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Direct Air Capture of CO_2 with an Amine Resin: A Molecular Modeling Study of the Deactivation Mechanism by CO_2

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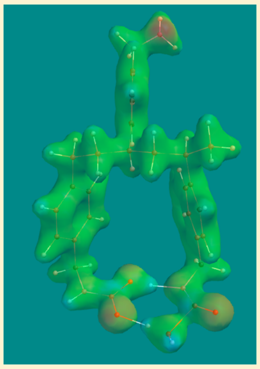
S *Supporting Information*

ABSTRACT: Since 2012, Lewatit R VP OC 1065 was reported as a promising material for direct air capture of CO_2. However, deactivation at a high pressure of CO_2 at 120 °C was reported with detrimental effects on its application. In this study, using density functional theory calculations, a quantitative description of the deactivation mechanism in the presence of CO_2 is presented. Deactivation by CO_2 follows a three-step mechanism. The first step in deactivation of the resin is self-catalyzed formation of a carbamic acid from an amine group and CO_2. The second step is decomposition of a carbamic acid to an isocyanate as the rate-determining step with an activation barrier of 144.4 kJ/mol. The third step is the H_2O-catalyzed addition of a benzyl amino group to the isocyanate, yielding an urea species, responsible for deactivation. However, the process can be made reversible by optimizing H_2O and CO_2 concentration and temperature. The identified deactivation mechanism quantitatively explains the differences between experimental CO_2 sorption data and the earlier reported dual site Langmuir model.



INTRODUCTION

Direct air capture of CO_2 (DAC CO_2) will become an unavoidable option and tool for CO_2 capture (and utilization) in general, as small point (transport, residential) emissions of CO_2 account for more than 40% of the U.S. CO_2 emissions.[1,2] In 2012 the polymeric resin Lewatit R VP OC 1065 was reported as a promising material for direct air capture of CO_2 with respect to aspects like rate of CO_2 uptake, limited H_2O uptake, CO_2 capacity, and CO_2 desorption under favorable conditions and energy requirements.[2,3] In 2017, a molecular modeling study was reported wherein the CO_2 capturing reactions of the polymeric resin Lewatit R VP OC 1065 were identified and quantitatively described in accordance with experimental data.[4] In 2017, Yu et al.,[5] reported significant oxidative degradation above 70 °C in air and, surprisingly, above 120 °C degradation in concentrated dry CO_2. Both types of deactivation in principle are detrimental for its practical application. Thus, determination of the reaction mechanisms of both types of deactivation is of utmost importance. In this molecular modeling study, various reactions on the resin in the presence of CO_2 are investigated. Oxidative degradation reactions will be reported separately.

MOLECULAR MODELING

All molecular modeling studies were performed using Wave function's Spartan '18 suite.[6] Molecular mechanics (MMFF) was used to explore the physisorption complexes of CO_2 with the previously obtained model for Lewatit R VP OC 1065, the saturated trimer of 4-aminomethyl vinylbenzene.[4] Results obtained with molecular mechanics were used as starting structures for various quantum chemical calculations wherein physisorption and particularly chemical reactions were investigated further. All structures were fully optimized using density functional theory (DFT) B3LYP/6-31-G*. Transition states were identified and characterized using their unique imaginary vibrational frequency or internal reaction coordinate (IRC).[9] Reaction enthalpies and activation barriers were calculated using total energies and enthalpy corrections. Entropy corrections were generally not used because of the huge simplifications of the QM-systems. However, in some specific cases the entropy contribution is explicitly mentioned.

RESULTS AND DISCUSSION

As mentioned above, in 2017 Yu et al.[5] reported degradation of Lewatit R VP OC 1065 in concentrated dry CO_2 above 120 °C. According to that study, formation of urea species seems to be responsible for the observed loss of CO_2 capacity. Already in 2012 the formation of urea species on (alkyl) amine containing resins, and the subsequent loss of CO_2 capacity, was reported in an extended experimental study of Sayari et al.[7] Furthermore, in 2014 Didas et al.[8] reported CO_2 induced degradation of primary amine-grafted mesoporous SBA-15 silica adsorbents with various alkyl linker lengths. This jointly experimental and computational study concluded that carbamic acid catalyzed formation of isocyanate from a carbamic acid precursor is the rate limiting step in the subsequent formation of a urea species from the isocyanate, as a reactive intermediate, and an amine. The activation barrier for *N*-ethyl carbamic acid catalyzed formation of an isocyanate

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from *N*-ethyl carbamic acid yielded 87.4 kJ/mol using CCSD(T)/6-311+G**//B3LYP/6-311+G**. The latter system was used as a smaller model for neighboring alkyl amines on mesoporous SBA-15 silica.

