carbamic acid) was hydrogen bonded to the surface silanol via its -COH group (Figure 4.5) and was denoted as type IV carbamic acid in accordance with the previous naming [118]. It was 35.0 kJ/mol less stable compared to the reference point due to the limited interactions with the surface and the adjacent amine. Activation energy was calculated as 164.7 kJ/mol that was much higher than the barrier calculated for the DCA route. This was indeed in excellent compliance with the previously published observations that formation of a carbamic acid without the involvement of an adjacent amine was extremely slow [118,139].

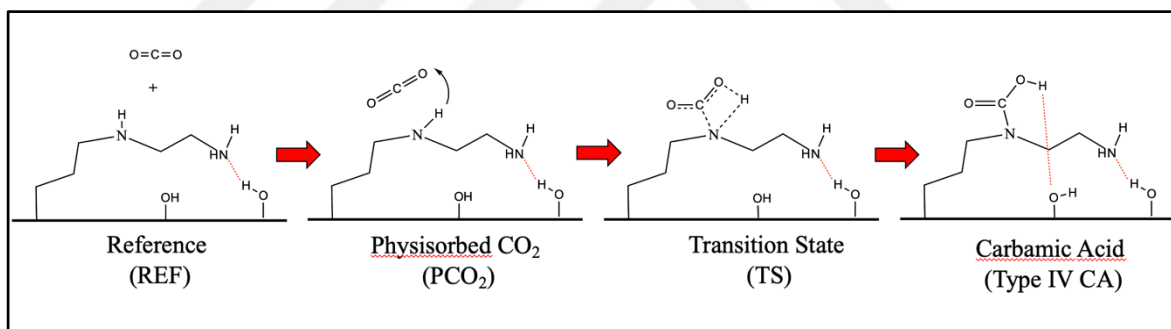


Figure 4.4. Diagrammatic representation of the ICA pathway over 5_5-single-AEAPS

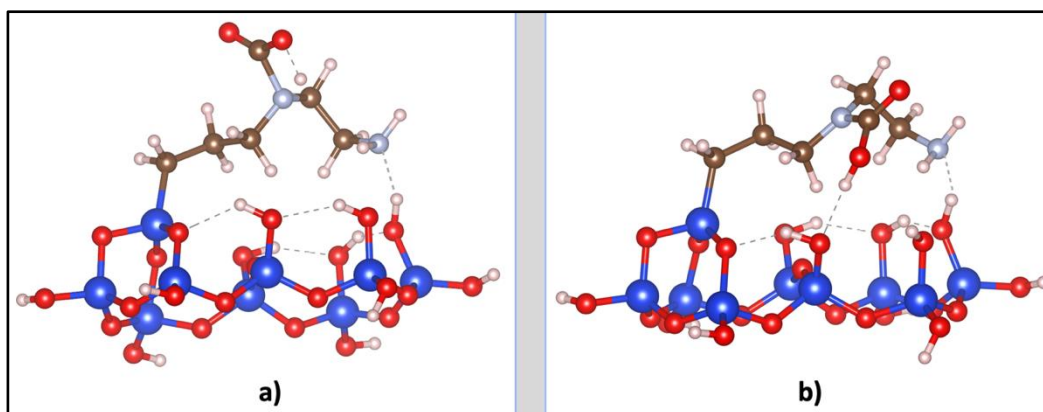


Figure 4.5. Molecular models of the (a) transition state, and (b) carbamic acid observed along the ICA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.1.3. Zwitterion to Carbamic Acid Evolution (ZCA) Pathway

Different from the DCA pathway, carbamic acid formation occurred in 2 steps in the ZCA path, i.e., physisorbed CO_2 was transformed into a zwitterionic intermediate first which was pursued by the simultaneous transfer of a hydrogen from the zwitterionic amine to the adjacent one and from this amine to the oxygen of the CO_2 (Figure 4.6). This pathway was observed over both primary and secondary amines of the AEAPS molecule, activation barriers and product stabilities of both cases being comparable. The carbamic acid obtained in the pathway (Figure 4.7) was hydrogen bonded to both the surface and the adjacent amine; and was denoted as being of type II. However, despite of the enhanced surface interactions of the end product, it was 0.4 kJ/mol less stable relative to the reference point. Observation of the zwitterionic intermediate was reported for APTMS (primary) and MAPS (secondary) before, only when the surface interactions were pronounced indeed [118]. Accordingly, due to the high number (5) of free silanols available at the surface and interaction of these silanols with the zwitterionic intermediate, formation of this structure was possible here but the obtained carbamic acid was considerably less stable compared to the type II carbamic acid structures reported for APTMS and MAPS before [118]. Activation barriers required for the formation of the intermediate and the product were determined as 16.1 kJ/mol and 50.7 kJ/mol, respectively. These values were reported as 8.9 kJ/mol and 36.3 kJ/mol for 5_4_5-APTMS (4 free silanols) and 7.1 kJ/mol and 41.0 kJ/mol for 5_4_5-MAPS (4 free silanols) showing that the barriers calculated for AEAPS were close to the formerly reported ones [118].

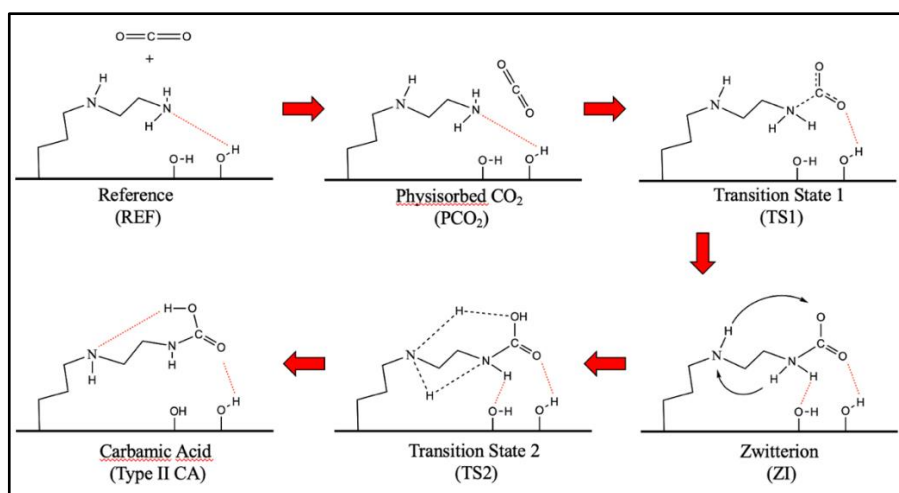


Figure 4.6. Diagrammatic representation of the ZCA pathway over 5_5-single-AEAPS

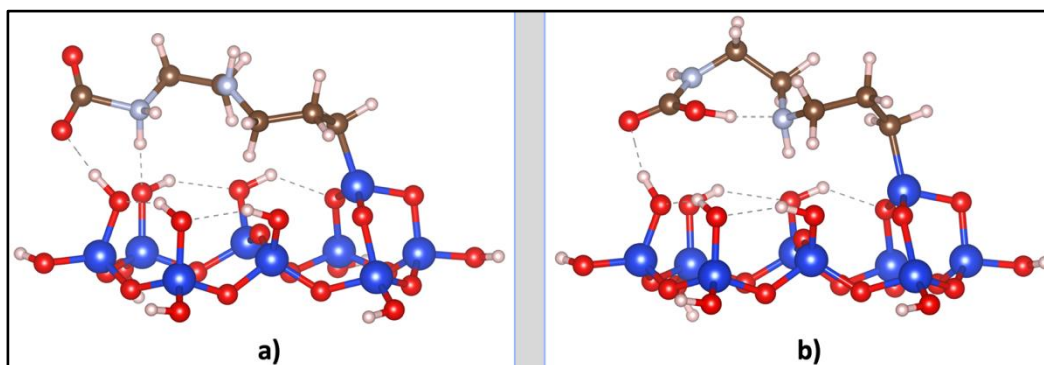


Figure 4.7. Molecular models of the (a) zwitterionic intermediate, (b) carbamic acid observed along the ZCA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.1.4. Surface-Assisted Carbamic Acid Evolution (SCA) Pathway

In the SCA pathway, physically adsorbed CO_2 (over the secondary amine) was converted directly into a carbamic acid where surface silanols took an active role in the proton migration. According to the observed pathway, a simultaneous proton transfer took place from the CO_2 -adsorbed amine to the nearest silanol, from this silanol to the adjacent amine and from this amine back to the oxygen of the CO_2 with a reaction barrier of 80.6 kJ/mol. The diagrammatic drawing of this pathway is given in Figure 4.8. The resulting product (type I carbamic acid) was hydrogen bonded to the adjacent amine via its $-\text{COH}$ group (Figure 4.9 (a)) and was 36.1 kJ/mol less stable in comparison to the reference point due to its limited interactions.

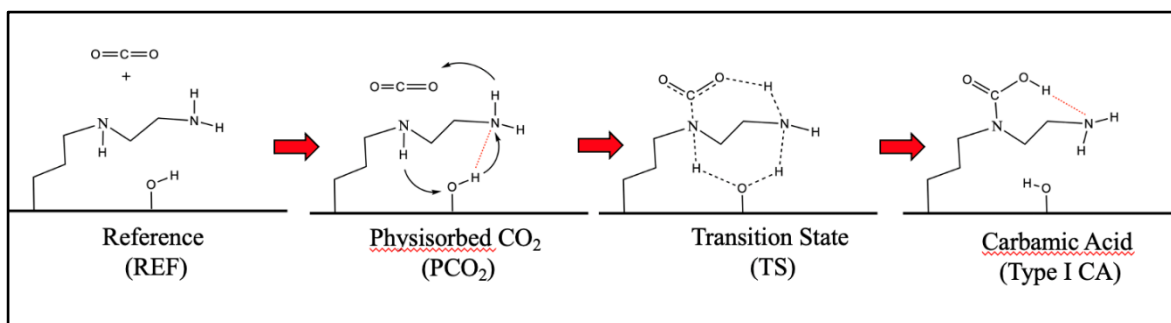


Figure 4.8. Diagrammatic representation of the SCA pathway over 5_5-single-AEAPS

When the activation barriers calculated for the DCA (113.7 kJ/mol) and SCA (80.6 kJ/mol) pathways were compared, it was realized that involvement of the surface OH groups in the proton migration did not increase the carbamic acid formation barrier as it was the case for APTMS but rather decreased. It was previously shown that the activation energy calculated for the proton transfer via the surface silanol (69.7 kJ/mol) was much higher than the one (36.3 kJ/mol) calculated for the protonation via the adjacent amine [118].

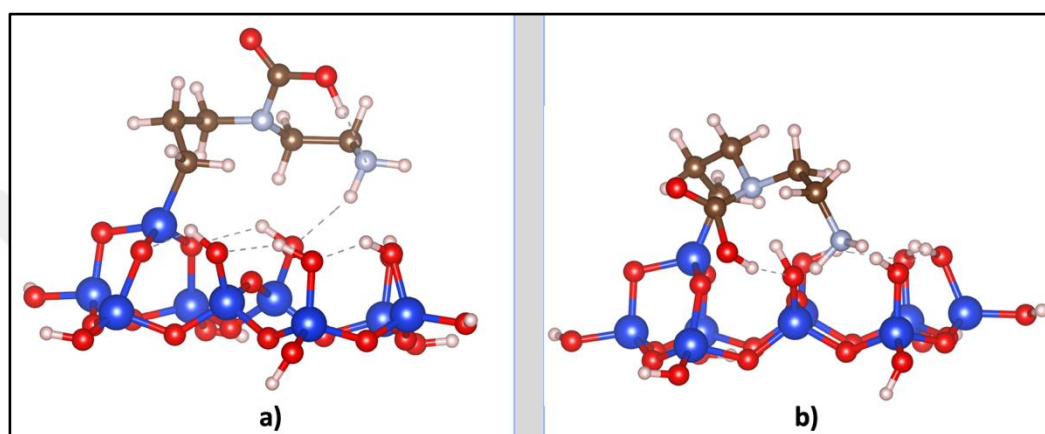


Figure 4.9. Molecular models of the carbamic acid observed along the (a) SCA, and (b) SCA* pathways. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

Another version of the SCA pathway that proceeded without the involvement of the adjacent amine was observable (SCA*) over both the primary and the secondary amine groups of the AEAPS molecule. In this version of the pathway, formation of the carbamic acid occurred via a simultaneous proton transfer from the CO₂-adsorbed amine to the nearest silanol and from this silanol directly back to the oxygen of the CO₂ (Figure 4.10). The estimated barrier for the secondary amine was comparable (88.9 kJ/mol) to that of the previous version of the pathway and the end product (carbamic acid) was of type IV (Figure 4.9 (b)), being 48.6 kJ/mol less stable relative to the reference point. In case of the primary amine group, however, the reaction was significantly slower (Activation Energy = 176.1 kJ/mol), the end product (type IV) possessing a relative energy of +36.8 kJ/mol in comparison to the reference point. Previous studies demonstrated that the functionality of the amine group (whether it is primary or secondary) was less deterministic on the product stability and activation barriers compared to the hydrogen bonding interactions involved [118]. Although the reaction species observed over primary and secondary amines had similar hydrogen bonding

interactions with the surface here, activation barriers differed significantly, the origin of which is not clear at this point.

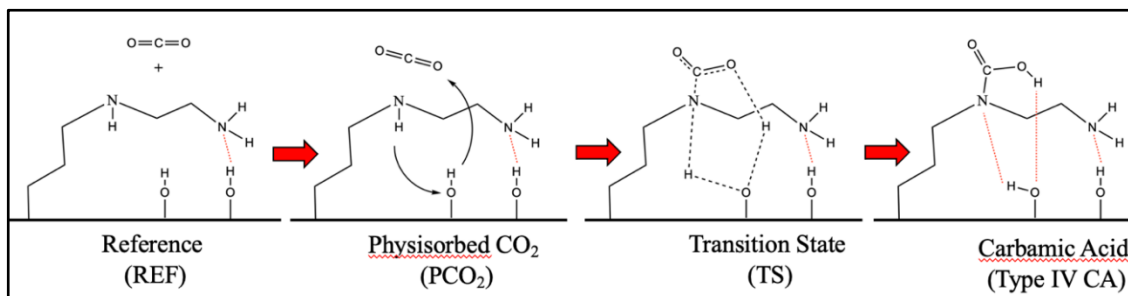


Figure 4.10. Diagrammatic representation of the SCA* pathway over 5_5-single-AEAPS

4.1.5. Surface-Assisted Carbamic Acid Evolution via an Intermediate (SICA*) Pathway

SICA* pathway was identified over the primary amine group of the model and was indeed similar to the SCA* pathway except for the formation of a surface intermediate. According to the observed path (Figure 4.11), physically bonded CO₂ removed a proton from a nearby surface silanol and this proton deficient silanol acquired another proton from the silanol next to it forming a complex made of -NH₂COOH and -SiO⁻ (surface intermediate) in the first step. Following this, a hydrogen atom was transferred from the CO₂-bonded amine to the surface siloxide (-SiO⁻) producing a carbamic acid that was hydrogen bonded to the surface via its -COH group. Being a type IV carbamic acid, this structure was calculated to be 32.5 kJ/mol less stable compared to the reference point. Activation energies, on the other hand, were estimated to be 107.1 kJ/mol and 0.3 kJ/mol, respectively for the first and second steps demonstrating that the reaction barriers were lower (compared to 176.1 kJ/mol of the SCA*) in the presence of a surface intermediate. Molecular models of the surface intermediate and the carbamic acid observed along the SICA* path are given in Figure 4.12.

