PCCP

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2018, **20**, 12149

A catalytic role of surface silanol groups in CO_2 capture on the amine-anchored silica support†

Moses Cho, Joonho Park, Cafer T. Yavuz and Yousung Jung*

Received 28th November 2017,
Accepted 5th April 2018

DOI: 10.1039/c7cp07973g

rsc.li/pccp

A new mechanism of CO_2 capture on the amine-functionalized silica support is demonstrated using density functional theory calculations, in which the silica surface not only acts as a support to anchor amines, but also can actively participate in the CO_2 capture process through a facile proton transfer reaction with the amine groups. The surface-mediated proton transfer mechanism in forming a carbamate–ammonium product has lower kinetic barrier (8.1 kcal mol^{-1}) than the generally accepted intermolecular mechanism (12.7 kcal mol^{-1}) under dry conditions, and comparable to that of the water-assisted intermolecular mechanism (6.0 kcal mol^{-1}) under humid conditions. These findings suggest that the CO_2 adsorption on the amine-anchored silica surface would mostly occur *via* the rate-determining proton transfer step that is catalyzed by the surface silanol groups.

Introduction

Carbon dioxide (CO_2) has been the major source of the global climate change due to the continuous increase in its concentration in the atmosphere and the resulting greenhouse effect. Because its impact on the environment is significant, there have been many efforts in developing materials that could efficiently capture CO_2 in order to bring down the CO_2 content in air. The amine based wet technology for CO_2 scrubbing has been widely used to capture CO_2 from flue gas streams from power plants, but restrained from continuous usage due to its corrosive nature, degradation, and high regeneration energy.[1,2] Because of these weaknesses, attention has been paid to the solid-state adsorbent materials, such as zeolites,[3,4] MOFs,[5–7] and carbon materials[8,9] in order to find alternatives to the use of monoethanolamine derivatives. Recently, in order to increase the selectivity of CO_2 from other impurities in the flue gas, amines have been impregnated/grafted on silica materials (MCM-41 or SBA-15), which showed high CO_2 capacities, selectivity, and stability towards humid conditions of flue gas or direct air capture.[10–21]

One of the issues in exploiting amine functionalized silica system is to unveil the intermediates and understand the reaction mechanism of formation of amine–CO_2 products. There have been many reports to address this question of reaction mechanism and intermediates through experimental techniques such as FTIR and NMR.[15,19,22–25] It is noted that in an aqueous amine system, carbamate–ammonium pair (denoted by CB to indicate carbamate–ammonium) is the dominant product as these ionic species can be stabilized through multiple hydrogen bonding (denoted by H-bonding) and solvation with water.[26–32] Moreover, neutral molecules such as carbamic acid (denoted by CA to indicate carbamic-acid) are expected to be stable in gaseous state because there are no solvents to stabilize charge separated species in gas phase (as shown by quantum chemistry calculations). However, a previous report highlights the CB pair as the dominant product even in dry conditions on the amine functionalized silica support.[33–35] Thus, different mechanisms seem to exist on the solid sorbent and it is expected that there might be other factors that stabilize the CB pair on the silica surface in dry condition, which then could affect the capture mechanism.

A few studies have offered insights to the formation of the CB pair on the amine-functionalized silica support; the experimental results hinted possible interaction between amine groups and the surface hydroxyl groups or silanol groups.[18,35–37] The FTIR study by Brunelli *et al.* suggested the formation of surface-bound carbamate on the silica surface. Recently, there have been theoretical and experimental efforts showing that silanols play a key role in stabilizing the CB products through multiple H-bonding.[34,38] Also, a recent study has shown that amine adsorbs CO_2 through a wrapping mechanism, where the amine–CO_2 product is stabilized through multiple intermolecular H-bonding interactions.[39] However, even though these studies have shown the nature of product stability on the surface, it still does not address the formation mechanism, in particular, the role of the surface on proton migration. Some other studies hint that the surface silanol groups on silica surface could play a role in CO_2 adsorption, but how the silanol groups could partake in the adsorption kinetics is not addressed.[37,40]

Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehakro, Daejeon 305-701, Korea. E-mail: ysjn@kaist.ac.kr

† Electronic supplementary information (ESI) available: Stable amine structure on the α-(100) SiO_2 surface, water assisted intermolecular mechanism pathways. See DOI: 10.1039/c7cp07973g

In addition, there have been several reports revealing that water enhances the CO_2 adsorption kinetics in amine containing adsorbents. The presence of small amounts of water vapor increases CO_2 adsorption in HKUST-1.[41] It is also determined that introducing water vapor enhanced CO_2 adsorption process in amine functionalized mesoporous silica systems (SBA-15 and MCM-41).[25,42,43] Although these papers demonstrated that water molecules improved CO_2 capture, there is no clear understanding of the effective role played by water molecules to enhance the reaction rate of the CO_2 adsorption in functionalized solid materials.

