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# Design of Effective Zeolite Catalysts for the Complete Hydrogenation of $CO_2$

Bun Chan* and Leo Radom*

*School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia*

Received January 22, 2006; E-mail: chan_b@chem.usyd.edu.au; radom@chem.usyd.edu.au

Carbon dioxide has been widely regarded as a potent greenhouse gas, linked to the problem of global warming. As a result, disposal of $CO_2$ has been a topic of intense research and a subject of discussion not only from a scientific but also from an ecopolitical point of view.[1] One possible solution that has received considerable attention is the *sequestering* of $CO_2$ in geological structures, but an attractive alternative is *renewal* of $CO_2$, for example through catalytic hydrogenation. Among various products that could be derived from hydrogenation of $CO_2$, methanol holds a central position, as it plays an important role among industrial chemicals. Methanol is normally produced from synthesis gas ($H_2$/CO), employing a catalyst that generally contains Cu and a mixture of oxides such as $ZnO/Al_2O_3$.

In this communication, we use theoretical calculations to help design zeolites that might efficiently convert $CO_2$ to methanol, and thus replace a waste chemical by one of considerable value.[2] In addition, we aim to do this without transition metals or heavy metals, in contrast to the majority of hydrogenation reactions in chemical and biological systems for which the catalysts contain such metals.[3] Among previous experimental studies of transition-metal-free hydrogenation reactions, it has been found that both strong acids and strong bases can be used as catalysts for the hydrogenation.[4] It has also been demonstrated that zeolites catalyze the hydrogenation of alkenes.[5] There have also been several theoretical studies of hydrogenation reactions catalyzed by acids, bases, and zeolites.[6]

Zeolites represent a particularly attractive class among the transition-metal-free catalysts for hydrogenation, due to the existence of a large variety of natural/synthetic zeolites having a wide range of acid/base properties.[7] Zeolite catalysis generally involves acid-catalyzed reactions, with many industrial applications in petroleum refining, synfuels production, and petrochemical production. However, a number of base-catalyzed zeolite reactions have also been reported.[8] In this communication, we aim to exploit both the acidic and basic properties to create a zeolite with particularly effective bifunctional catalysis.

We employ quantum chemistry calculations to examine the zeolite-catalyzed, three-stage hydrogenation of $CO_2$ to methanol:

$$CO_2 + H_2 \rightarrow HCO_2H \qquad (A)$$

$$HCO_2H + H_2 \rightarrow CH_2(OH)_2 \rightarrow CH_2O + H_2O \qquad (B)$$

$$CH_2O + H_2 \rightarrow CH_3OH \qquad (C)$$

Only the concerted pathway is considered, as a previous study has found that the alternative stepwise mechanism in similar systems is less favorable.[6c] Standard ab initio molecular orbital theory and density functional theory calculations were carried out with the GAUSSIAN 03 program.[9,10]

We have chosen to explore the catalytic properties of the zeolite catalysts from a microscopic point of view, as simulated by the small clusters shown in Figure 1. It has been previously found that this type of model provides an adequate qualitative picture of chemical rearrangements that occur locally on the active site.[11] Indeed, our further calculations indicate that the qualitative trends obtained with these 4T-clusters are consistent with those calculated with larger 28T-clusters, while quantitatively the barriers are somewhat lower for the smaller system. We employ **1** as a model for a typical acidic zeolite catalyst such as H−ZSM-5. The other model systems **2**−**5**, selected from numerous possibilities that we have examined, illustrate the effect on the reaction barrier of various chemical compositional changes to the standard zeolite model **1**. Thus, **2** is the alkali metal analogue of **1**, while **3** and **4** have N and Ge incorporation, respectively. Recent theoretical studies have shown that amine-based zeolites have higher catalytic activity than the conventional analogue with O linkages.[12] It has also been demonstrated that the catalytic activity of zeolites for both acid- and base-catalyzed reactions can be improved by Ge incorporation.[13] To the best of our knowledge, a zeolite based on cluster **5** has not been previously investigated. The rationale for the design of model **5** is that the catalytic activity may be enhanced by combining several favorable features.