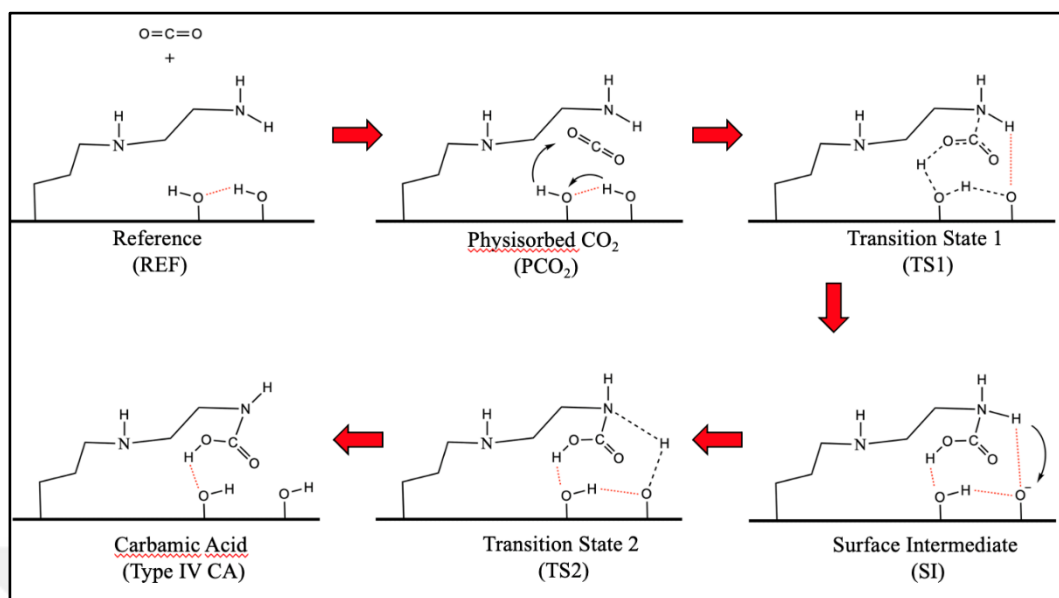


Figure 4.11. Diagrammatic representation of the SICA* pathway over 5_5-single-AEAPS

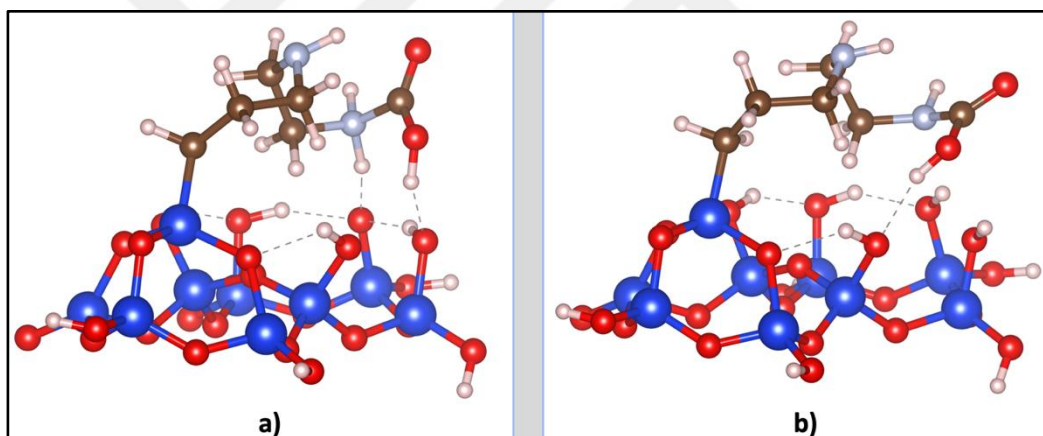


Figure 4.12. Molecular models of the (a) surface intermediate, and (b) carbamic acid observed along the SICA* pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.1.6. Surface-Assisted Carbamic Acid to Carbamic Acid Evolution (CASA) Pathway

CASA pathway was identified over the secondary amine of the AEAPS structure and involved the formation of a carbamic acid in the first step directly from the physisorbed CO₂, as it was the case in the DCA pathway. This step required an activation barrier of 69.1 kJ/mol that was much smaller than the value estimated for the DCA pathway (113.7 kJ/mol). This was probably due to the increased hydrogen bonding interactions of the transition state

structure obtained in this route. The resulting product (type I carbamic acid) was hydrogen bonded to the adjacent amine via its -COH group and was 34.7 kJ/mol more stable in comparison to the reference point. The extreme stability of this type I carbamic acid structure seemed to be originating from the additional interactions of its =CO group with the surface silanols due to its proximity to the surface. Following this, a simultaneous proton transfer from the -COH of the obtained carbamic acid back to the adjacent amine, from this amine to the nearest surface silanol, from this silanol to another silanol and from the second silanol back to the hydrogen deficient carbamic acid took place leading to the formation of a second carbamic acid that was hydrogen bonded to the surface via its -COH group (type IV). Similar to the first structure, the =CO group was located close to the surface making the obtained product quite stable (39.0 kJ/mol more stable than the reference point). The activation barrier calculated for this step was 70.4 kJ/mol. The diagrammatic drawing of the CASA pathway is given in Figure 4.13, whereas the molecular models of the two carbamic acids obtained are presented in Figure 4.14.

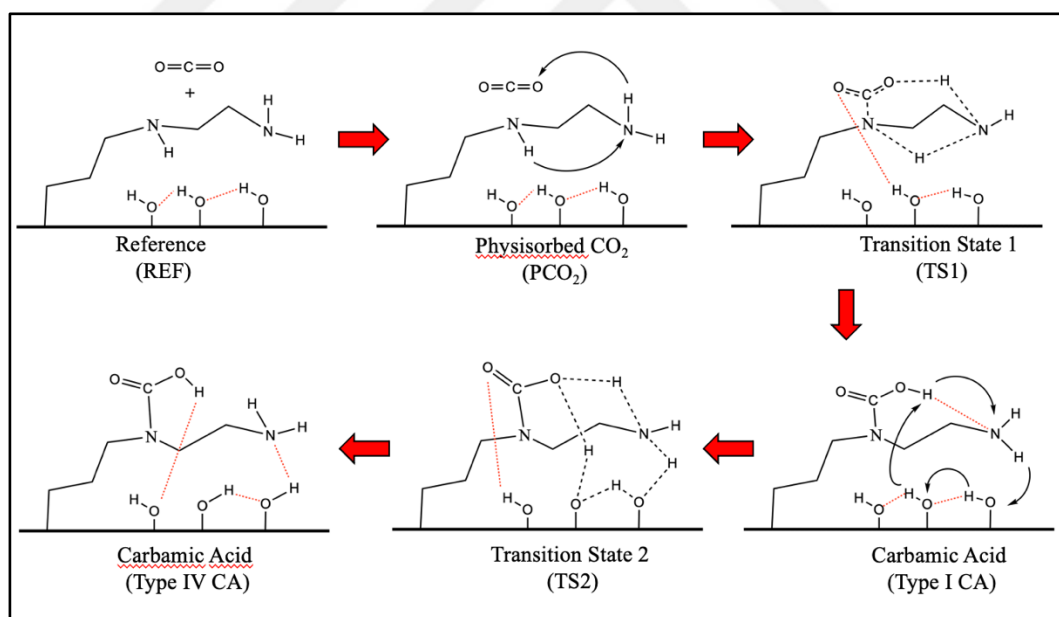


Figure 4.13. Diagrammatic representation of the CASA pathway over 5_5-single-AEAPS

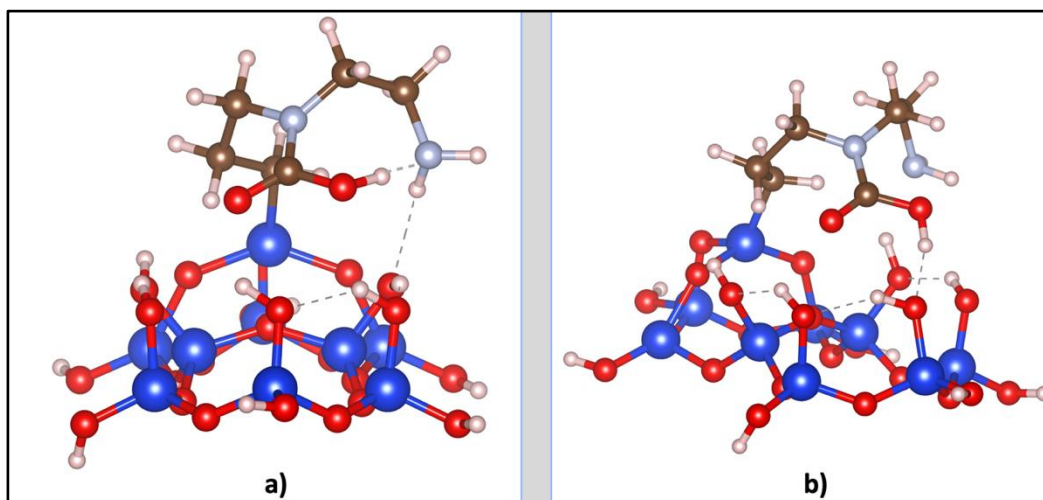


Figure 4.14. Molecular models of the (a) first (type I), and (b) second (type IV) carbamic acids observed along the SICA* pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.1.7. Carbamic Acid to Surface-assisted Carbamic Acid Evolution via an Intermediate (CAISA) Pathway

CAISA pathway (Figure 4.15) was identified over the secondary amine group of the AEAPS and was almost identical to the CASA pathway except for the formation of a surface intermediate. According to the calculated pathway, direct carbamic acid formation from the physisorbed CO_2 took place in the first step, which was followed by the production of a reaction intermediate (a complex made of $-\text{NCOOH}$, $-\text{NH}_3^+$, and $-\text{SiO}^-$) via a proton transfer from the $-\text{COH}$ of the carbamic acid back to the adjacent amine and from a nearby silanol to the hydrogen deficient carbamic acid. Finally in the third step, this surface siloxide (SiO^-) acquired a proton spontaneously from the $-\text{NH}_3^+$ group leading to the formation of another carbamic acid. The activation barrier calculated for the first step (99.0 kJ/mol) was close to that of the DCA pathway (113.7 kJ/mol) but much higher than the one obtained in the first step of the CASA pathway (69.1 kJ/mol) discussed above, probably due to the decreased interactions of the transition state with the surface and the adjacent amine. The second barrier (69.0 kJ/mol) was, on the other hand, was comparable to that of the formation of the second carbamic acid in the CASA pathway (70.4 kJ/mol) despite of the formation of the surface intermediate. Both carbamic acid structures (Figure 4.16) were of type I (hydrogen bonded to the adjacent amine via its $-\text{COH}$) and were 0.2 kJ/mol more stable in comparison to the

reference point. Nevertheless, formation of a carbamic acid via this pathway seemed to be unlikely since the physisorbed CO_2 was thermodynamically more stable (-10.5 kJ/mol relative energy in comparison to the reference).

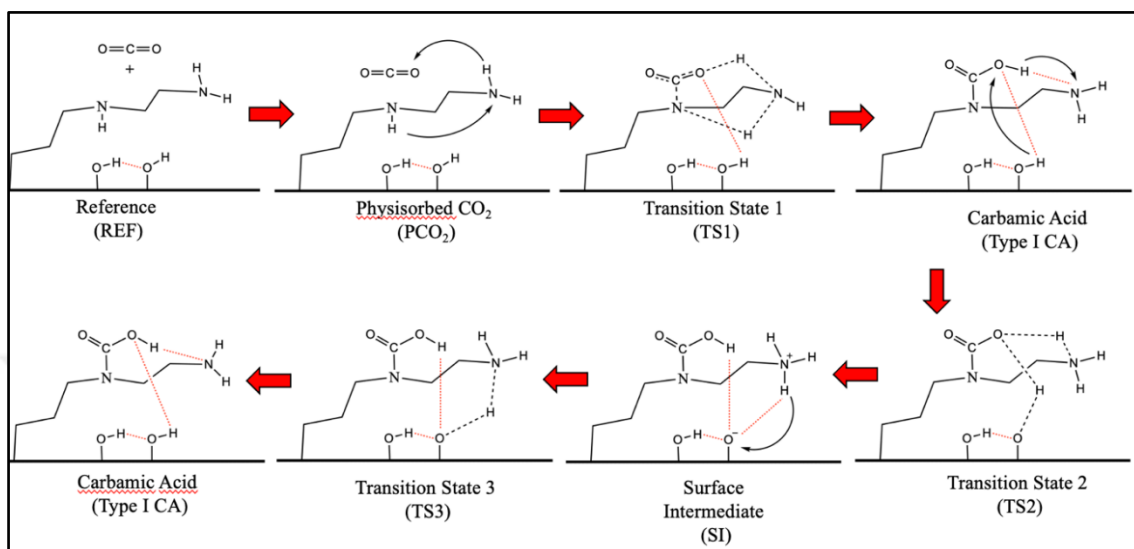


Figure 4.15. Diagrammatic representation of the CAISA pathway over 5_5-single-AEAPS

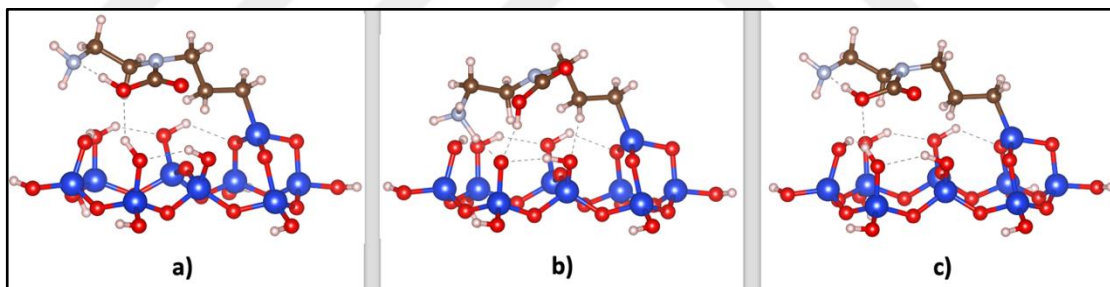


Figure 4.16. Molecular models of the (a) first carbamic acid (type I), (b) surface intermediate, and (c) second carbamic acid (type I) observed along the CAISA pathway.

Colors represent: red = oxygen, blue = silicon, pink = hydrogen

Another version of this pathway (CAISA+) was observed over the secondary amino group of the molecule in which the formation of the first carbamic acid took place via the involvement of the surface (via the SCA path rather than the DCA pathway). The estimated barrier (124.2 kJ/mol) was much higher compared to both the values obtained in the first version of the CAISA (99.0 kJ/mol) and the SCA pathway (80.6 kJ/mol). Next, a surface intermediate complex that was made of $-\text{NCOOH}$, $-\text{NH}_3^+$, and $-\text{SiO}^-$ was produced with an activation barrier of 46.0 kJ/mol, which was followed by the spontaneous back protonation of the surface siloxide ($-\text{SiO}^-$) by the $-\text{NH}_3^+$ group. The activation energy calculated for the

second step was slightly lower than that of the second step of the first version (69.0 kJ/mol). The first carbamic acid (type II) was bonded to the adjacent amine via its -COH group and to the surface silanol via the =CO group, while the second one (type IV) was hydrogen bonded to only the surface silanol via its -COH. Estimated relative energies for those two structures in comparison to the reference point were +13.6 kJ/mol and +16.1 kJ/mol, respectively for the first and second carbamic acid. The diagrammatic drawing of this version of the CAISA pathway is given in Figure 4.17 and the molecular models of the carbamic acids and the surface intermediate are displayed in Figure 4.18.