In the above-mentioned molecular modeling study on Lewatit R VP OC 1065 describing the CO_2 capturing reactions,[4] it was found that in the resin alternating benzyl amine groups are in close vicinity of each other leading to two catalytic reactions: amine-H_2O and amine catalyzed formation of the corresponding carbamic acid. A third CO_2 capturing reaction, carbamic acid catalyzed formation of a carbamic acid from an amine and CO_2, was considered not to be important at low (400 ppm) atmospheric CO_2 concentration due to the low complexation enthalpy for CO_2 of −2.9 kJ/mol at such a site. The two above-mentioned CO_2 capturing reactions show a complexation enthalpy for CO_2 of −19.1 and −19.8 kJ/mol, respectively. This leads to an approximately 1000 times higher equilibrium amount of CO_2 on these two sites compared to the third site. However, as the equilibrium amount of CO_2 will increase largely at a high CO_2 partial pressure (80% CO_2), this reaction will become very feasible as it has a very low activation barrier of 27.4 kJ/mol and a favorable reaction enthalpy of −45.0 kJ/mol.

Figure 1 shows the CO_2 physisorption complex of the carbamic acid amine (a), the transition state of the CO_2 capturing reaction (b), and the initial product of the reaction, the bis carbamic acid. The CO_2 complex (a) shows two rather weak H-bridges, one between a hydrogen of the benzyl amino group and the C═O of the carbamic acid, and one between the OH-group of the carbamic acid and the O═C of CO_2. In addition, there is an electrostatic interaction between the amine lone pair and the C from CO_2. It should be noted that the complex without CO_2 shows a (normal) much stronger H-bridge between the OH of the carbamic acid and amine lone pair of the neighboring benzyl amino group. The transition state (b) shows an imaginary frequency of i885 cm^{-1}, wherein simultaneously a hydrogen from the benzyl amino group is transferred to the C═O of the carbamic acid, and the hydrogen of the OH of the carbamic acid is transferred to the O═C of the CO_2 being captured. The bis carbamic acid shows the OH-group formed with the CO_2 captured still in antiposition, which is approximately 57 kJ/mol less stable, as the normal dimeric structure of the bis carbamic acid (a) shown in Figure 2.

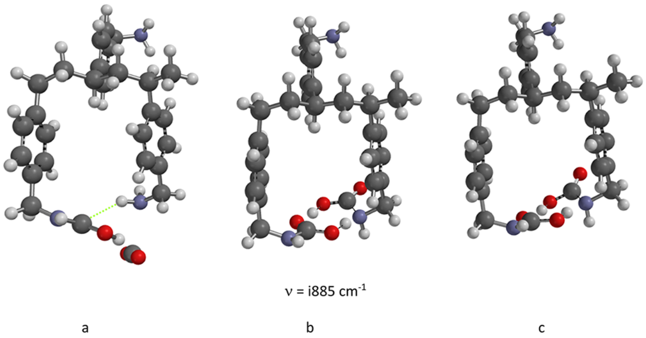

Figure 1. CO_2 physisorption complex of the carbamic acid amine (a), the transition state of the CO_2 capturing reaction (b), and the bis carbamic acid (c). Display: ball and spoke; B3LYP/6-31G*.

Figure 2 shows the “normal” bis carbamic acid complex (a). “Normal” refers to the well-known dimeric structure of carboxylic acids. The bis carbamic acid prereaction complex (b) shows H-bridges between the NH−amide and O═C−amide and between the two OH-groups of the carbamic acids. The prereaction complex is only 26.2 kJ/mol higher in enthalpy as the normal bis carbamic acid complex because the distance between alternating aromatic groups in (a) is not ideal for stabilization by *π*-stacking. The transition state for isocyanate formation (c) is a rather late one with an imaginary frequency of i130 cm^{-1}, wherein the amide hydrogen, and the leaving OH-group of the carbamic acid, almost completely have been transferred to yield the isocyanate and H_2O. The activation barrier is 144.4 kJ/mol and the overall process turns out be endothermic by 109.0 kJ/mol. Thus, the isocyanate is a reactive intermediate.

The next step in the formation of an urea species would be the addition of a benzyl amino group to the isocyanate group as formed above. The benzyl amino group can be available on the next alternating position of the isocyanate group. Figure 3 shows the first step in the process, H_2O catalyzed addition of the amine to the isocyanate group. H_2O, formed as a the side product in the formation of the isocyanate in the former step, is still present in the amine isocyanate complex (a). It now acts as a proton transfer catalyst in the transition state for addition of the amine to the isocyanate (b). The transition state (b) shows an imaginary frequency of i1433 cm^{-1} and the activation barrier is 52.8 kJ/mol. The initial product is the enol tautomer of the cyclic urea trimer, still complexed with H_2O (c).