In this study, we investigated the role of silanols as well as water molecules in CO_2 adsorption by surface grafted amines, and for that, several key reaction mechanisms were examined (Fig. 1). In all cases, the formation of zwitterion is commonly the first elementary reaction step. After forming zwitterion there are three possible pathways. In a commonly accepted model, a proton from the first amine is migrated to the second amine and the proton of the second amine is migrated to O. The interchange of protons between the two amines could then occur at the same time, thus forming the six-membered ring in the transition state. This mechanism is denoted as 'InterM', *i.e.*, intermolecular proton transfer mechanism, a mechanism well accepted in literature. In a second reaction model, water acts as the proton transfer medium between both the amine molecules and between the amine and the carboxylate molecules. This mechanism is denoted by 'W-InterM', *i.e.*, the water-assisted intermolecular proton transfer mechanism. These two mechanisms are assumed to proceed without the help of the surface, and reaction products can be both CB and CA. A new third model, also the key proposed mechanism under consideration in this study, is the proton migration from zwitterion to surface as denoted by 'SurfM', in which the silanol mediates proton transfer. The resulting CB and CA products are bound to the SiO_2 surface and denoted as sCB (surface-bound carbamate–ammonium pair) and sCA (surface-bound carbamic-acid), respectively. We have to note that another mechanism discussed in the literature is the intramolecular mechanism, in which the proton migrates from N to O directly. However, recent studies have shown the unfeasibility of intramolecular mechanism (IntraM) due to the high kinetic barrier, and thus, IntraM was not considered in this study.[30,40]

Herein, we found an active role of the surface silanols in amine–CO_2 reactions to promote the kinetics of product formation. The key step for the observed sCB formation in dry condition is found to be the facilitated proton transfer steps between the amine and surface silanol groups. This new mechanism unveils for the first time the active involvement of silica surface in CO_2 adsorption mechanism. Furthermore, we find that the presence of water molecules accelerates the reaction kinetics through catalyzing the proton transfer process between the amine and CO_2. We expect that these fundamental concepts could be useful for further designing of materials for gas capture as well as amino silica catalyst that involve the proton transfer, for example, for aldol and nitroaldol condensation reactions.[44,45]

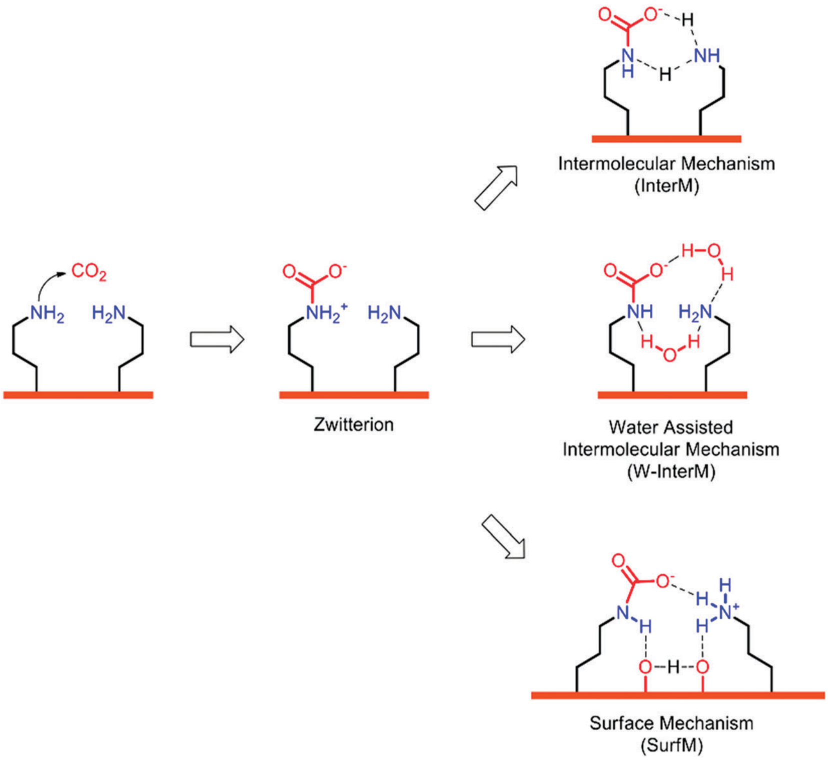

Fig. 1 Mechanisms of amine–CO_2 binding considered in this work are intermolecular mechanism (InterM), water assisted intermolecular mechanism (W-InterM), and surface mechanism (SurfM).

Computational method

Total electronic energies were calculated using the Vienna *ab initio* Simulation Package (VASP)[46] with the revised Perdew–Burke–Ernzerhof (RPBE)[47] exchange–correlation functional. Additionally, the dispersion correction of Grimme's D3[48] with Becke–Johnson damping[49] was employed. A plane wave basis set and the projector-augmented wave (PAW) method[50] with a cut-off energy of 450 eV was used. Geometries were fully optimized until the force was less than 0.025 eV Å^{-1}. All energies were sampled at gamma point. The transition state barriers were calculated by a climbing image nudged elastic band (CI-NEB) method with eight intermediate images.[51] The structures were visualized using the VESTA program.[52]

The slab model was based on SiO_2 since the most commonly used adsorbents are MCM-41 or SBA-15, which are silica derivatives. SiO_2 exists in many crystalline forms. Among them, α-quartz was chosen for this study as it is the most stable polymorph at normal ambient conditions. It is shown that naturally grown SiO_2 has silanol groups on the surface.[53] Thus, the surface sites were hydroxylated (Si–OH). The surface silanol groups consist of either geminal or terminal silanol groups,[54] and it has been experimentally shown that the most used adsorbents such as SBA-15 or MCM-4 have 90% terminal silanol groups.[55] As the model surface, the (100) facet of α-quartz was selected as the calculation platform since this surface consists of terminal silanol sites very similar to experimental adsorbents[55–57] and its ordered structure will make it more systematic in energy minimizations. As for the amine, 3-aminopropyltrimethoxysilane (APS) was used since it often serves as a benchmark for the amine functionalized silica support and it can be easily compared with the experimental results.[16,19,35] The models and the most stable functionalization configurations used in the present calculations are shown in Fig. S1–S3 (ESI†).