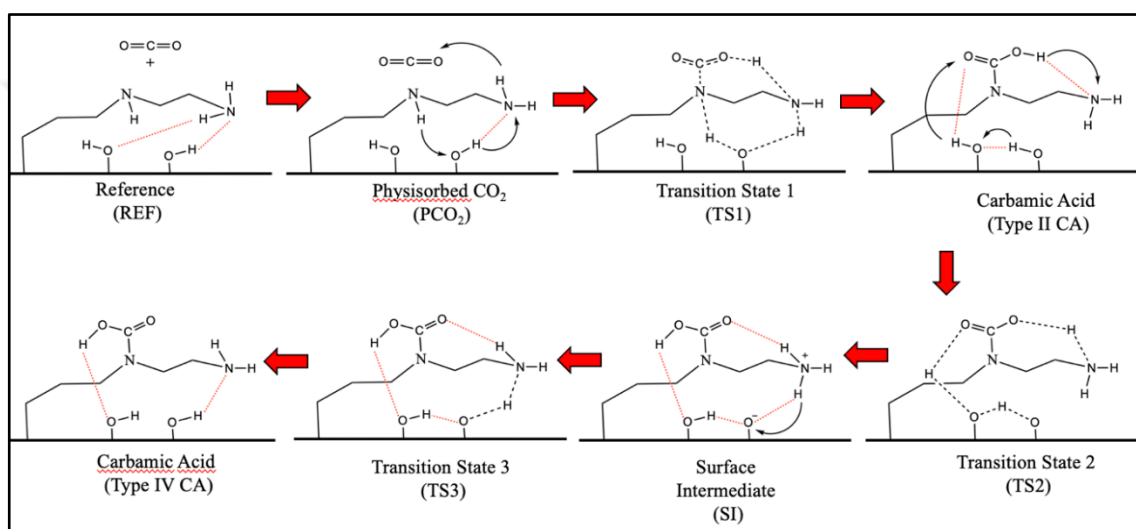


Figure 4.17. Diagrammatic representation of the of the CAISA+ pathway over 5_5-single-AEAPS

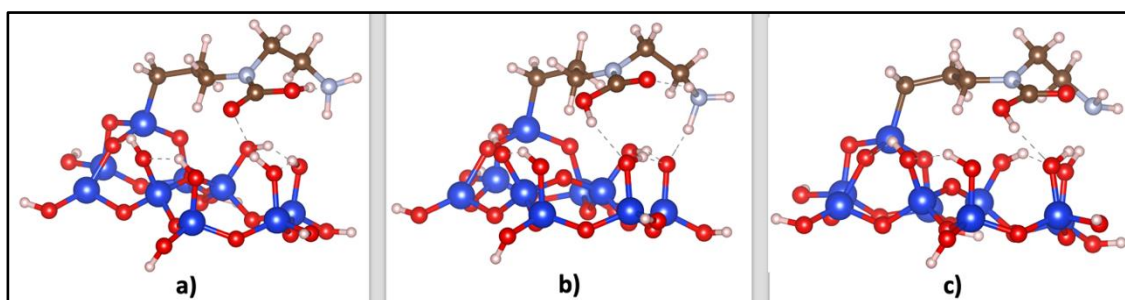


Figure 4.18. Molecular models of the (a) first carbamic acid (type II), (b) surface intermediate, and (c) second carbamic acid (type IV) observed along the CAISA+ pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.1.8. Surface-Assisted Carbamate to Carbamic Acid Evolution via Zwitterion (ZSCBA) Pathway

In the ZSCBA pathway (Figure 4.19) that was identified over the secondary amine, physisorbed CO₂ was converted into a zwitterionic intermediate (with a +15.1 kJ/mol relative energy in comparison to the reference) which was then transformed into an ammonium carbamate via a simultaneous proton transfer from the zwitterionic amine to a nearby silanol and from this silanol to the adjacent amine. The activation barriers calculated for the first and second steps were 29.4 kJ/mol and 45.9 kJ/mol, respectively. The first barrier associated with the zwitterion formation was slightly higher than the values calculated for 5_4_5-MAPS (secondary) in various pathways (20.5 kJ/mol and 11.5 kJ/mol) [118]. The second one, on the other hand, was close to the value calculated for the conversion of the zwitterionic intermediate into a carbamic acid structure in the ZCA path (50.6 kJ/mol) discussed above despite of the involvement of the surface. Obtained carbamate was thermodynamically unstable possessing a relative energy of 45.8 kJ/mol in comparison to the reference and was further back protonated in the third step via a hydrogen transfer from the ammonium to a nearby silanol, from this silanol to another silanol, and from the second silanol to the oxygen of the carbamate. This final step required a barrier of 29.4 kJ/mol that was much lower than that of the previous step. The resulting carbamic acid was hydrogen bonded to the surface silanols via its -COH and =CO groups and was denoted as type VI carbamic acid. Despite of the two hydrogen bonding interactions of the end product, it was 49.1 kJ/mol less stable in comparison to the reference point. Molecular models of the zwitterionic intermediate, ammonium carbamate and carbamic acid are given in Figure 4.20.

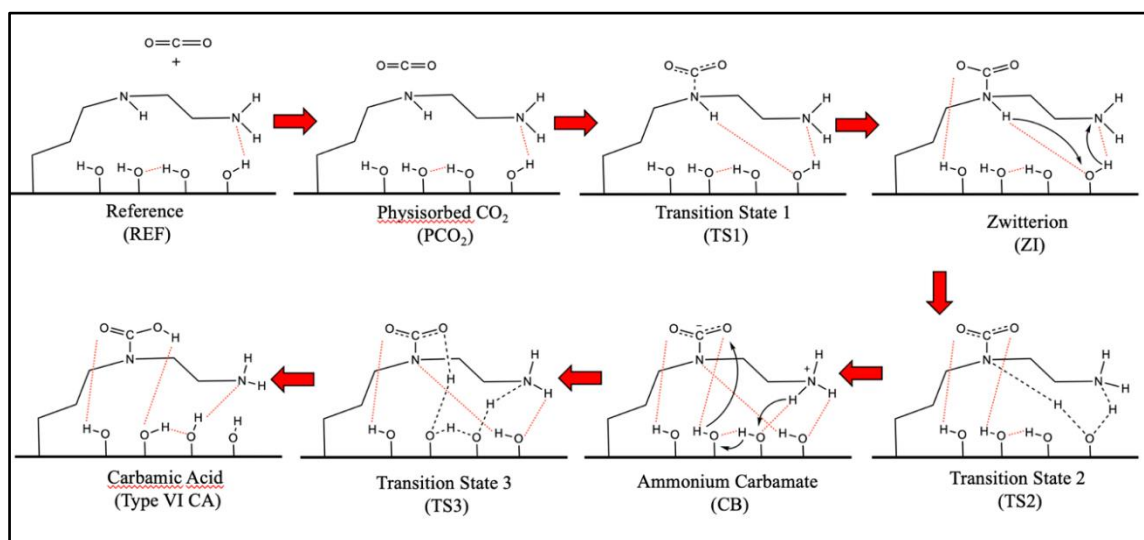


Figure 4.19. Diagrammatic representation of the ZSCBA pathway over 5_5-single-AEAPS

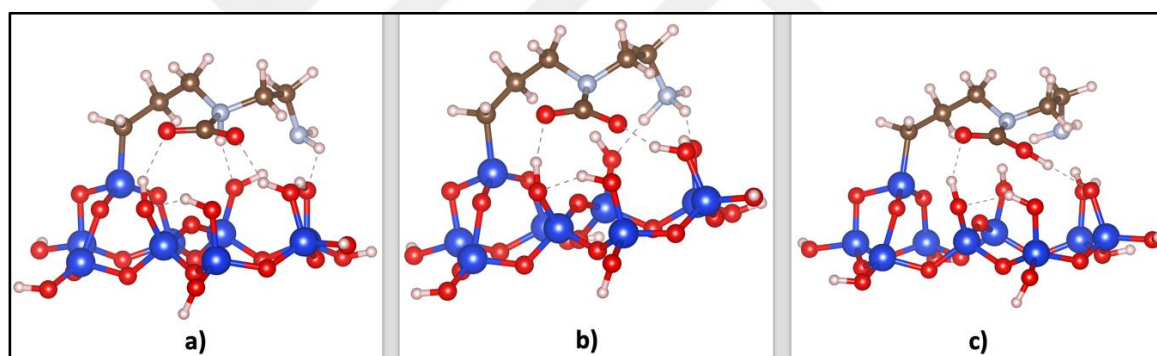


Figure 4.20. Molecular models of the (a) zwitterion, (b) ammonium carbamate, and (c) carbamic acid (type VI) observed along the ZSCBA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

Our calculations performed over 5_5-single-AEAPS demonstrated that intramolecular adsorption of CO₂ was possible and carbamic acid was the main product. Formation of the carbamic acid seemed to take place via the CASA pathway under the conditions studied, where the conversion of one carbamic acid (type I) to another (type IV) was achieved via the surface silanols. Although the CASA route was identified over secondary amines only, both the primary and the secondary amino groups were observed to be active in the adsorption of CO₂ as suggested by the previous experiments, as long as the products could be stabilized via strong hydrogen bonding interactions [14,111]. Previous studies implemented over APTMS and MAPS indeed underlined the critical role of surface and

neighbor interactions on the reaction kinetics and thermodynamics, more interactions meaning more stable products and lower activation barriers [118]. The number of free silanols remaining at the surface after grafting was 5 in case of 5_5-single-AEAPS and strong amine-amine and amine-surface interplays were expected. However, reaction pathways involving strong hydrogen bonding interactions were rare here, illustrating that the required interactions were somehow limited compared to the cases of APTMS and MAPS [118]. This could indeed originate from the short alkyl chain length between the primary and secondary amine groups of the AEAPS molecule restricting the amine-amine interactions as suggested previously by Yoo et.al. or the increased steric hindrance around the amino groups of the AEAPS molecule [140].

4.2. ANALYSIS OF ADSORPTION MECHANISM OVER 5_5-DOUBLE-AEAPS

When two AEAPS molecules are grafted onto the mesoporous silica (5_5) surface, there were 2 free silanols remaining at the surface. In this sense, these models were similar to the previously-studied 5_5-APTMS (primary) and 5_5-MAPS (secondary) models [118]. The total number of amino groups was, on the other hand, 4 indicating that the adsorption of a second CO₂ molecule was also possible since most of the former studies demonstrated that the CO₂/N ratio was 0.5 [118,138]. Accordingly, different from the previous section, adsorption of both 1 and 2 CO₂ molecules was investigated over 5_5-double-AEAPS models and the corresponding findings will be discussed in two different subsections.

4.2.1. Analysis of Adsorption Mechanism of The First CO₂ over 5_5-Double-Aeaps

Several different conformers were considered for the study of the first CO₂ adsorption and 9 different pathways were identified, namely direct carbamic acid evolution (DCA), isolated carbamic acid evolution (ICA), zwitterion to carbamic acid evolution (ZCA), surface-assisted carbamic acid evolution (SCA), carbamate to carbamic acid evolution (CBA), zwitterion to carbamate evolution (ZCB), multi-step carbamate to carbamic acid evolution (MCBA), multi-step carbamate to carbamic acid evolution via a zwitterion (MZCBA) and multi-step surface-assisted carbamate to carbamic acid evolution (MSCBA) pathways. All

the pathways except for the multi-step ones have been identified over APTMS (primary), MAPS (secondary) or 5_5-single-AEAPS before [118].

Of these 9 pathways observed in this part, only 5 of them resulted in thermodynamically stable products and of these 5 pathways, one of them was unlikely to occur (MZCBA). Accordingly, Figure 4.21 presents the reaction energetics of the most feasible (thermodynamically) 4 pathways in order keep the diagram as simple as possible. The reference point in the diagrams is denoted as REF and has a free energy that is equal to the total energies (free) of the gaseous CO₂ and the matching 5_5-double-AEAPS cluster.

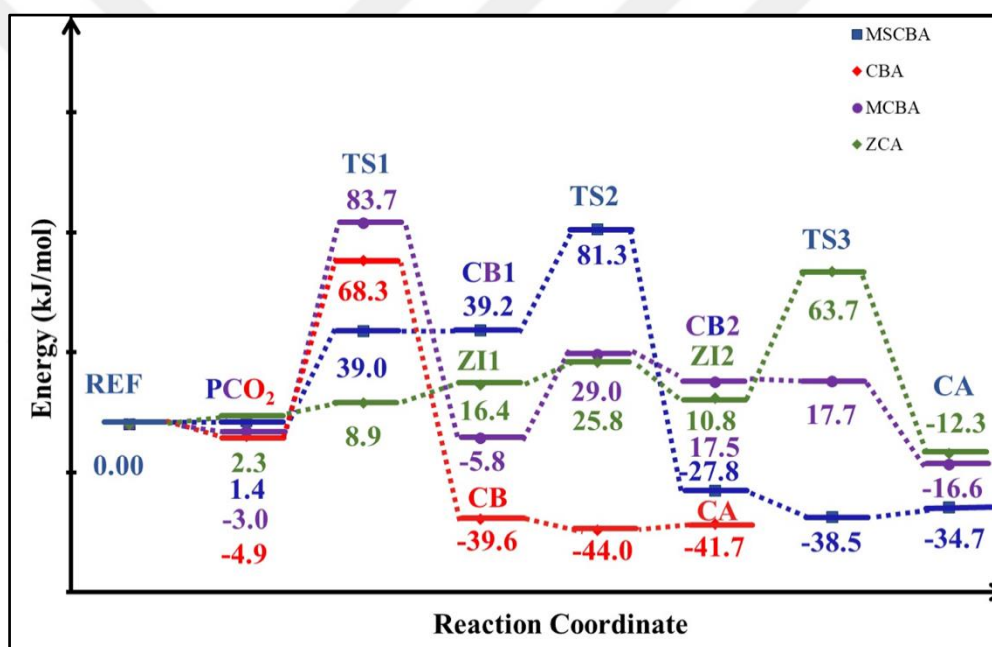


Figure 4.21. Energy diagrams regarding the First CO₂ Chemisorption over 5_5-double-AEAPS. REF refers Reference point, PCO₂ refers Physisorbed CO₂, TS refers Transition state, ZI refers Zwitterionic intermediate, CB refers Ammonium carbamate, CA refers Carbamic acid

4.2.1.1. Direct Carbamic Acid Evolution (DCA) Pathway

Two different versions of the DCA path were identified over 5_5-single-AEAPS models depending on whether the pathway took place intramolecularly (as it was the case in the previous section) or intermolecularly (as it was the case for APTMS and MAPS reported

before [118]). In the intramolecular DCA pathway which can occur in case of low surface amine densities, the simultaneous proton transfer from the CO₂-adsorbed amine to the adjacent amine and from this amine back to the -CO of the CO₂ took place within the same AEAPS molecule (Figure 4.2). This version of the pathway was observed over only secondary amines when two AEAPS molecules were grafted onto the surface, but it was shown in the previous section (single AEAPS) that both amino groups (primary and secondary) were active in the reaction pathway resulting in similar energetics. The activation energy was calculated as 107.7 kJ/mol, while the end product (Type I carbamic acid, Figure 4.22 (a)) possessed a relative energy of +12.7 kJ/mol in comparison to the reference point. Both the reaction barrier and the stability of the carbamic acid were close to the values (activation energy = 113.7 kJ/mol, relative energy = +2.3 kJ/mol in comparison to the reference) obtained in the previous section suggesting that the number of free surface silanols was not so deterministic on the reaction energetics.