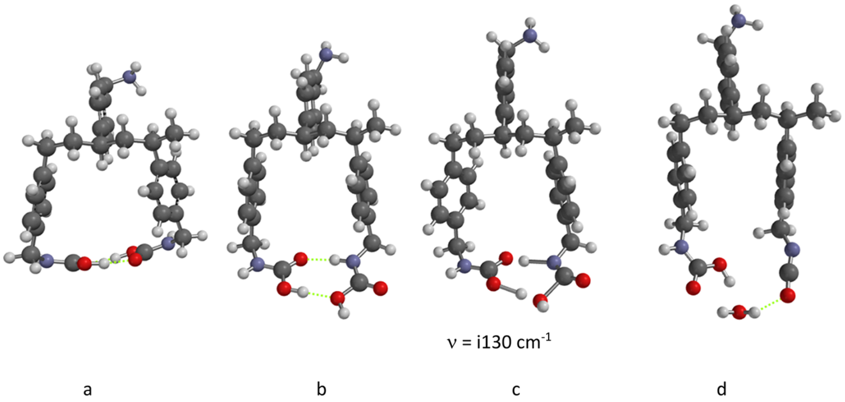

Figure 2. Bis carbamic acid complex (a), the bis carbamic acid prereaction complex (b), the transition state for isocyanate formation (c), and the product carbamic acid isocyanate H_2O complex (d). Display: ball and spoke; B3LYP/6-31G*.

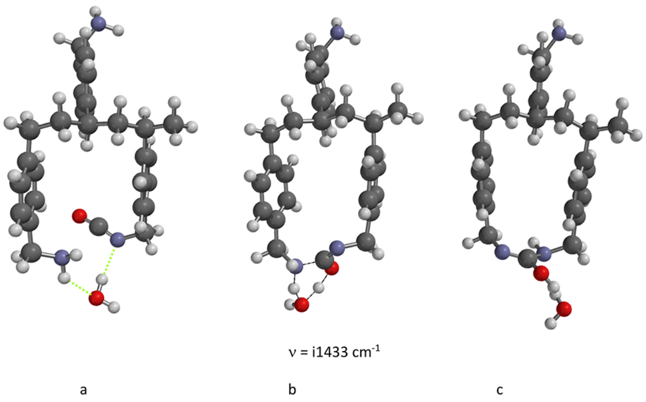

Figure 3. Amine isocyanate complex (a), the transition state for H_2O catalyzed amine to isocyanate addition (b), the (enol) urea H_2O complex (c). Display: ball and spoke; B3LYP/6-31G*.

A similar H_2O catalyzed process with an activation barrier of 16.7 kJ/mol only finally leads to the cyclic urea trimer in its keto form. The overall enthalpy change of the net formation of the cyclic urea and H_2O from an amine carbamic acid complex is −0.6 kJ/mol, built up from the following:

(1) The formation of the bis carbamic acid at high CO_2 concentration: (−45.0 kJ/mol);

(2) The formation of the isocyanate and H_2O: (+109.0 kJ/mol);

(3) The formation of the cyclic urea and H_2O: (−64.6 kJ/mol).

Thus, the formation of urea species is a macroscopic equilibrium reaction which in principle could be reversed. This is in line with the experimental finding of Yu et al.[5] that treatment with wet N_2 recovers 7% CO_2 uptake capacity of the initially lost CO_2 uptake of 9%. However, the cyclic urea H_2O complex (c), easily loses H_2O at 120 °C, as its enthalpy gain is +12.2 kJ/mol only while its entropy gain is −42.8 kJ/mol, yielding −30.6 kJ/mol for the ΔG of the overall reaction. Thus, under dry conditions at 120 °C, the formation of urea could almost go to completion because for the reverse reaction H_2O, as the necessary catalyst, is removed from the urea resin sites.