As for InterM, the molecular calculation was performed by having two propylamines configuration aligned right next to each other in the periodic cell, and the terminal carbon atoms were fixed in order to mimic the surface anchoring, as shown in Fig. S4 (ESI†). For all calculations relating to InterM, it was assumed that the reaction proceeds through simultaneous two proton migration steps, yielding CA as the product as suggested in previous studies.[40,58,59]

Results and discussion

The effect of silanols in stabilizing carbamate–ammonium on the silica surface

Recent studies have demonstrated that the amine actively interacts with the surface *via* H-bonding between organic molecules and silica surface.[22,34,60] Thus, we have considered H-bonding of the amine to the surface as the preferred ground state with the most stable geometry given in Fig. S2 (ESI†). While the backbone of propylamine preserves the anti-conformer, H-bond lowers the optimized energy by *ca.* 2 kcal mol^{-1}. As for two-amine location, the validity of its structure was checked by comparing the sCB formation energy with the experimental initial heat of adsorption, which lies in between −17 to −22 kcal mol^{-1}.[19,33,34]

To gain insight on how products are stabilized on the silica surface, the CO_2 binding energy (BE) values of sCB and sCA products were compared. The optimized structures with the reaction energies and different H-bond lengths are shown in Fig. 2. The computed BE of sCB was −19.4 kcal mol^{-1}, which falls within the energy range of experimental values (between −17 to −22 kcal mol^{-1}).[19,33,34] In the optimized structure, an O of carbamate is anchored in between two silanol groups with two H-bonds with distances of 1.37 D and 1.59 D. Together with the intermolecular H-bond (1.49 D) in between carboxylate and ammonium, the strong interaction between carboxylate group and surface silanol groups make the binding energy of CO_2 as high as −20 kcal mol^{-1}. The overall geometry of sCA is similar to sCB-Amm, but H was migrated from ammonium to carboxylate, forming the non-ionized terminal carboxylate form. Due to the H-adsorption on O atoms, the charges on the anchored O are diminished, which weakens the H-bonds between the anchored O and two silanol groups. The bond lengths of two H-bonds increased to 1.55 D and 1.69 D from 1.37 D and 1.59 D, respectively. Therefore, the BE of sCA is lowered (−15.1 kcal mol^{-1}) than that of sCB (−19.4 kcal mol^{-1}) by 4.3 kcal mol^{-1}, which can explain why the experiment shows that the major product is carbamate.

Interestingly, we observed in our calculations another reaction product of carbamic acid–ammonium complex while searching for diverse optimized structures. The extra proton was provided from the surface, changing sCB into deprotonated siloxide (SiO^-)–carbamic acid–ammonium complex, which is referred to as sCA(SiO^-/NH_3^+). The energy difference between sCA(SiO^-/NH_3^+) and sCB is negligible and there is only a small geometrical change in sCA(SiO^-/NH_3^+) compared to sCB. Due to the H-migration to carboxylate group, the charges of O in carboxylate groups decreased, which make the H-bonds with O of carboxylate elongated from 1.59 D and 1.49 D to 1.67 D and 1.62 D, respectively. However, the loss of the stabilization energy due to H-bonds is compensated from the strong H-bond between siloxide (SiO) and carbamic acid. This negligible energy difference shows a possible sign of easy proton migration between amine–CO_2 product and surface, interconverting between different products (sCA(SiO^-/NH_3^+)) without the help of neighboring amine. Therefore, we propose that the surface could actively participate in the CO_2 adsorption process *via* proton transfer mediated by the surface silanol.

Proposed CO_2 adsorption mechanism through the surface proton transfer

Based on the obtained CO_2 adsorption energy, it was found that the stability of sCB arises from the multiple H-bonding interactions with the surface silanols together with neighboring amine. Additionally, sCA(SiO^-/NH_3^+) was shown to be formed through an active proton exchange between carboxylic group and surface, showing the possibility that silanols participate in the CO_2 adsorption mechanism.