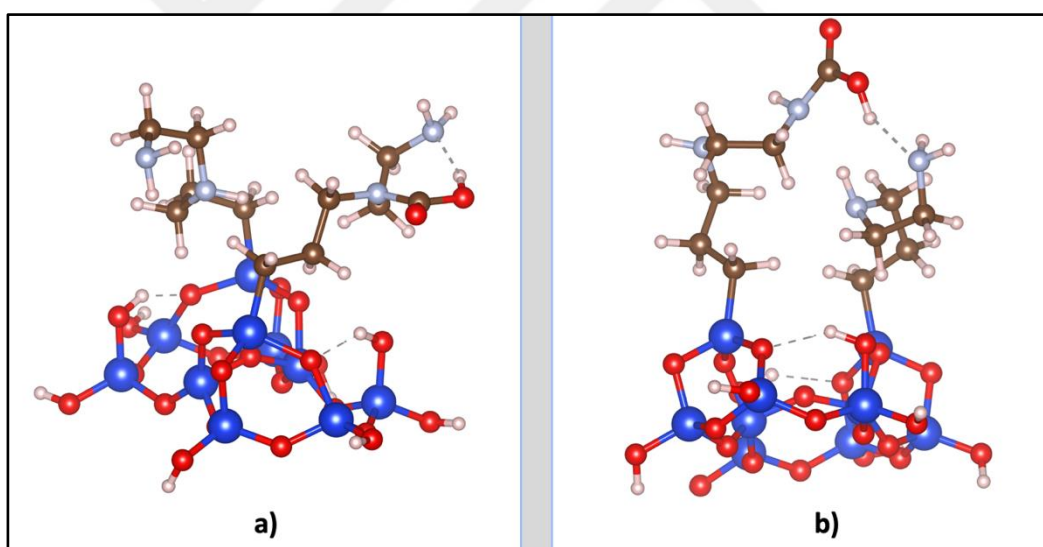


Figure 4.22. Molecular models of the carbamic acids observed along the (a) intramolecular DCA, and (b) intermolecular DCA pathways. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

In the intermolecular version of the pathway (Figure 4.23), the proton transfer needed to form the carbamic acid took place between two amino groups of the two different AEAPS molecules, as it was the case for APTMS (primary) and MAPS (secondary). This pathway was observed over both primary and secondary amine groups, reaction barriers and product stabilities being similar in both cases. According to the identified path, formation of a type I

carbamic acid (Figure 4.22 (b)) required a reaction barrier of 93.1 kJ/mol that was slightly lower than the value (107.7 kJ/mol) of the intramolecular DCA but higher than its counterparts in case of 5_5-APTMS (67.3 kJ/mol) and 5_5-MAPS (79.8 kJ/mol) [118]. Since the pathway seemed to involve no interplay with the surface -OH groups at any point along the pathway, our estimated barrier in terms of electronic energy (19.5 kcal/mol) was compared to the formerly published barriers for SiO₂-eliminated APTMS structures (12.7 kcal/mol and 15.3 kcal/mol (with zero point corrections)) and it was found to be slightly higher than the reported numbers [117,139]. This suggested that additional factors other than the surface interactions like the steric hindrance over the amino groups might also be effective on the reaction energetics.

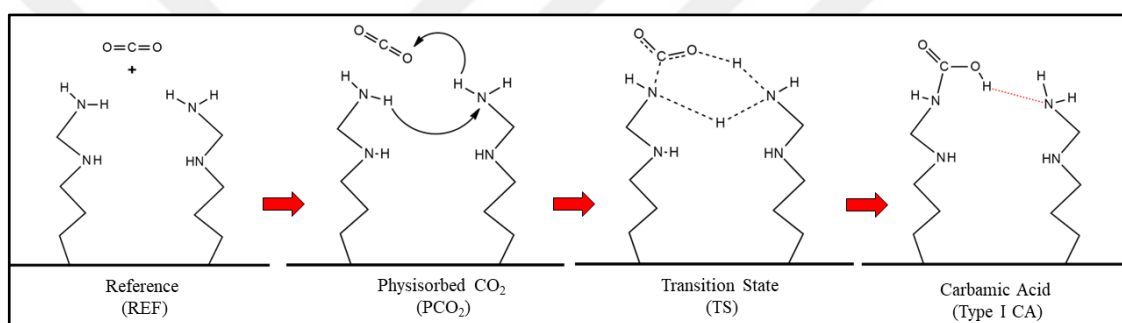


Figure 4.23. Diagrammatic representation of the DCA (intermolecular) pathway over 5_5-double-AEAPS

The product (Figure 4.22 (b)) was, on the other hand, found to be 20.2 kJ/mol less stable in comparison to the reference. Relative product energies of +4 kJ/mol and -35.7 kJ/mol were formerly reported in comparison to the reference for 5_5-APTMS and 5_5-MAPS, respectively; the extreme stability of the latter originating from the proximity of the =CO of the carbamic acid to the surface [118].

4.2.1.2. Isolated Carbamic Evolution (ICA) Pathway

ICA pathway (Figure 4.4), which took place via a direct hydrogen transfer from the CO₂-adsorbed amine to the oxygen of the CO₂ without needing any amine-amine interactions was observed over both primary and secondary amine groups. Obtained carbamic acid was of type I and hydrogen bonded to the adjacent amine in the same AEAPS molecule via its -COH group, being 21.8 kJ/mol less stable in comparison to the reference point. Activation

energy for this step was estimated as 110 kJ/mol. It was lower than the value calculated over 5_5-single-AEAPS (164.7 kJ/mol) and the ones reported for 5_5-APTMS (155.8 kJ/mol) and 5_5-MAPS (168.8 kJ/mol) [118]. Nevertheless, the reaction barrier was still high indicating that the formation of a carbamic in this way was slow.

4.2.1.3. Zwitterion to Carbamic Acid Evolution (ZCA) Pathway

In the ZCA pathway observed over 5_5-double-AEAPS, formation of the carbamic acid took place via a zwitterionic intermediate both intramolecularly and intermolecularly. Although the formation of the zwitterion was discovered to occur in case of increased hydrogen bonding interactions with the surface, the intermediate was still detectable here due to the strong adjacent amine interactions present in the structures. Both versions of the pathway were observed over the primary amino groups of the AEAPS molecules.

According to the intramolecular ZCA pathway, physically adsorbed CO₂ was converted into a zwitterionic intermediate that was 16.4 kJ/mol less stable than the reference point with an activation energy of 6.6 kJ/mol. This was followed by the transformation of this intermediate to a slightly more stable (relative energy being 10.8 kJ/mol in comparison to the reference point) zwitterionic structure with a barrier of 9.3 kJ/mol. Finally in the third step, a simultaneous proton transfer from the zwitterion to the adjacent amine in the same AEAPS molecule and from this adjacent amine to the nearest oxygen of the CO₂ took place giving rise to the formation of a type I carbamic acid with an activation energy of 52.9 kJ/mol. This path was indeed similar to the ZCA pathway discussed above for the 5_5-single-AEAPS (Figure 4.6), except for the transformation of one zwitterion to another. Estimated barriers for the formation of the zwitterion (16.0 kJ/mol) and carbamic acid (50.6 kJ/mol) were comparable but the end product obtained for the 5_5-double-AEAPS was slightly more stable (relative energy of -12.3 kJ/mol in comparison to the reference) due to the proximity of this carbamic acid to the amino groups of the other AEAPS molecule (increased adjacent interactions). Molecular models of the zwitterionic intermediates and the carbamic acid are given in Figure 4.24.

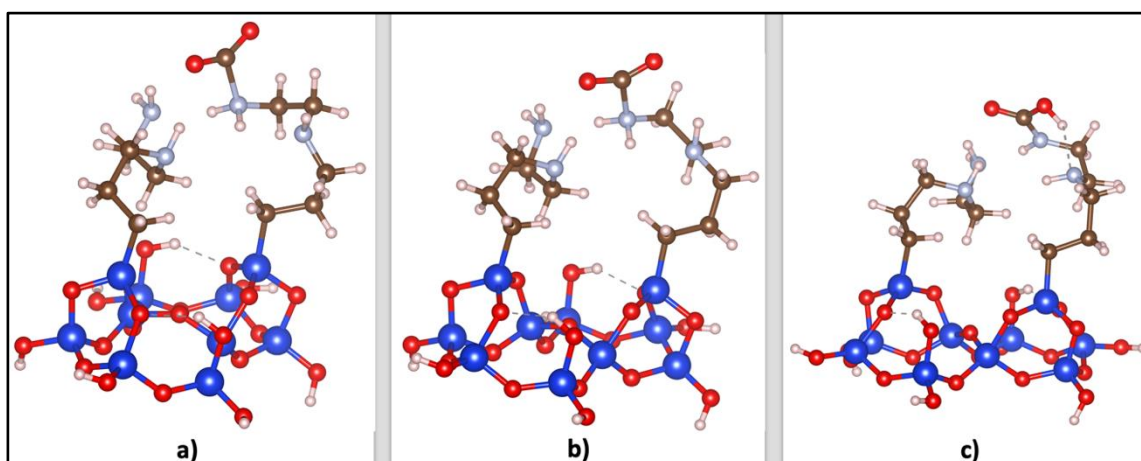


Figure 4.24. Molecular models of the (a) zwitterion 1, (b) zwitterion 2, and (c) carbamic acid (type I) observed along the intramolecular ZCA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

In the intermolecular version of the pathway, the reaction proceeded identically until the formation of the carbamic acid (Figure 4.25) but then the second zwitterionic intermediate was converted into another type I carbamic acid via a simultaneous hydrogen transfer between the zwitterion and an adjacent amine (primary) of the other AEAPS molecule. The resulting product was 1.1 kJ/mol more stable in comparison to the reference and the activation barrier corresponding to this step was 40.1 kJ/mol, being slightly lower than that of the intramolecular path. A complementary pathway without the observation of the second zwitterion was reported for 5_5-APTMS before with similar barriers (8.9 kJ/mol and 36.3 kJ/mol, respectively for the first and second steps) but a more stable end product that was stabilized via hydrogen bonding interactions with the adjacent amine and surface silanol (-27.6 kJ/mol) [118]. The zwitterionic intermediates as well as the end product (type I carbamic acid) can be seen in Figure 4.26.

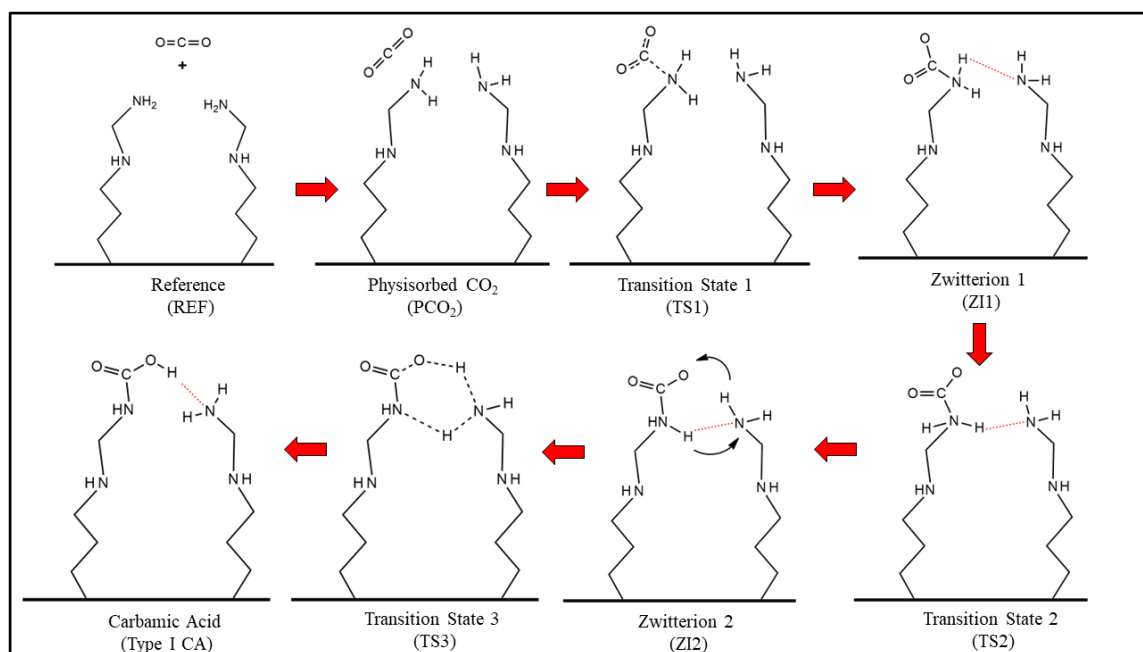


Figure 4.25. Diagrammatic representation of the ZCA (intermolecular) pathway over 5_5-double-AEAPS

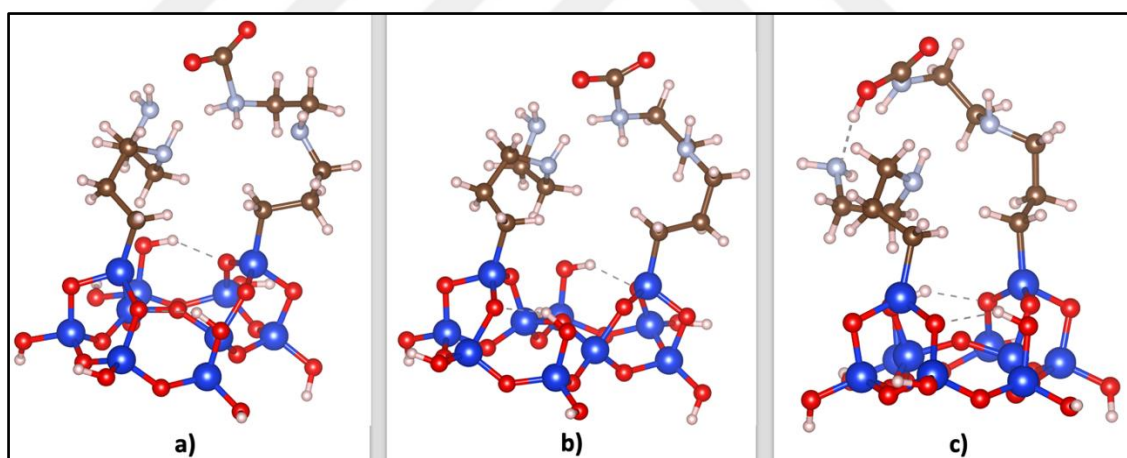


Figure 4.26. Molecular models of the (a) zwitterion 1, (b) zwitterion 2, and (c) carbamic acid (type I) observed along the intermolecular ZCA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.2.1.4. Surface-Assisted Carbamic Acid Evolution (SCA) Pathway

SCA pathway, which took place via a simultaneous hydrogen transfer from the CO₂-adsorbed amine to the surface silanol, from this silanol to the adjacent amine and from the second amine to the nearest oxygen of the CO₂ (Figure 4.8), was observed to take place only

intramolecularly. Due to the longer chain length of the molecule probably, no two amino groups from different AEAPS molecules could approach to each other, being close to the surface at the same time so the reaction could not proceed intermolecularly. CO₂ adsorption was achieved over one of the primary amines involved and obtained carbamic acid was of type I (Figure 4.27) and 37.5 kJ/mol less stable relative to the reference point. Formation of this product required a barrier of 56.6 kJ/mol, which was lower than the value estimated for the 5_5-single-AEAPS (secondary amine, 80.6 kJ/mol).