From the results of Yu et al.,[5] a rough estimate of the activation barrier for the degradation reaction can be obtained too. Assuming that the CO_2 related degradation of Lewatit R VP OC 1065 at the surface of the resin particles initially is not seriously hindered by mass transfer limitation, the reaction rate can be expressed as $k = k_0 \times e^{-\mathrm{Ea}/RT}$ with $k_0 = k_\mathrm{B} \times T/h = 8.2 \times 10^{18}\ \mathrm{s}^{-1}$ at 393 K (120 °C). At 120 °C, a loss of 9% CO_2 adsorption capacity was observed under continuous 80% CO_2 exposure for 72 h. Substituting all data in the rate expression results in an estimate for E_a of 145.5 kJ/mol. The latter is in excellent agreement with the computationally obtained value of 144.4 kJ/mol. Finally the use of these data quantitatively explains the deviations from the dual site Langmuir isotherm model[4] at high CO_2 pressures and high T. At 120 °C and pCO_2 = 81 000 Pascal, the dual site Langmuir isotherm model predicts a CO_2 adsorption of 1.71 mol CO_2/kg resin where experimentally 1.55 mol CO_2/kg resin is observed which corresponds to the 9% loss observed by Yu et al.[5] exactly.

Alternatively the effect of a high CO_2 concentration on the resin at a high temperature was investigated by trying CO_2 itself as a catalyst. This would offer a direct explanation of the phenomena observed too. Figure 4 shows the transition states of two possible options: the transition state for CO_2 catalyzed formation of an isocyanate (a) and the transition state for CO_2 catalyzed addition of an amine to a carbamic acid. While taking up an H_2O molecule, CO_2 is converted in both processes temporarily into H_2CO_3 which in turn easily decomposes into CO_2 and H_2O, thus making it net CO_2-catalysis. The latter processes show low activation barriers, however the transition state for CO_2 catalyzed formation of an isocyanate (a) shows an activation barrier of 187.4 kJ/mol and the transition state for CO_2 catalyzed addition of an amine to a carbamic acid shows an activation barrier of 163.0 kJ/mol.

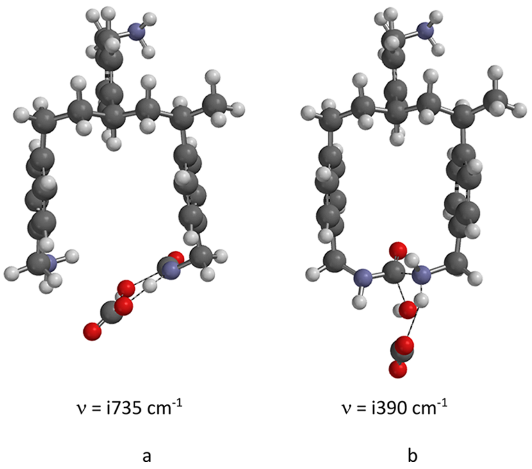

Figure 4. The transition state for CO_2 catalyzed formation of an isocyanate (a) and the transition state for CO_2 catalyzed addition of an amine to a carbamic acid. Display: ball and spoke; B3LYP/6-31G*.

Applying the same formula as above, an activation barrier of 163.0 kJ/mol would lead to 0.05% loss of CO_2 capacity of the resin at 120 °C under continuous 80% CO_2 exposure for 72 h; this rules out these options.

■ CONCLUSIONS

This molecular modeling study toward experimentally observed formation of urea species and subsequent loss of CO_2 capacity of Lewatit R VP OC 1065 at high CO_2 pressure and temperature, shows the following:

(1) Carbamic acid catalyzed formation of a carbamic acid from an amine and CO_2 is a very feasible reaction at high CO_2 pressure (80% CO_2) and high temperature (120 °C).

(2) The resulting product, wherein two alternating carbamic acids groups are within close vicinity undergoes carbamic acid catalyzed decomposition at high temperature to an isocyanate as a reactive intermediate and H_2O. This is the rate limiting step with an activation barrier of 144.4 kJ/mol which is in excellent agreement with an estimate from experimental data (145.5 kJ/mol).

(3) The thus formed highly reactive isocyanate undergoes H_2O catalyzed addition of an amine from an alternating benzyl amine group to yield a cyclic urea species eventually which easily can lose its complexed H_2O molecule.

(4) Whereas the reaction enthalpy of urea formation indicates a macroscopic equilibrium reaction, the actual process conditions (dry or wet) determine the level of (indirectly) CO_2-induced loss of CO_2 adsorption capacity at high temperature of Lewatit R VP OC 1065.

(5) The experimentally observed and computationally explained loss of CO_2 capacity at high CO_2 pressure and high temperature quantitatively explains the observed differ-

ences between experimental CO_2 sorption data and the previously reported dual site Langmuir model.

(6) The computational data obtained can be used in a kinetic model to optimize both CO_2 adsorption and desorption conditions with respect to (partial) pressure of H_2O and CO_2 to minimize overall energy consumption and resin deactivation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b02637.

Molecular modeling data (XLSX)
All molecular structures and how to use the molecular structures (ZIP)
Additional information (PDF)

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Notes

The author declares no competing financial interest.

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