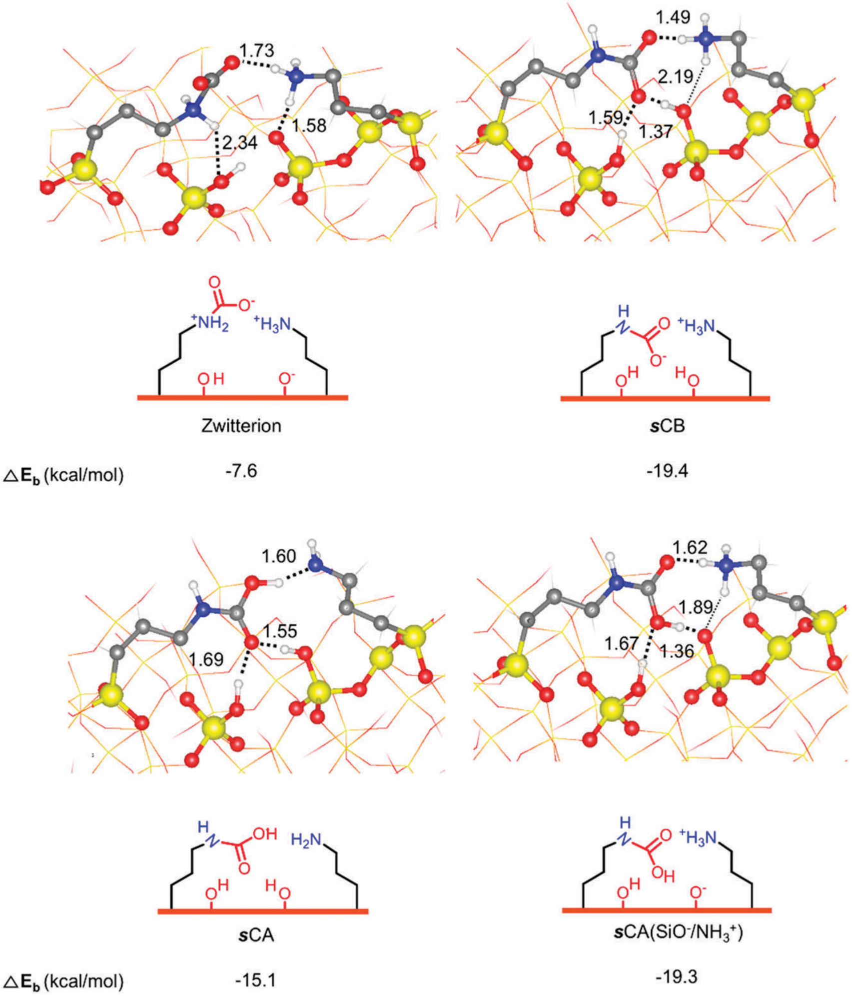

Fig. 2 Optimized structures of amine–CO_2 products: zwitterion, sCB (surface-bound carbamate–ammonium), sCA (surface-bound carbamic-acid), and sCA (SiO^-/NH_3^+) (surface bound siloxide–carbamic acid–ammonium complex). The CO_2 binding energy is denoted by ΔE_b. Color codes: blue = nitrogen, gray = carbon, yellow = silicon, red = oxygen, white = hydrogen. Hydrogen bond lengths are in Å.

It is generally accepted that a proton transfer is an essential step in the CO_2 adsorption process using amines or amine derivatives and thus must be facilitated through either the second amine or a protic molecule in the medium, such as an alcohol, for example.[30,40] Because the silanol group is considered as a protic group and the amine–CO_2 products can be bound to the surface through multiple H-bonding, possible surface effects could exist during the reaction process. Thus, we examined the possible reaction pathways that explicitly involve the silica surface in the amine–CO_2 binding reaction.

Energetics of the surface involved mechanism (SurfM) is presented in Fig. 3 and the schematic representations of reaction intermediates and transition states are shown in Fig. 4. First, a CO_2 molecule is adsorbed to the amine physically and then reacts to form a zwitterion, while the other amine accepts a proton from the surface forming the zwitterion–ammonium pair, leaving the surface silanol in a deprotonated state of siloxide. This finding is somewhat different from existing studies, where the ammonium is thought to be formed through the proton abstraction from neighboring amine. In a recent study, it has been shown that the ammonium formation can take place even in the absence of CO_2 with the amine protonating the silanol group, thus demonstrating that silanols are able to exchange protons with the functionalized molecules.[15,34] The 2nd transition state (I-TS2) is for proton migration between the two silanol moieties, namely, between silanol and siloxide (SiO^-). Then, proton of the zwitterion migrates to siloxide ion on the surface and the carbonyl group (–COO) of carbamate is rearranged to make H-bonds with the two silanols in the 3rd transition state (I-TS3) with an activation energy of 8.1 kcal mol^{-1} as the rate determining step. Then, the facile formation of sCA(SiO^-/NH_3^+) from sCB is expected with a kinetic energy barrier of 0.6 kcal mol^{-1}. Additionally, the calculated activation barrier energy from sCB to sCA is 5.1 kcal mol^{-1}. These results show that sCA(SiO^-/NH_3^+) is likely to form rather than sCA at the silanol interface. We have also evaluated kinetic barriers for InterM mechanism without surface involvement for comparison (black line in Fig. 3 and Fig. S4, ESI†). The calculated energy barrier for the InterM is found to be 12.7 kcal mol^{-1} (II-TS), which shows good agreement with previous results (11.9[59] and 15.3[40] kcal mol^{-1}). Indeed, the