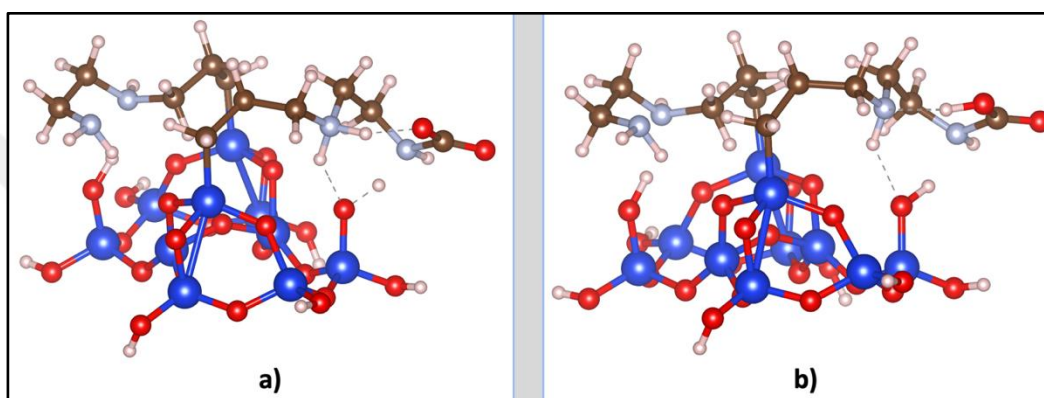


Figure 4.27. Molecular models of the (a) transition state, and (b) carbamic acid (type I) observed along the intramolecular SCA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

This pathway was not reported before for APTMS and MAPS structures, but previous calculations performed over 5_4_5-APTMS and 5_4_5-MAPS demonstrated that it was possible for the surface silanols to take an active role in the proton migration (as it was the case observed here) when there are sufficient surface silanols present at the surface and the amine structures could approach to the surface (in case of lower surface amine densities) [117,118]. However, although the proton migration achieved from the amine to the surface silanol and from this silanol to the adjacent amine was shown to be much slower compared to its counterpart from the CO₂-adsorbed amine directly to the adjacent one in case of APTMS and MAPS, the situation was just the opposite here. Activation energy of the DCA (intra being 107.7 kJ/mol, inter being 93.1 kJ/mol) was much higher than that of the SCA (56.6 kJ/mol), the reason of which is unclear at the moment.

4.2.1.5. Carbamate to Carbamic Acid Evolution (CBA) Pathway

CBA pathway was a two-step, intermolecular reaction pathway that could take place over both primary and secondary amines. According to the observed route, formation of an ammonium carbamate structure was achieved in the first step via a hydrogen transfer from the CO₂-adsorbed amine to a adjacent one present in the other AEAPS molecule (Figure 4.28). This step required a reaction barrier of 73.2 kJ/mol that was close to the values calculated for the carbamate formation observed in the DCB pathway of 5_5-APTMS (68.7 kJ/mol) and 5_5-MAPS (66.4 kJ/mol) as well as the CBA pathway of 5_5-APTMS (74.9 kJ/mol) [118]. Obtained ammonium carbamate was hydrogen bonded to two adjacent amino groups and one surface silanol, being 39.6 kJ/mol more stable relative to the reference point. This structure was in total agreement with the previously proposed ammonium carbamate structure for the species corresponding to the frequently observed ¹³C NMR resonance at ~164 ppm [138]. This carbamate was next back protonated spontaneously by the ammonium forming a carbamic acid that was hydrogen bonded to one of the adjacent amines via its -COH (type I) and was 41.7 kJ/mol more stable in comparison to the reference. The extreme stability of these carbamate and type I carbamic acid structures (Figure 4.29) was probably originating from the much stronger amine-amine interactions noticed here due to the proximity of the four amino groups to one another forming a reactive quaternary-amine-center, underlining the significance of amine-amine interactions.

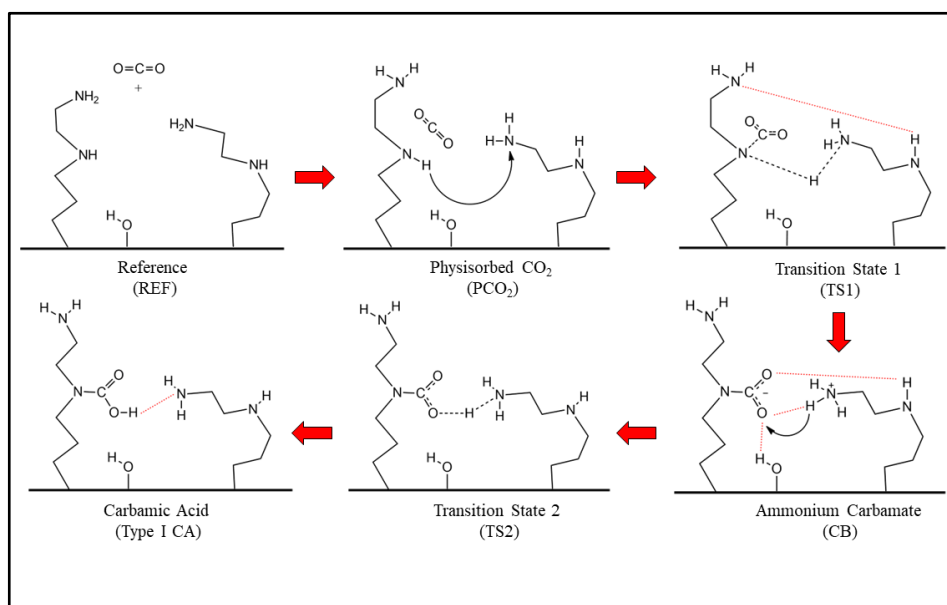


Figure 4.28. Diagrammatic representation of the CBA pathway over 5_5-double-AEAPS

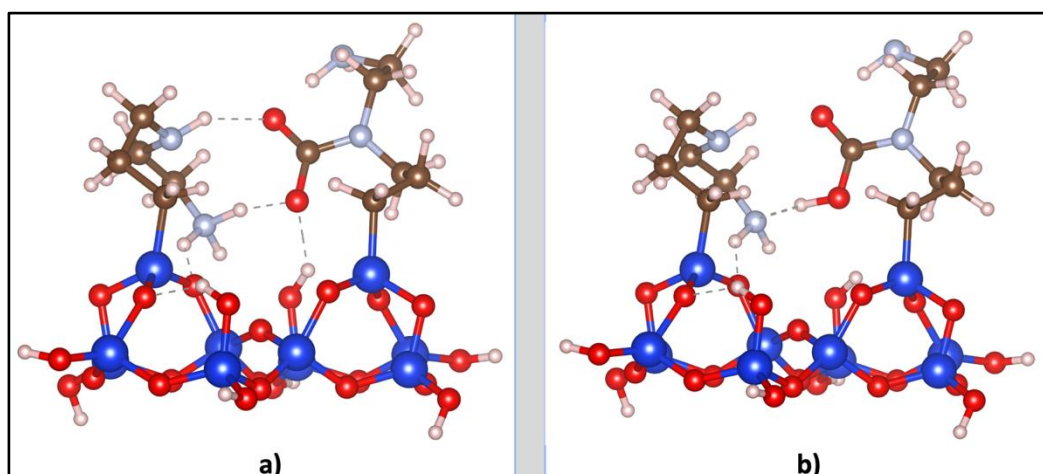


Figure 4.29. Molecular models of the (a) ammonium carbamate, and (b) carbamic acid (type I) observed along the CBA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.2.1.6. Zwitterion to Carbamate Evolution (ZCB) Pathway

According to the ZCB path observed over a primary amine group (Figure 4.30), physisorbed CO_2 was first transformed into a zwitterion that was 12.4 kJ/mol less stable in comparison to the reference with an activation energy of 16.0 kJ/mol. Following this, deprotonation of the zwitterion was achieved with the help of an adjacent amine (primary) of the other AEAPS molecule, resulting in the formation of an ammonium carbamate (Figure 4.31) that had no hydrogen bonding interactions and was 34.4 kJ/mol less stable than the reference point. The second step required a barrier of 16.9 kJ/mol which was comparable to the values estimated for the conversion of the zwitterion into an ammonium carbamate species in case of 5_4_5-APTMS (12.3 kJ/mol) and 5_4_5-MAPS (19.0 kJ/mol) [147]. Identification of the zwitterion, on the other hand, seemed to enhance the rate of carbamate formation when the barrier estimated for the direct carbamate formation observed in the CBA pathway (73.2 kJ/mol) was considered.

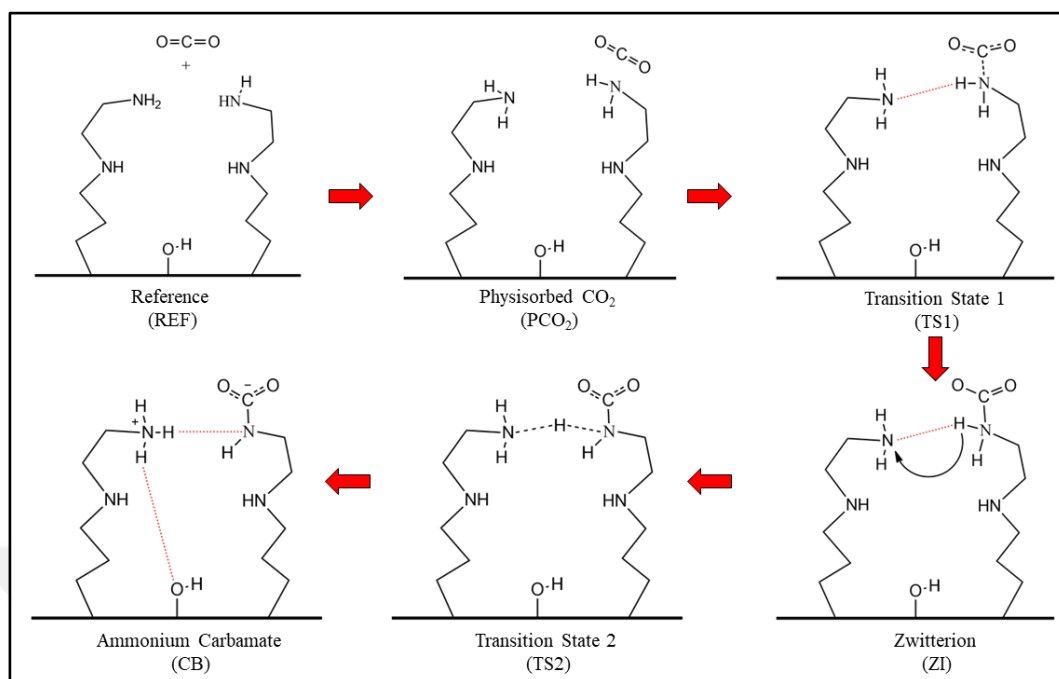


Figure 4.30. Diagrammatic representation of the ZCB pathway over 5_5-double-AEAPS

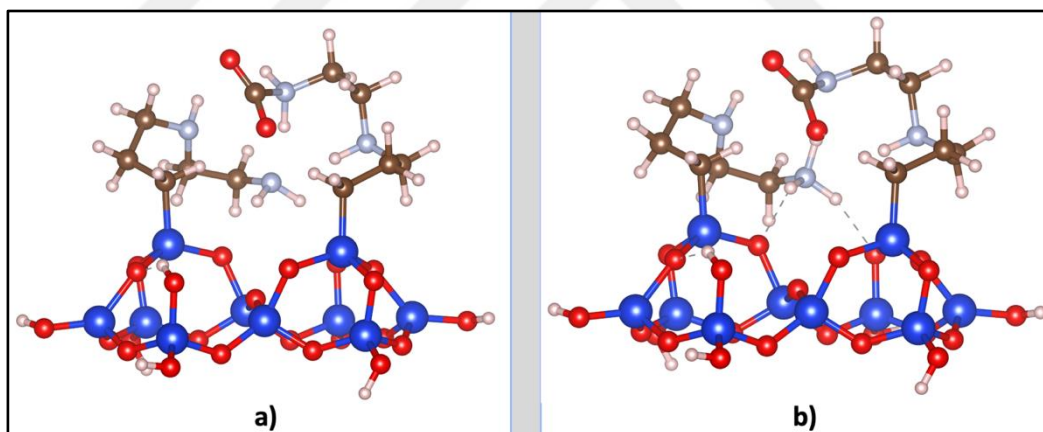


Figure 4.31. Molecular models of the (a) zwitterionic intermediate, and (b) ammonium carbamate observed along the ZCB pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.2.1.7. Multi -Step Carbamate to Carbamic Acid Evolution (MCBA) Pathway

MCBA route (Figure 4.32) was indeed the multi-step version of the CBA that could take place over both primary and secondary amines. The pathway consisted of 4 steps. In the first one, physisorbed CO_2 was converted into an ammonium carbamate structure via a proton transfer from the CO_2 -adsorbed amine to a nearby amine of the adjacent AEAPS molecule

with a reaction barrier of 86.7 kJ/mol. The resulting ammonium carbamate structure (Figure 4.33) was hydrogen bonded to two different amino groups and was 5.8 kJ/mol more stable than the reference point. Following this, the ammonium was deprotonated by the adjacent amine of the same AEAPS molecule with an activation energy of 34.8 kJ/mol leading to the formation of another ammonium carbamate that was 17.5 kJ/mol less stable than the reference. Finally, in the last step, a hydrogen was spontaneously transferred from the ammonium to the nearby amino group of the adjacent AEAPS molecule, and from this amine to the nearest oxygen of the CO₂ leading to the formation of a type I carbamic acid. Final product had a relative energy of -16.6 kJ/mol in comparison to the reference. Reaction barriers calculated for the formation of the first ammonium carbamate and the end product (carbamic acid) were close to the values obtained for the CBA pathway of 5_5-double-AEAPS as well as the 5_5-APTMS [118].

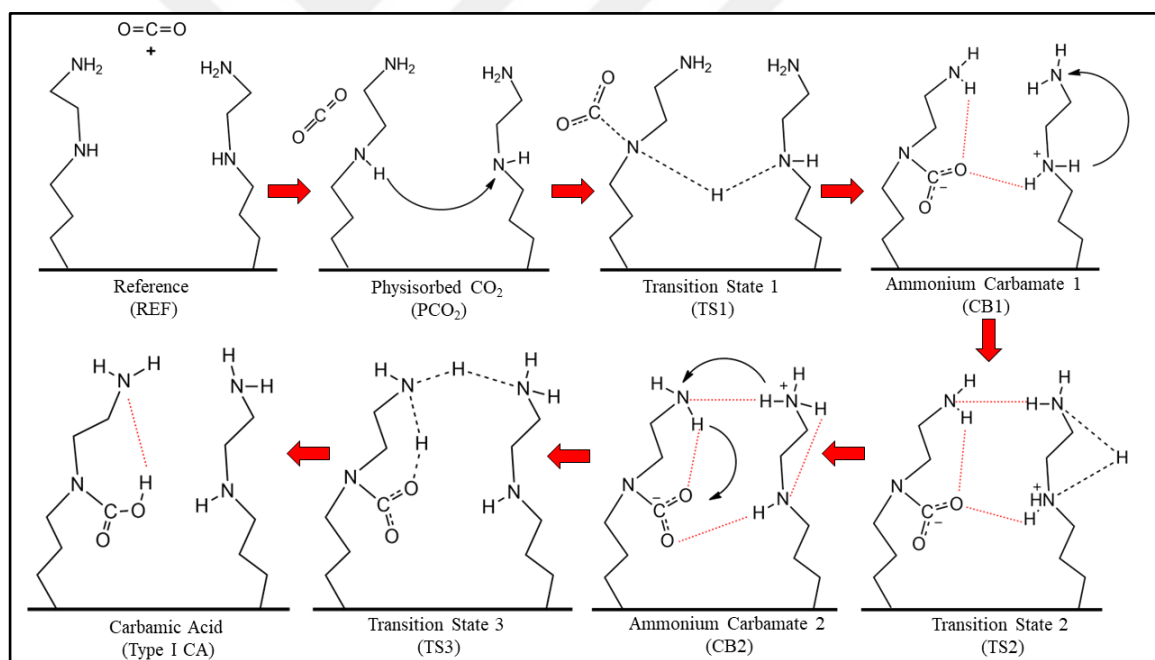


Figure 4.32. Diagrammatic representation of the MCBA pathway over 5_5-double-AEAPS

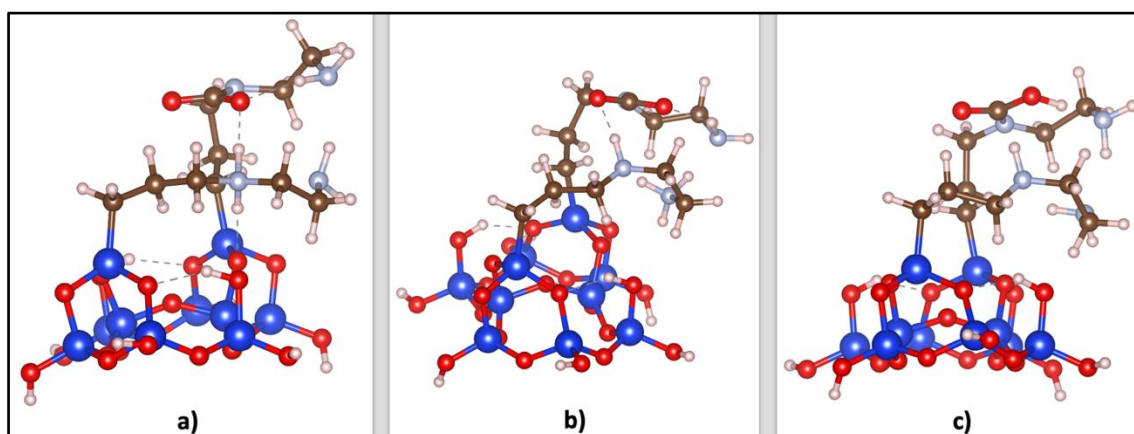


Figure 4.33. Molecular models of the (a) carbamate 1, (b) carbamate 2, and (c) carbamic acid (type I) observed along the MCBA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.2.1.8. Multi-Step Carbamate to Carbamic Acid Evolution via a Zwitterion (MZCBA) Pathway

MZCBA pathway (Figure 4.34) was indeed quite similar to the MCBA path except for the formation of a zwitterionic intermediate. According to the intermolecular pathway observed over a primary amine group, physisorbed CO_2 was transformed into a zwitterionic intermediate which was next deprotonated by a nearby primary amino group of the other AEAPS molecule to give an ammonium carbamate structure. Activation barriers estimated for these steps were 29.9 kJ/mol and 6.2 kJ/mol, that were close to the values obtained for the ZCB path discussed above. Formation of this zwitterionic structure seemed to decrease the activation energy required for the formation of the ammonium carbamate significantly when the corresponding barrier of the MCBA path (86.7 kJ/mol) was considered.

Successive transfer of a proton from the ammonium to the secondary amine of the same AEAPS molecule, from this amine to the secondary amine of the other AEAPS molecule and finally from this amine to the nearest oxygen of the zwitterion took place then, forming the carbamate 2, carbamate 3, and carbamic acid structures (Figure 4.35), respectively. Reaction barriers calculated for these steps were 2.5 kJ/mol, 18.8 kJ/mol, and 1.1 kJ/mol, respectively. Conversion barriers from one carbamate structure to another was found to be slightly lower compared to the case observed for MCBA (34.8 kJ/mol). Obtained type I carbamic acid was hydrogen bonded to a adjacent amine and a surface silanol via its -COH

group but was only 1.0 kJ/mol more stable than the reference implying that the pathway was unlikely to occur. Hence, the reaction energy diagram of this pathway was excluded from Figure 4.21 in order to keep the figure as simple as possible.



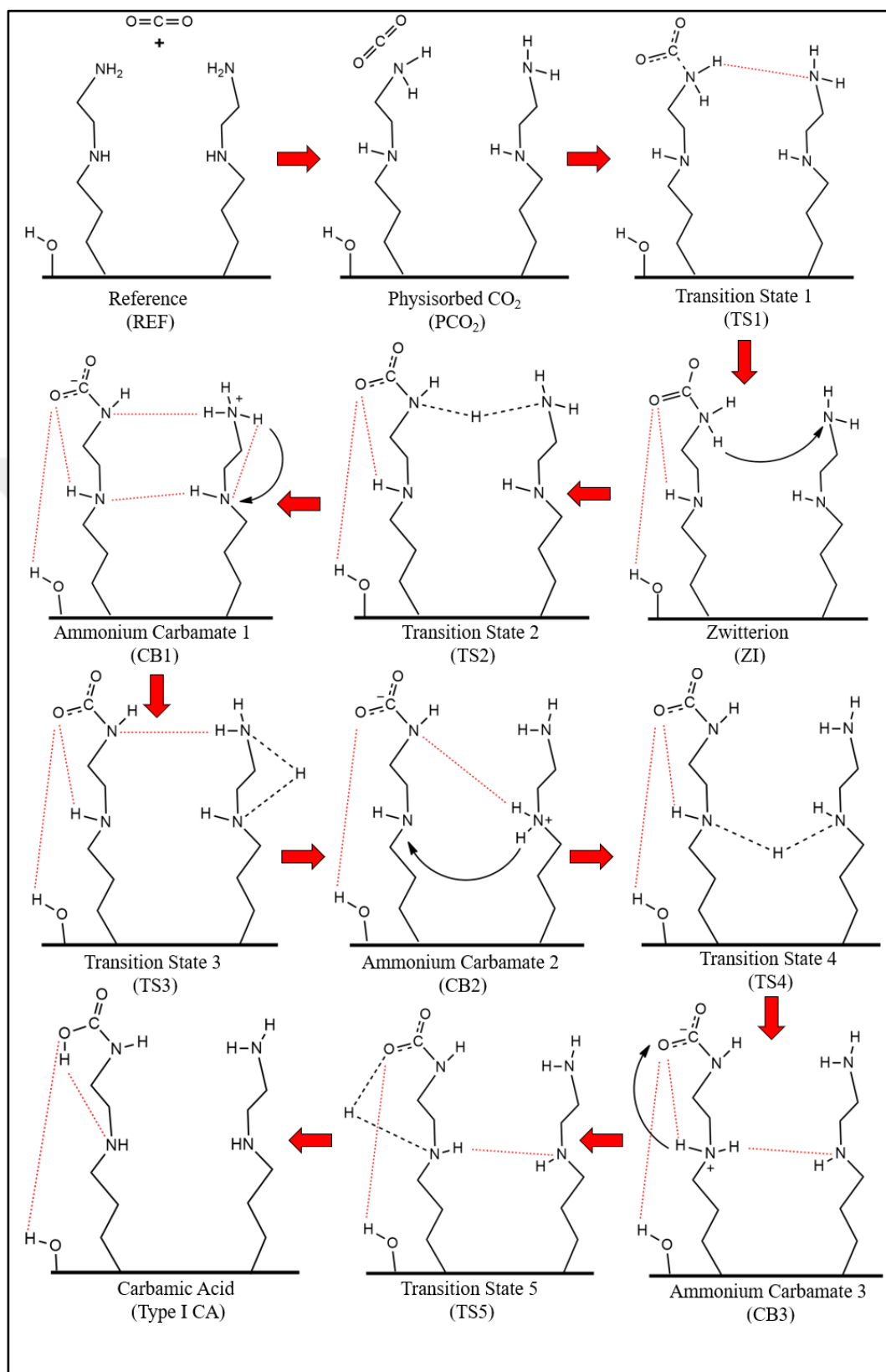


Figure 4.34. Diagrammatic representation of the MZCBA pathway over 5_5-double-AEAPS

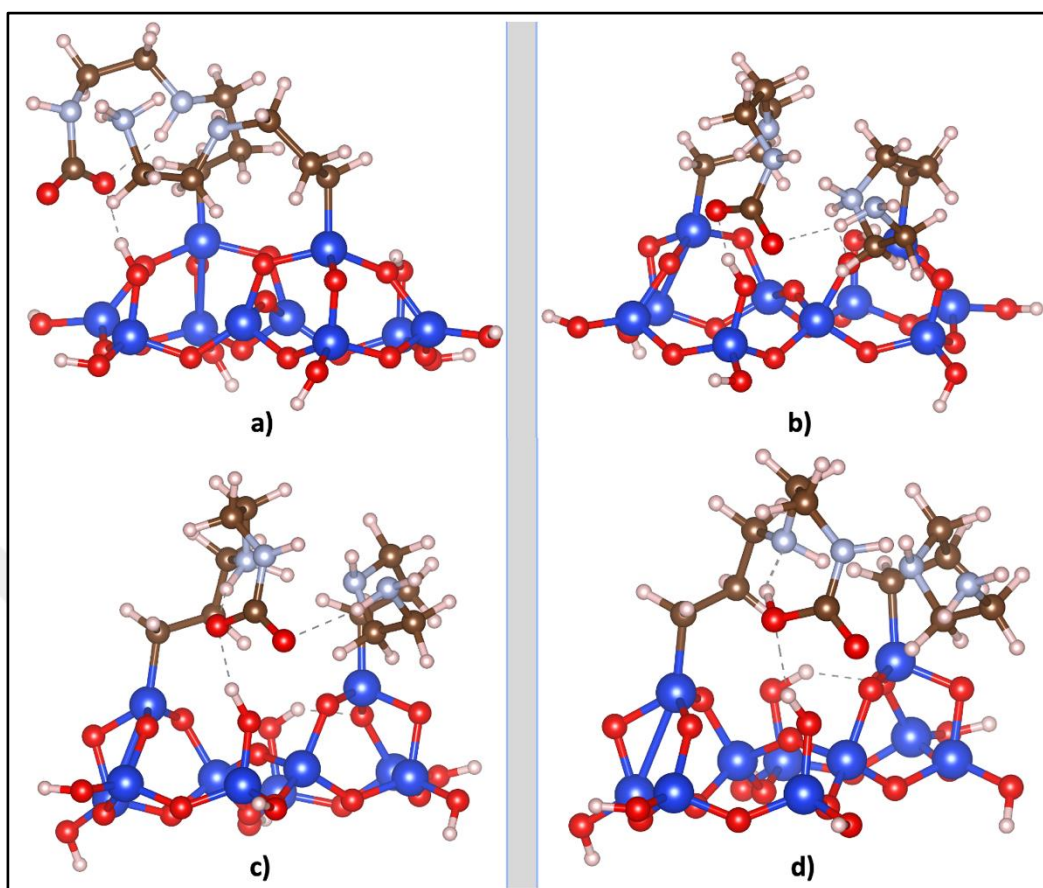


Figure 4.35. Molecular models of the (a) carbamate 1, (b) carbamate 2, (c) carbamate 3, and (d) carbamic acid (type I) observed along the MZCBA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.2.1.9. Multi-Step Surface-Assisted Carbamate to Carbamic Acid Evolution (MSCBA) Pathway

Finally, MSCBA (Figure 4.36) was an intermolecular reaction pathway that was observed over a primary amine group. Similar to the MCBA route, it involves the steps of formation of an ammonium carbamate structure, conversion of this structure into another ammonium carbamate and finally deprotonation of this second ammonium to give a carbamic acid structure. What differed in the MSCBA path was that formation of the second carbamate was achieved via a proton transfer from the ammonium to a nearby silanol and from this silanol to the adjacent amine. Activation energies calculated for the first and second steps were 37.6 kJ/mol and 42.0 kJ/mol, respectively, while the formation of the carbamic acid took place spontaneously. Compared to the MCBA case (86.7 kJ/mol and 34.8 kJ/mol,

respectively), formation of the first carbamic acid was found to be much faster whereas involvement of the surface silanol in the formation of the second carbamate seemed to have no significant effect on the reaction kinetics.

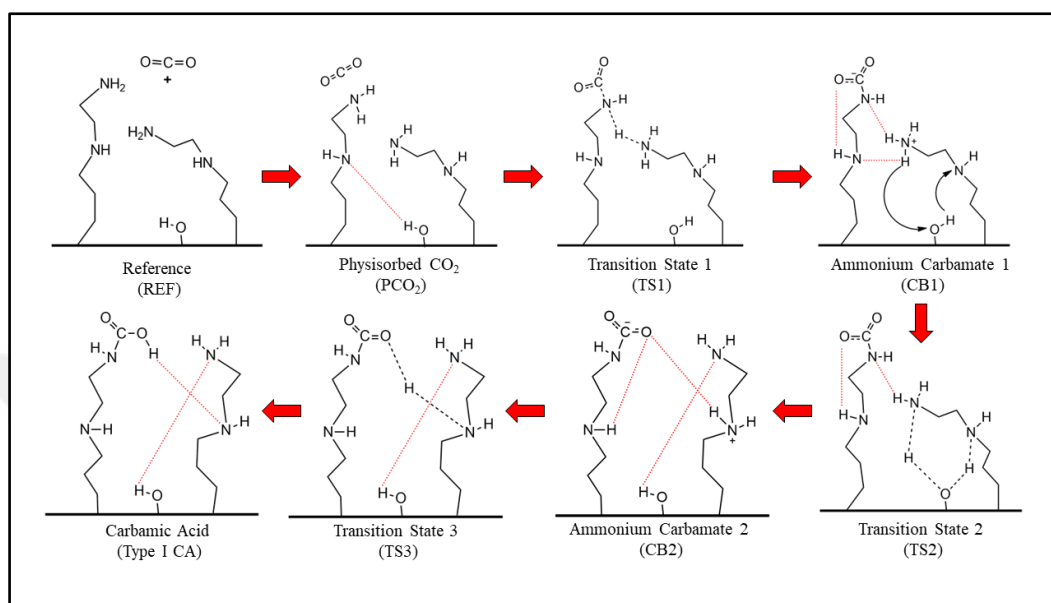


Figure 4.36. Diagrammatic representation of the MSCBA pathway over 5_5-double-AEAPS

The first ammonium carbamate (Figure 4.37) was hydrogen bonded to one of the adjacent amines and was found to be unstable (with a relative energy of +39.2 kJ/mol) in comparison to the reference point. The second carbamate, on the other hand, interacted with two different amino groups and was found to be 27.8 kJ/mol more stable than the reference. Finally, the end product was a carbamic acid of type I that was hydrogen bonded to one of the adjacent amines via its -COH group and was 34.7 more stable than the reference point.