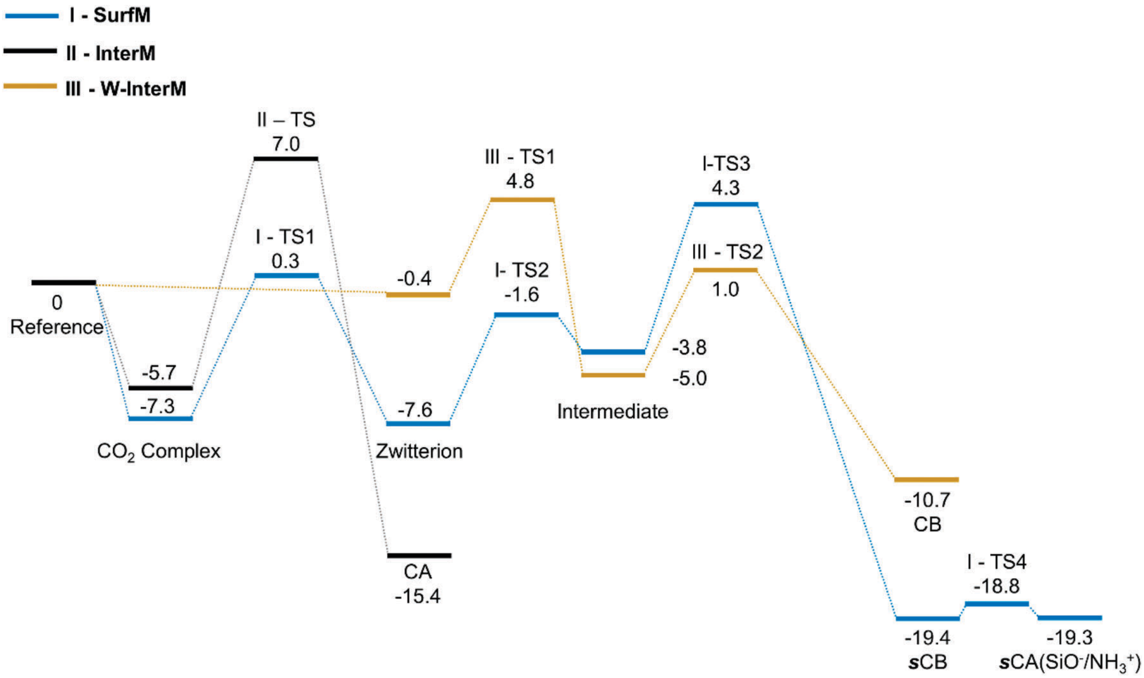

Fig. 3 The energy profile of three different CO_2 binding mechanisms (surface mechanism (SurfM), intermolecular mechanism (InterM), and water assisted intermolecular mechanism (W-InterM)) are presented.

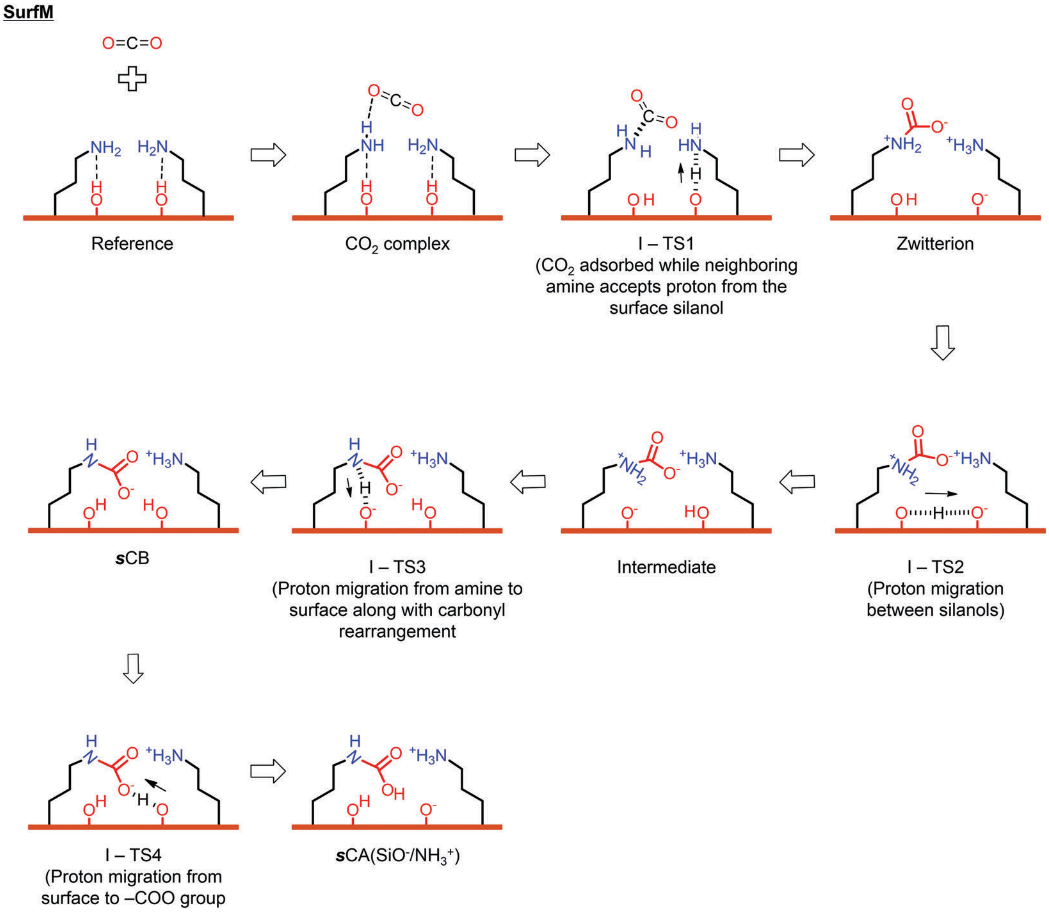

Fig. 4 Schematics of intermediates/transition state structures for surface mechanism (SurfM).

surface promotes the key proton transfer step by 4.6 kcal mol^{-1} compared to conventional intermolecular CO_2 capture mechanism.

Next, we considered the possibility of water assisting CO_2 capture process because the power plant flue gases always contain water vapor. Thus, we examined the water effect on InterM to see how it affects the activation barrier by employing the molecular model in the absence of silica surface. Fig. S5 (ESI†) shows the various pathways for the active role of water molecules as proton transfer bridges for the formation of amine–CO_2 products in a manner similar to that of the silica surface. The calculations showed that adding two and three water molecules lowered the activation energy from 12.7 (gas phase) to 6.0 (two water molecules) and 5.2 (three water molecules) kcal mol^{-1}, respectively (Fig. S7, ESI†). Since there is a small activation energy change as the number of water molecules increases from two to three, we used the two water molecules model as a representative water assisted InterM (W-InterM) in this study for all remaining cases due to the large computational cost of using 3 water molecules. Hence, the two water molecules assisted path is shown as W-InterM in Fig. 3 (path III, drawn in yellow line), with schematics shown in Fig. 5. The 1st TS (III-TS1) from the zwitterion is the concerted four-proton migration step, where H migrates from N of zwitterion to water molecule and carboxylate becomes carboxylic acid. Then, the CA donates a proton to a nearby amine to become CB and this step is the rate determining step with the activation energy of 6.0 kcal mol^{-1}. This mechanism supports the aforementioned assumption that CA is formed first and then the CB is constructed.