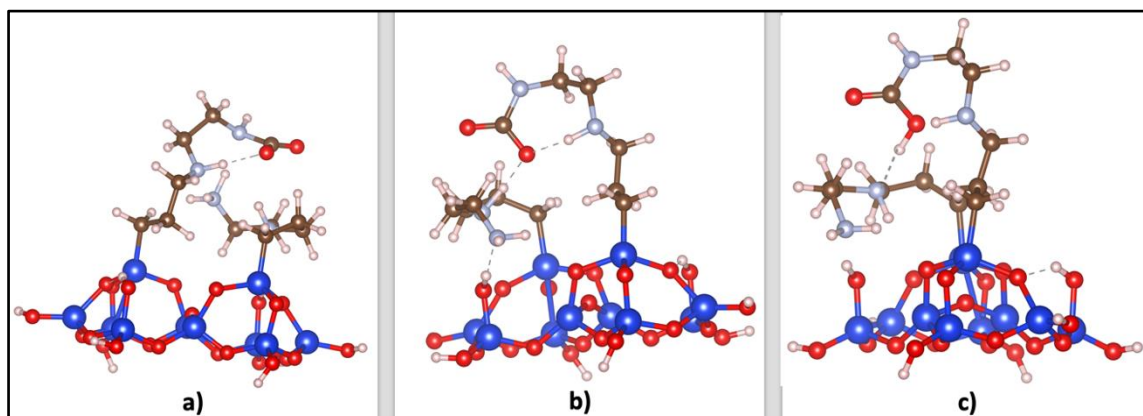


Figure 4.37. Molecular models of the (a) carbamate 1, (b) carbamate 2, and (c) carbamic acid (type I) observed along the MSCBA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

Our calculations performed over 5_5-double-AEAPS showed that the hydrogen bonding interactions were much stronger in case of 2 AEAPS molecules resulting in more reaction pathways with thermodynamically stable products. These interactions were mostly of the amine-amine type; amine-surface interactions were more restricted under the conditions studied (high surface amine density) due to the long chain length of the molecule. Accordingly, the amino groups were mostly located close to one another but far away from the surface.

Of the 9 reaction pathways identified over the selected model, CBA and MSCBA were the most feasible two routes. Relative stabilities of the carbamic acid and carbamate products indicated that both species might be found in the adsorption stream as proposed by the previous IR and NMR studies [6,104,112,114,139,141,142,143]. In both cases, the products were found to be stabilized via complex hydrogen bonding networks involving interactions with the surface and/or the adjacent amine, underlining once more the critical role of the interplays in CO₂ adsorption as suggested before [118,138].

4.2.2. Analysis of Adsorption Mechanism of The Second CO₂ over 5_5-Double-Aeaps

Several different conformers were included in the study of the second CO₂ adsorption and 3 different pathways were identified, namely carbamate to carbamic acid to carbamic acid (CBAA), direct carbamic acid to carbamate (DCAB), and multi-step carbamate to carbamic

acid formation via various carbamates (MCBBA) pathways. Adsorption of both CO₂ molecules were found to be thermodynamically feasible for none of the 3 pathways. CBAA route resulted in a stable product for the first CO₂ adsorption while the capture of the second CO₂ was calculated to be thermodynamically feasible for the MCBBA pathway.

4.2.2.1. Carbamate to Carbamic Acid to Carbamic Acid Evolution (CBAA) Pathway

In the CBAA route (Figure 4.38), the adsorption of the first CO₂ was achieved via a standard CBA pathway that was discussed in the previous section for 5_5-double-AEAPS. Accordingly, physisorbed CO₂ was converted into an ammonium carbamate structure via a hydrogen migration from CO₂-adsorbed amine to a nearby amino group that was present in the adjacent AEAPS molecule. This step required an activation barrier of 65.6 kJ/mol and created a carbamate that was 52.6 kJ/mol less stable than the reference point. A simultaneous proton transfer from the ammonium to a adjacent amine and from this amine to the oxygen of the CO₂ took place then with a barrier of 10.9 kJ/mol, forming the first carbamic acid structure that was of type I and possessed a relative energy of -33.9 kJ/mol relative to the reference (REF 1). Figure 4.39 presents the reaction energy diagram of the CBAA path. The Reference points in the diagram are denoted as REF1 and REF2. REF1 has a free energy that is equal to the total energies (free) of the gaseous CO₂ and the matching 5_5-double-AEAPS cluster, while REF2 has an energy that is equal to the sum of the free energies of the gaseous CO₂ and the carbamic acid obtained as a result of the adsorption of the first CO₂.

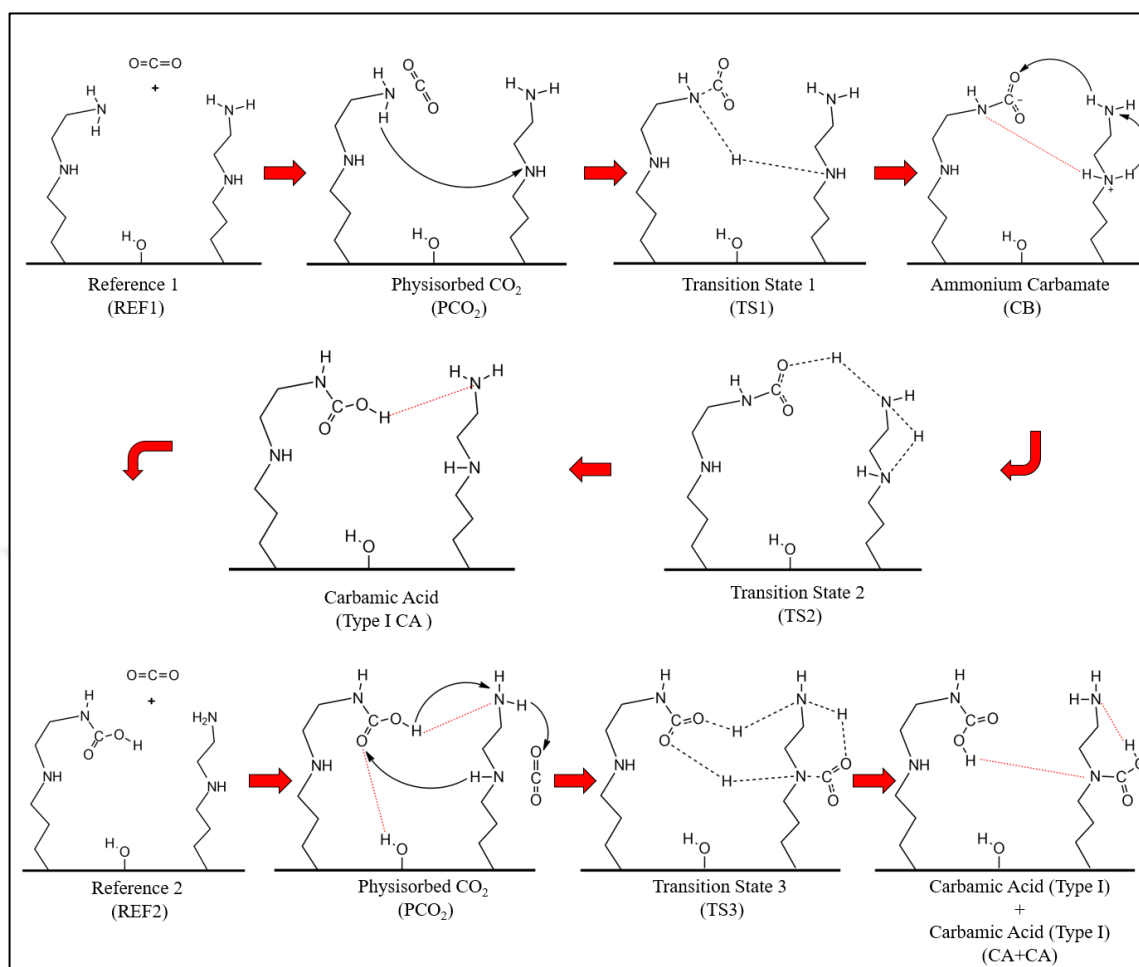


Figure 4.38. Diagrammatic representation of the CBAA pathway over 5_5-double-AEAPS

Following this, a second CO₂ was physisorbed over one of the free amino groups with a binding energy of 34.1 kJ/mol. During this physisorption, the carbamic acid that was already present at the surface was transformed into another carbamic acid structure (type II) that was hydrogen bonded to the adjacent amine via its -COH and to one of the surface silanols via its =CO and the extreme stability of this physisorption state seemed to be originating from this fact. Following the physisorption, the second CO₂ molecule was converted into a second carbamic acid structure via a simultaneous proton transfer from the second physisorption state to the =CO of the first carbamic acid, from the -COH of the first carbamic acid to an adjacent amine, and from this amine to the nearest oxygen of the second physisorbed state. Estimated barrier was 71.0 kJ/mol that was lower than the values obtained for the DCA pathway (107.7 kJ/mol and 93.1 kJ/mol) discussed above and the end product was a carbamic acid of type I that was 15.6 kJ/mol less stable in comparison to the reference (REF 2). Molecular models of the two carbamic acids are given in Figure 4.40.

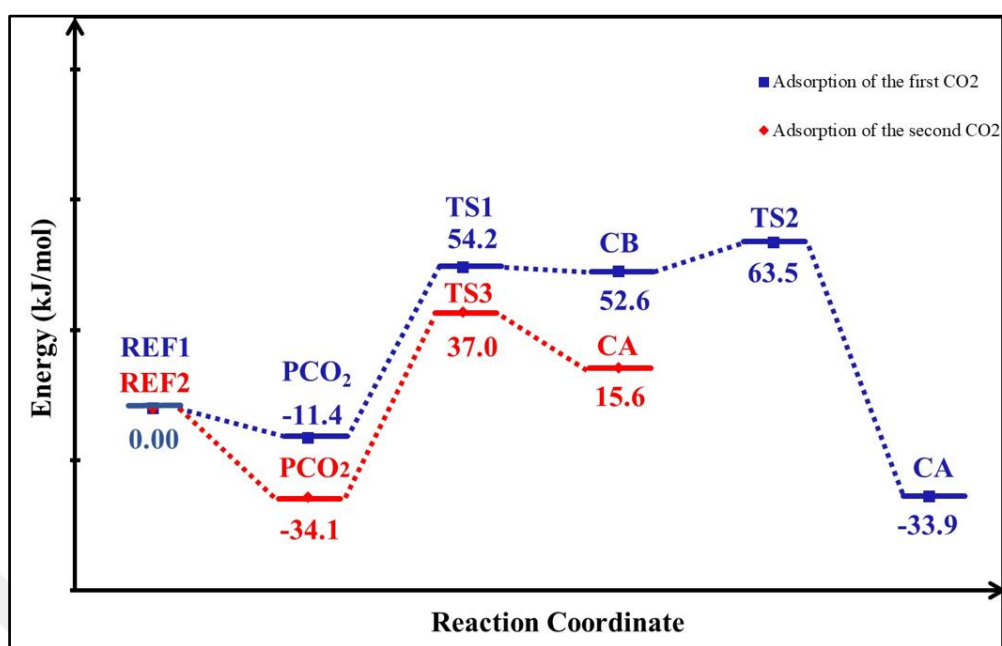


Figure 4.39. Energy diagram regarding the CBAA route over 5_5-double-AEAPS. REF refers Reference point, PCO₂ refers Physisorbed CO₂, TS refers Transition state, CB refers Ammonium carbamate, CA refers Carbamic acid

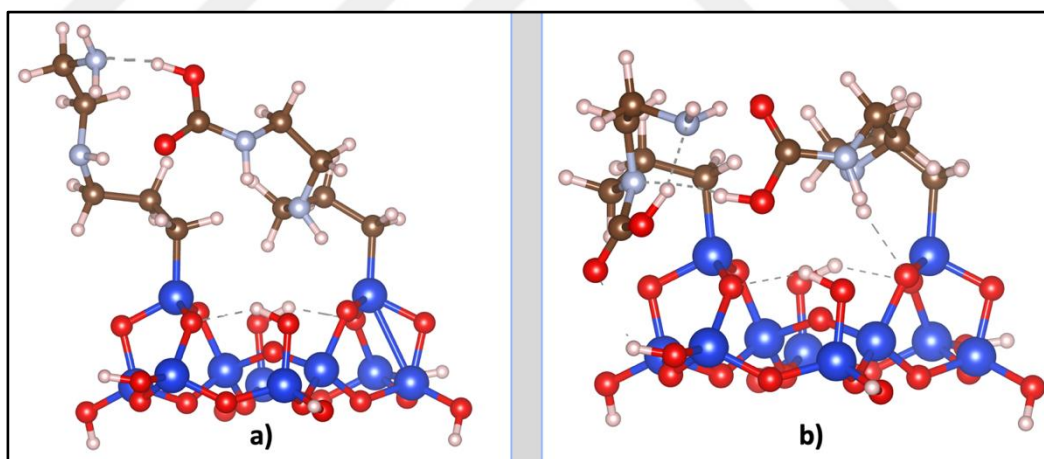


Figure 4.40. Molecular models of the (a) first carbamic acid (type I), and (b) two carbamic acids (type I and type I) observed along the CBAA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.2.2.2. Direct Carbamic Acid to Carbamate Evolution (DCAB) Pathway

DCAB (Figure 4.41) was a pathway that achieved the adsorption of both CO₂ molecules intramolecularly. The adsorption of the first CO₂ took place via the intramolecular DCA

(Figure 4.2) pathway whereas that of the second one occurred via the intramolecular direct carbamate formation (DCB) pathway that involved the evolution of an ammonium carbamate via the deprotonation of the CO_2 -adsorbed amine by an adjacent amine. Reaction barriers calculated for the adsorption of the first and second CO_2 molecules were 107.7 kJ/mol and 111.4 kJ/mol, respectively. The first value was identical to that of the intramolecular DCA pathway observed over 5_5-double-AEAPS (107.7 kJ/mol) while the second one was slightly higher than the one (73.2 kJ/mol) calculated for the intermolecular carbamate formation step of the CBA. Both the carbamic acid (type I, 12.7 kJ/mol less stable relative to the reference) and the ammonium carbamate (111.4 kJ/mol less stable than the reference) structures were unstable. The molecular models of these species are presented in Figure 4.42.