We also searched for a possible water effect on SurfM (W-SurfM) (Fig. S9 and S10, ESI†). In the presence of water, H-bonding occurred on both the deprotonated siloxide and the carbonyl group of carbamate and hence, we obtained a lowered activation energy by 1.5 kcal mol^{-1} due to the stabilization of the transition state *via* H-bonding with water. When water participates in the capture process actively, by mediating proton transfer, the activation barrier was interestingly raised by 6.6 kcal mol^{-1}. We find that this observation is due to an extra water molecule on SurfM positioned such that the H of nitrogen and O of water is 1.86 Å, which is somewhat elongated compared to that (the distance between H of nitrogen and the

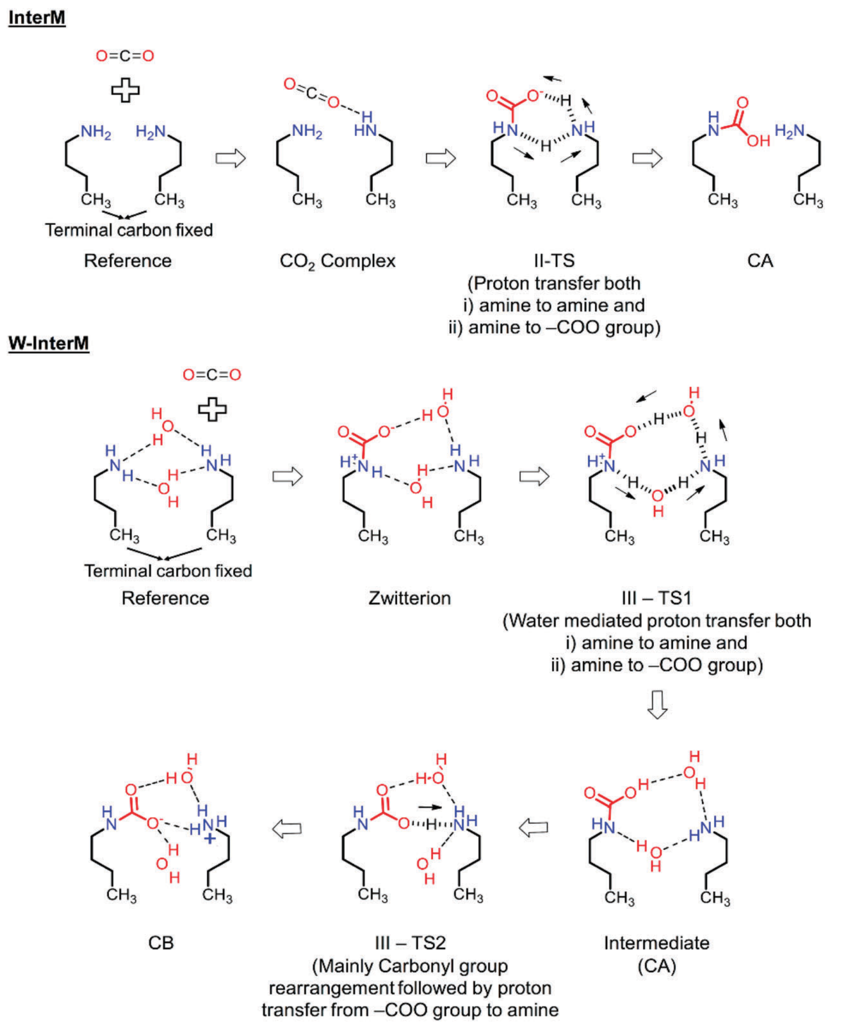

Fig. 5 Schematics of intermediates/transition state structures for both intermolecular mechanism (InterM) and water assisted intermolecular mechanism (W-InterM).

oxygen of siloxide) in the dry state SurfM intermediate (1.66 Å). Therefore effect of water seems less important in the reaction mechanism of SurfM (since surface silanol groups already play a similar role), while water has a significant effect in case of InterM.

Additionally, we further elaborated the water effect by employing the implicit solvent environment to compare the stability of the carbamate product (CB) in both W-InterM and SurfM in the solvent condition. The calculated surfM CB (sCB) energy in the solvated state is -19.7 kcal mol^{-1}, which is very similar to that in the dry state (-19.4 kcal mol^{-1}). Moreover, the solvated W-InterM CB is -15.8 kcal mol^{-1}, energetically more stabilized compared to that of dry condition (-10.7 kcal mol^{-1}). This overall energy shows that solvated sCB is more stable by -3.9 kcal mol^{-1} compared to the solvated W-InterM.

Comparing the reaction mechanism and energetics, there exists a similarity between surface-assisted and water-assisted pathways. First, the formation of ionic products (zwitterion and carbamate) was observed in both SurfM and W-InterM. The presence of water molecules around the carboxylate moiety stabilizes ionic species even in gas phase, suggesting that silanols on the SiO_2 surface and water play a similar role of stabilizing the ionic structures through multiple H-bonding. Second, the kinetic barrier of W-InterM path shows comparable barrier (6.0 kcal mol^{-1}) to that of the SurfM (8.1 kcal mol^{-1}) in the proton-donation step of the zwitterion. Water plays a catalytic role by actively participating in intermolecular proton relays between amine to amine as well as amine to carboxylate moieties, similar to the silanol groups on the silica surface. Collectively, these results indicate that SurfM is the most favorable path in dry conditions, while in humid conditions, both SurfM and water-assisted InterM mechanisms are plausible depending on the local surroundings such as amine density, dispersity of silanol groups on the surface or the accessibility of water molecules to amines on adsorbent.

We note that the present finding in which the support material itself is actively involved in the CO_2 capture process of the amine-functionalized solid sorbent is in line with recent reports on the amine-anchored MOF-74.[61] In the latter example, CO_2 was revealed to be captured by the cooperative mechanism of the anchored amine and the open metal sites of the support MOF framework to form carbamate–ammonium products, and carbamate–ammonium product was stabilized by the reactive open metal sites of the MOF-74. On the basis of the present finding, we further suggest that it might be possible that the open metal sites in MOF-74 support also played a catalytic role in CO_2 capture to lower the activation barrier of the proton migration of the amines.

Conclusions

It is demonstrated that silanol groups on silica surface can actively participate in the CO_2 capture process through a facile proton transfer reaction with the amine group. The calculations show that surface proton migration is the main proton transfer process in dry condition. Moreover, when water molecules are present under humid conditions, water can act as a proton transfer bridge and the activation barrier is reduced to as low as that obtained in the surface mechanism. Thus, it is likely that the surface mechanism will be prominent in the dry condition, but in the humid condition, both surface- and water-assisted intermolecular mechanism is likely to occur. This finding enlightens us to study the nature of amine–CO_2 reaction mechanism on the amine-anchored protic support, and offers physical insights to further optimize the density and acidity of silanols on incorporating different functional groups on the surface of silica to facilitate the proton transfer.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was supported by Korea CCS R&D Center (NRF-2014M1A8A1049256). J. P. was partly supported by NRF Korea (NRF-2015R1D1A4A01018697). Generous computing time from KISTI is gratefully acknowledged.

References

1 G. T. Rochelle, *Science*, 2009, **325**, 1652–1654.
2 R. S. Haszeldine, *Science*, 2009, **325**(5948), 1647.
3 R. V. Siriwardane, M.-S. Shen, E. P. Fisher and J. Losch, *Energy Fuels*, 2005, **19**(3), 1153–1159.
4 M. R. Hudson, W. L. Queen, J. A. Mason, D. W. Fickel, R. F. Lobo and C. M. Brown, *J. Am. Chem. Soc.*, 2012, **134**(4), 1970–1973.
5 S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870.
6 K. Sumida, D. L. Rogow, J. A. Mason, T. M. Mcdonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.
7 W. L. Queen, M. R. Hudson, E. D. Bloch, J. A. Mason, M. I. Gonzalez, J. S. Lee, D. Gygi, J. D. Howe, K. Lee, T. A. Darwish, M. James, V. K. Peterson, S. J. Teat, B. Smit, J. B. Neaton, J. R. Long and C. M. Brown, *Chem. Sci.*, 2014, **5**, 4569–4581.
8 T. C. Drage, J. M. Blackman, C. Pevida and C. E. Snape, *Energy Fuels*, 2009, **23**(5), 2790–2796.
9 G. Sethia and A. Sayari, *Energy Fuels*, 2014, **28**(4), 2727–2731.
10 R. A. Khatri, S. S. C. Chuang, Y. Soong, M. Gray, R. V. December, V. Re, M. Recei and V. May, *Energy Fuels*, 2006, **196**, 1514–1520.
11 X. Xu, C. Song, B. G. Miller and A. W. Scaroni, *Ind. Eng. Chem. Res.*, 2005, **44**, 8113–8119.
12 R. Serna-Guerrero, E. Da'na and A. Sayari, *Ind. Eng. Chem. Res.*, 2008, **47**(23), 9406–9412.
13 Z. Bacsik, R. Atluri, A. E. Garcia-Bennett and N. Hedin, *Langmuir*, 2010, **26**(12), 10013–10024.
14 Z. Sun, M. Fan and M. Argyle, *Ind. Eng. Chem. Res.*, 2011, **50**, 11343–11349.

15 Z. Bacsik, N. Ahlsten, A. Ziadi, G. Zhao, A. E. Garcia-Bennett, B. Martín-Matute and N. Hedin, *Langmuir*, 2011, **27**(17), 11118–11128.

16 Y. G. Ko, S. S. Shin and U. S. Choi, *J. Colloid Interface Sci.*, 2011, **361**, 594–602.

17 S. A. Didas, A. R. Kulkarni, D. S. Sholl and C. W. Jones, *ChemSusChem*, 2012, **5**, 2058–2064.

18 N. A. Brunelli, S. A. Didas, K. Venkatasubbaiah and C. W. Jones, *J. Am. Chem. Soc.*, 2012, **134**(34), 13950–13953.

19 M. A. Alkhabbaz, P. Bollini, G. S. Foo, C. Sievers and C. W. Jones, *J. Am. Chem. Soc.*, 2014, **136**(38), 13170–13173.

20 M. Jahandar Lashaki, H. Ziaei-Azad and A. Sayari, *ChemSusChem*, 2017, **10**(20), 4037–4045.

21 H. A. Patel, J. Byun and C. T. Yavuz, *ChemSusChem*, 2017, **10**(7), 1303–1317.

22 A. Danon, P. C. Stair and E. Weitz, *J. Phys. Chem. C*, 2011, **115**(23), 11540–11549.

23 C. S. Srikanth and S. S. C. Chuang, *J. Phys. Chem. C*, 2013, **117**(18), 9196–9205.

24 W. C. Wilfong, C. S. Srikanth and S. S. C. Chuang, *ACS Appl. Mater. Interfaces*, 2014, **6**(16), 13617–13626.

25 S. A. Didas, M. A. Sakwa-Novak, G. S. Foo, C. Sievers and C. W. Jones, *J. Phys. Chem. Lett.*, 2014, **5**(23), 4194–4200.