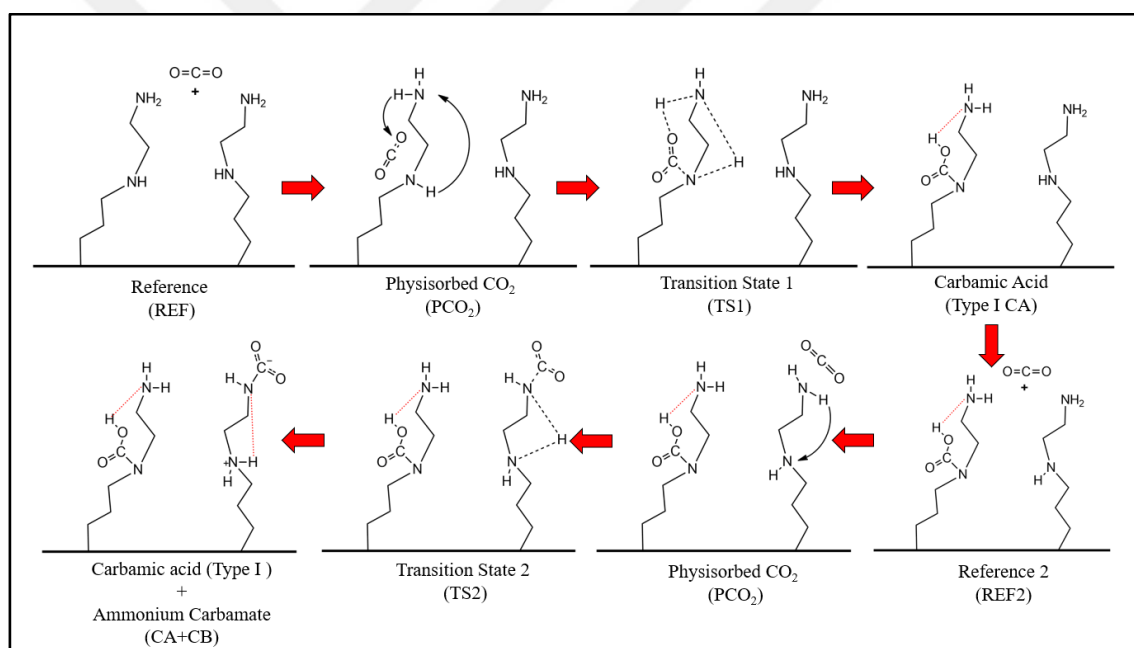


Figure 4.41. Diagrammatic representation of the DCAB pathway over 5_5-double-AEAPS

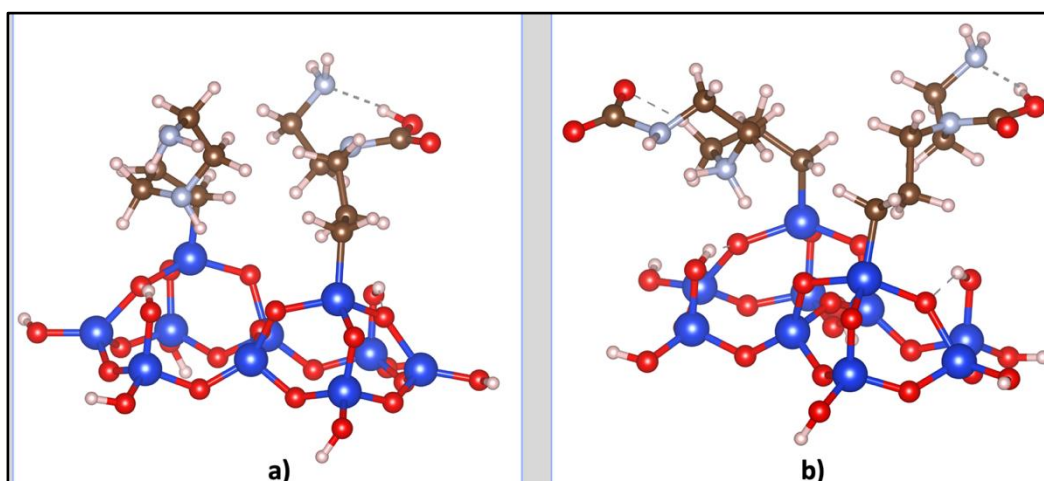


Figure 4.42. Molecular models of the (a) first carbamic acid (type I), and (b) carbamic acid (type I) + ammonium carbamate observed along the DCBA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

4.2.2.3. Multi-Step Carbamate to Carbamic Acid Evolution via Various Carbamates (MCBBA) Pathway

According to the calculated pathway (Figure 4.43), once the second ammonium carbamate structure that was observed in the MCBA path was formed, a second CO_2 molecule was physisorbed over one of the free amino groups with an adsorption energy of 5.1 kJ/mol. Following this, a simultaneous hydrogen migration from the ammonium to a nearby free amine and from this amine to the nearest oxygen of the carbamate took place forming a complex of a carbamic acid and a physisorbed CO_2 . Activation energy of this step was estimated as 16.1 kJ/mol and the obtained carbamic acid was hydrogen bonded to two different amine sites via its $-\text{COH}$ and $=\text{CO}$ groups (Type VII). Being involved in two hydrogen bonding interactions with the neighbors, this complex was 46.2 kJ/mol more stable than the reference point. Physisorbed CO_2 was then converted into an ammonium carbamate via a hydrogen transfer taking place from the CO_2 -physisorbed amine to the $=\text{CO}$ of the first carbamic acid and from the $-\text{COH}$ of this carbamic acid to a nearby free amine at the same time. In this way a complex of ammonium carbamate + carbamic acid was obtained with a reaction barrier of 53.6 kJ/mol, the complex being 0.4 kJ/mol less stable than the reference. The ammonium was then spontaneously deprotonated and a complex of two carbamic acid structures was formed with a relative energy of -7.2 kJ/mol in comparison to the reference.

Figure 4.44 presents the reaction energy diagram of the MCBBA path. The reference points in the diagram are denoted as REF1 and REF2. REF1 has a free energy that is equal to total energies (free) of the gas-phase CO_2 and the matching 5_5-double-AEAPS cluster, while REF2 has an energy that is equal to the sum of the free energies of the gaseous CO_2 and the ammonium carbamate as a result of the adsorption of the first CO_2 . Molecular models of the adsorption species of the first and second CO_2 may be seen in Figure 4.45.

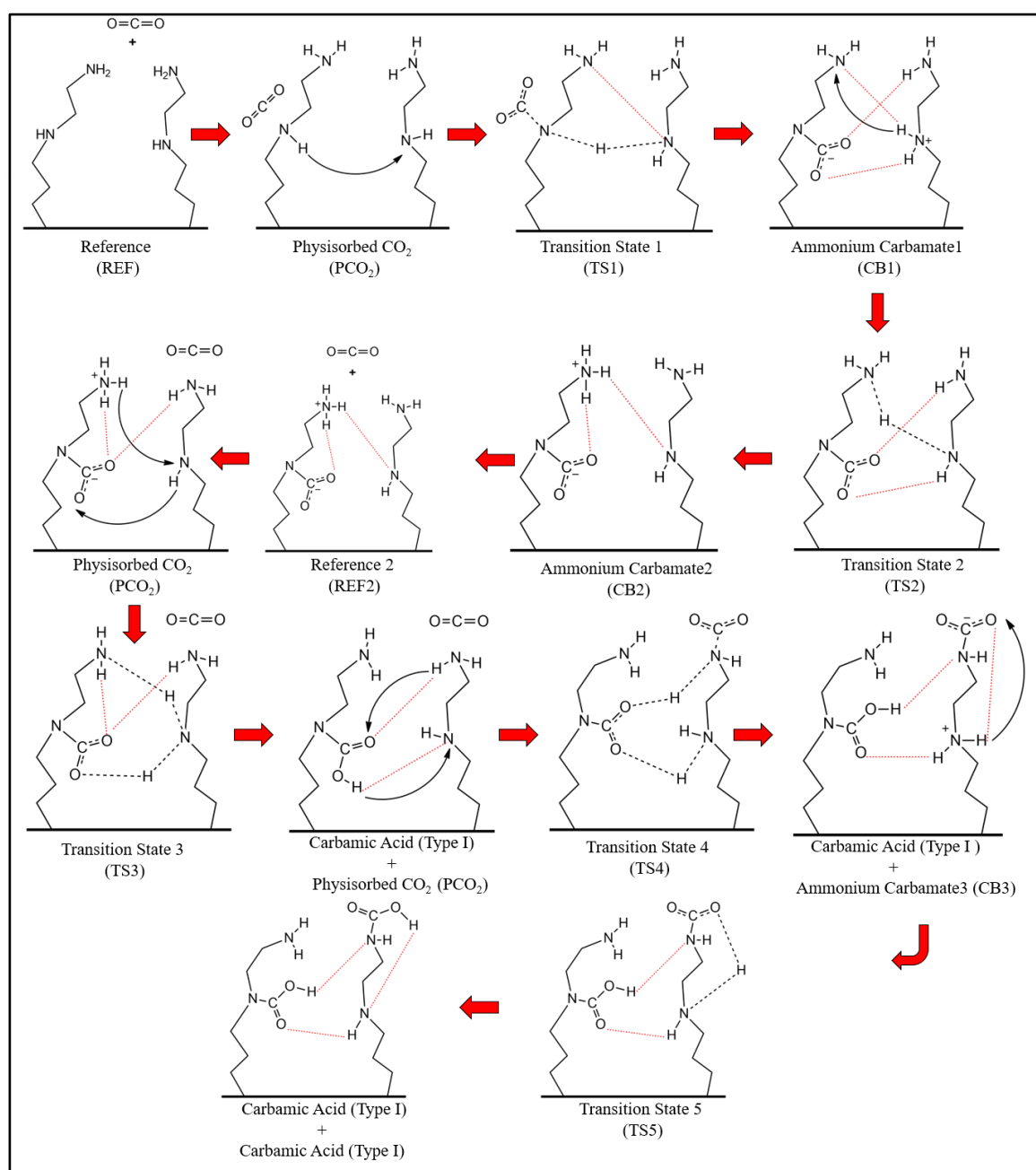


Figure 4.43. Diagrammatic representation of the MCBBA pathway over 5_5-double-AEAPS

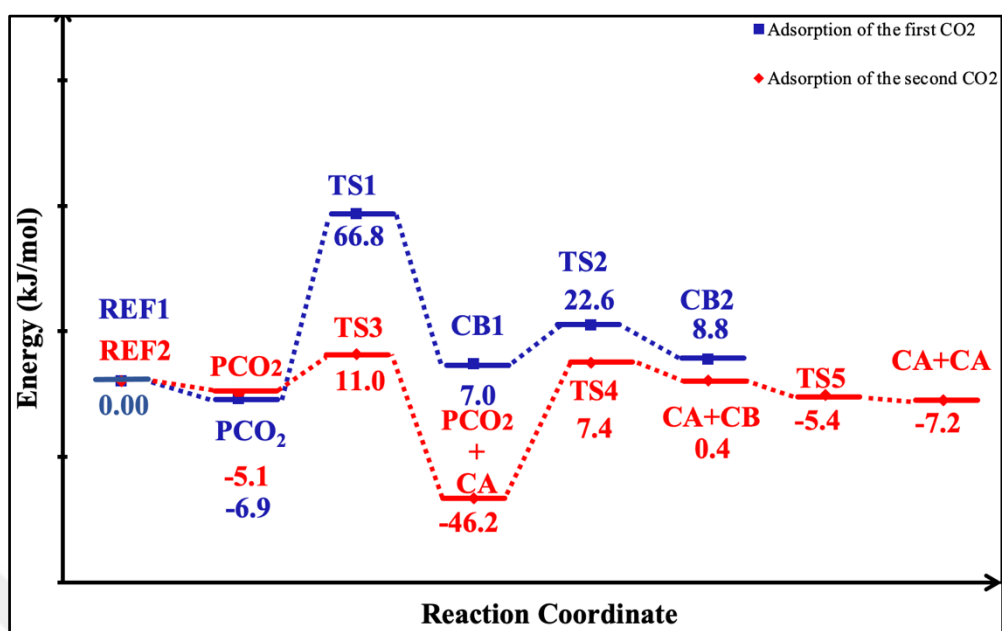


Figure 4.44. Energy diagram regarding the MCBBA route over 5_5-double-AEAPS. REF refers Reference point, PCO₂ refers Physisorbed CO₂, TS refers Transition state, CB refers Ammonium carbamate, CA refers Carbamic acid

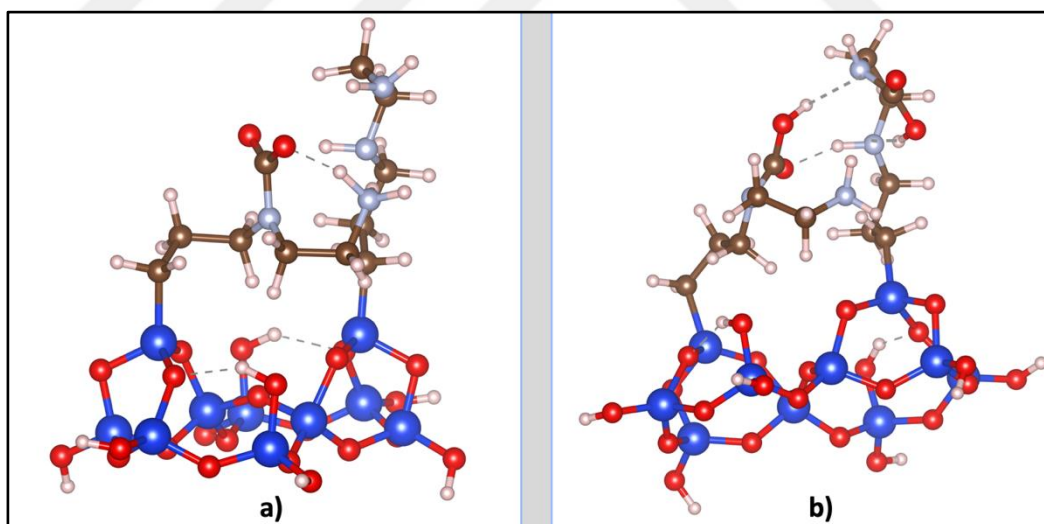


Figure 4.45. Molecular models of the (a) ammonium carbamate, and (b) carbamic acid (type I) + carbamic acid (type VII) observed along the MCBBA pathway. Colors represent: red = oxygen, blue = silicon, pink = hydrogen

Our calculations performed over 5_5-double-AEAPS demonstrated that adsorption of two CO₂ molecule was possible parallel to the previously observed reaction stoichiometry [118,138]. Although the adsorption of both CO₂ molecules was found to be thermodynamically feasible in none of the pathways, our observations implied that this may

be possible if the adsorption species can be stabilized via complex hydrogen bonding networks. Nevertheless, the number of conformers resulting in the adsorption of two CO₂ molecules were low suggesting a lower amine efficiency (C/N) under the conditions exploited in this study.



5. CONCLUSION AND RECOMMENDATIONS

This study aimed to examine the interaction pathways of CO₂ over AEAPS-modified mesoporous silica by using quantum mechanical calculations with the purpose of elucidating (i) the amino groups that contributed to the capture, (ii) the function of surface -OH groups on the reaction pathway, and (iii) whether intramolecular adsorption was possible. Following conclusions have been derived based on the calculations performed:

- CO₂ was captured both intramolecularly and intermolecularly.
- Both amine groups contributed the capture of CO₂, generally resulting in similar product stabilities and reaction barriers.
- Intramolecular adsorption was dominant under low surface amine density conditions, but strong amine-amine interactions were lacking leading generally to higher barriers and lower product stabilities.
- Hydrogen bonding interactions (both amine-amine and amine-surface) rather than the amine functionality was more deterministic on the thermodynamics and kinetics of the adsorption.
- Under low surface amine density conditions, carbamic acid was the only product that was stabilized via the interactions with surface.
- Long chain length of the molecule seemed to decrease the flexibility of the AEAPS structure preventing amine-amine interactions.
- Intermolecular adsorption was dominant under high surface amine density conditions, amine-amine interactions being the primary interplay stabilizing the reaction species.
- Both carbamic acid and ammonium carbamate species could be identified in case of high surface amino densities.
- Adsorption of the second CO₂ was observed but no reaction pathways resulting in two stable adsorption species could be obtained.
- Lower fraction of conformers resulting the adsorption of two CO₂ molecules suggested a lower amine efficiency under the conditions studied.
- Various forms of carbamic acid (that differed from each other in the hydrogen bonds that they included) were obtained with varying stabilities.

Following recommendations may be useful for a complete study of the adsorption pathways over amine-based adsorbents that would result in the development of sorbents with high performance:

- Much larger silica models may be used for the grafting of two AEAPS molecules since they can result in conformers with amine-amine and amine-surface interactions at the same time.
- Impact of humidity on the adsorption kinetics and thermodynamics may be studied.
- Effect of the structural properties of amines may be studied with the purpose of establishing a structure-activity relationship between the amine characteristics and their CO₂ capture performances.

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