26 Y. Matsuzaki, H. Yamada, F. A. Chowdhury, T. Higashii and M. Onoda, *J. Phys. Chem. A*, 2013, **117**(38), 9274–9281.

27 K. Iida and H. Sato, *J. Phys. Chem. B*, 2012, **116**(7), 2244–2248.

28 B. Arstad, R. Blom and O. Swang, *J. Phys. Chem. A*, 2007, **111**(7), 1222–1228.

29 T. Davran-Candan, *J. Phys. Chem. A*, 2014, **118**(25), 4582–4590.

30 B. Han, C. Zhou, J. Wu, D. J. Tempel and H. Cheng, *J. Phys. Chem. Lett.*, 2011, **2**(6), 522–526.

31 C. A. Guido, F. Pietrucci, G. A. Gallet and W. Andreoni, *J. Chem. Theory Comput.*, 2013, **9**(1), 28–32.

32 H.-B. Xie, N. He, Z. Song, J. Chen and X. Li, *Ind. Eng. Chem. Res.*, 2014, **53**(8), 3363–3372.

33 L. Pinto, L. Mafra and M. Guil, *Chem. Mater.*, 2011, **23**, 1387–1395.

34 M. W. Hahn, J. Jelic, E. Berger, K. Reuter, A. Jentys and J. A. Lercher, *J. Phys. Chem. B*, 2015, 1988–1995.

35 A. Danon, P. Stair and E. Weitz, *J. Phys. Chem. C*, 2011, **115**, 11540–11549.

36 M. B. Yue, L. B. Sun, Y. Cao, Z. J. Wang, Y. Wang, Q. Yu and J. H. Zhu, *Microporous Mesoporous Mater.*, 2008, **114**(1), 74–81.

37 L. Wang and R. T. Yang, *J. Phys. Chem. C*, 2011, **115**, 21264–21272.

38 K. C. Kim, E. G. Moschetta, C. W. Jones and S. S. Jang, *J. Am. Chem. Soc.*, 2016, **138**(24), 7664–7672.

39 D. Thirion, V. Rozyyev, J. Park, J. Byun, Y. Jung, M. Atilhan and C. T. Yavuz, *Phys. Chem. Chem. Phys.*, 2016, **18**(21), 14177–14181.

40 S. A. Didas, R. Zhu, N. A. Brunelli, D. S. Sholl and C. W. Jones, *J. Phys. Chem. C*, 2014, **118**, 12302–12311.

41 A. Ö. Yazaydın, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis and R. Q. Snurr, *Chem. Mater.*, 2009, **21**(8), 1425–1430.

42 A. Sayari and Y. Belmabkhout, *J. Am. Chem. Soc.*, 2010, **132**(18), 6312–6314.

43 P. J. E. Harlick and A. Sayari, *Ind. Eng. Chem. Res.*, 2007, **46**(2), 446–458.

44 J. Lauwaert, E. G. Moschetta, P. Van Der Voort, J. W. Thybaut, C. W. Jones and G. B. Marin, *J. Catal.*, 2015, **325**, 19–25.

45 V. E. Collier, N. C. Ellebracht, G. I. Lindy, E. G. Moschetta and C. W. Jones, *ACS Catal.*, 2016, **6**(1), 460–468.

46 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**(1), 15–50.

47 B. Hammer, L. B. Hansen and J. K. Nørskov, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**(11), 7413–7421.

48 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**(15), 154104.

49 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**(7), 1456–1465.

50 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**(24), 17953–17979.

51 G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901–9904.

52 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2008, **41**(3), 653–658.

53 M. L. Schlegel, K. L. Nagy, P. Fenter and N. C. Sturchio, *Geochim. Cosmochim. Acta*, 2002, **66**, 3037–3054.

54 A. Rimola, D. Costa, M. Sodupe, J.-F. Lambert and P. Ugliengo, *Chem. Rev.*, 2013, **113**, 4216–4313.

55 M. Ide, M. El-Roz, E. De Canck, A. Vicente, T. Planckaert, T. Bogaerts, I. Van Driessche, F. Lynen, V. Van Speybroeck, F. Thybault-Starzyk and P. Van Der Voort, *Phys. Chem. Chem. Phys.*, 2013, **15**(2), 642–650.

56 T. C. dos Santos, S. Bourrelly, P. L. Llewellyn, J. W. de, M. Carneiro and C. Machado Ronconi, *Phys. Chem. Chem. Phys.*, 2015, **17**(16), 11095–11102.

57 K. Sim, N. Lee, J. Kim, E.-B. Cho, C. Gunathilake and M. Jaroniec, *ACS Appl. Mater. Interfaces*, 2015, **7**(12), 6792–6802.

58 J. E. Crooks and J. P. Donnellan, *J. Chem. Soc., Perkin Trans. 2*, 1989, 331–333.

59 K. Li, J. D. Kress and D. S. Mebane, *J. Phys. Chem. C*, 2016, **120**(41), 23683–23691.

60 A. Rimola, M. Sodupe, S. Tosoni, B. Civalleri and P. Ugliengo, *Langmuir*, 2006, **22**, 6593–6604.

61 T. M. McDonald, J. a. Mason, X. Kong, E. D. Bloch, D. Gygi, A. Dani, V. Crocellà, F. Giordanino, S. O. Odoh, W. S. Drisdell, B. Vlaisavljevich, A. L. Dzubak, R. Poloni, S. K. Schnell, N. Planas, K. Lee, T. Pascal, L. F. Wan, D. Prendergast, J. B. Neaton, B. Smit, J. B. Kortright, L. Gagliardi, S. Bordiga, J. a. Reimer and J. R. Long, *Nature*, 2015, **519**, 303–308.