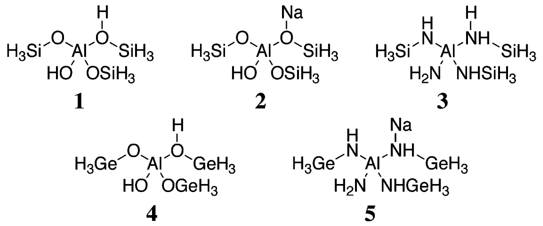

***Figure 1.*** Model zeolites employed in this study.

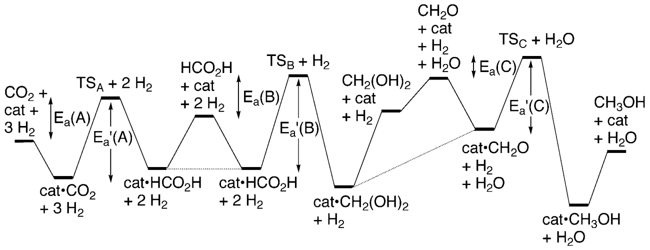

***Figure 2.*** Reaction profile for zeolite-catalyzed three-stage hydrogenation of $CO_2$ to methanol.

The general reaction profile for the sequence of reactions A−C is shown in Figure 2. Each hydrogenation reaction is characterized by a two-well energy profile. For instance, in reaction A, the $CO_2$ substrate forms a complex (cat•$CO_2$) with the zeolite catalyst. This complex reacts with $H_2$, proceeding via the transition structure $TS_A$ to form a complex (cat•$HCO_2H$) between the $HCO_2H$ product and the catalyst. The optimized structures for **1** and **2** and the complexes and TSs involved in the corresponding catalytic hydrogenation of $CO_2$ to form $HCO_2H$ (reaction A) are shown in Figure 3 as representative examples for species involved in the series of hydrogenation reactions.[14]

Table 1 presents the overall barriers ($E_a$), measured from the adjacent isolated substrate plus catalyst, and the central barriers

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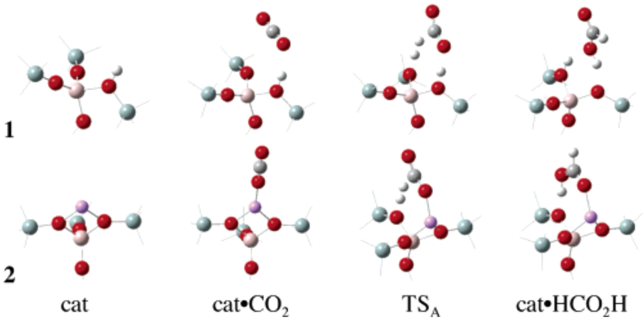

***Figure 3.*** Optimized structures for reaction intermediates and transition structures in reaction A involving catalysts **1** and **2**.

***Table 1.*** Overall ($E_a$) and Central ($E_a'$) Barriers for Zeolite-Catalyzed Hydrogenation Reactions (MP2/G3MP2Large, kJ $mol^{-1}$, 0 K)

| | Overall barrier ($E_a$) | | | Central barrier ($E_a'$) | | |
|---|---|---|---|---|---|---|
| catalyst | $CO_2$ | $HCO_2H$ | $CH_2O$ | $CO_2$ | $HCO_2H$ | $CH_2O$ |
| 1 | 148 | 107 | 61 | 174 | 151 | 115 |
| 2 | 112 | 108 | 66 | 142 | 183 | 119 |
| 3 | 139 | 134 | 96 | 162 | 168 | 125 |
| 4 | 127 | 105 | 61 | 156 | 159 | 106 |
| 5 | 67 | 56 | 17 | 103 | 120 | 74 |

($E_a'$), measured from the adjacent substrate−catalyst complex plus $H_2$, for each reaction. With only a few exceptions, the variation of $E_a'$ follows that of $E_a$, and the discussion is therefore focused on $E_a$ for simplicity. It is evident that the various catalysts have varying effects on the three hydrogenation reactions, that is, the three component reactions respond differently toward a change in the acid/base properties of the catalyst. For instance, while the use of **2** leads to a much lower $E_a(CO_2)$ compared with that using **1**, the $E_a$ values for the other two reactions catalyzed by **2** are somewhat higher than with **1**. The use of the amine-substituted zeolite **3** leads to an $E_a(CO_2)$ comparable to that with **1**. However, the $E_a$ values for hydrogenation of $HCO_2H$ and $CH_2O$ with **3** are substantially higher than those with **1**. The effects of Ge incorporation (**4**) on the $E_a$ values are similar to those of $Na^+$ incorporation (**2**), namely, lowering of $E_a(CO_2)$ relative to that with **1** while giving comparable $E_a$ values for the hydrogenation of $HCO_2H$ and $CH_2O$.

The changes in chemical composition from **1**, as illustrated by **2**−**4**, give moderate to substantial lowering of $E_a(CO_2)$. However, none of **2**−**4** are significantly more reactive toward hydrogenation of $HCO_2H$ and $CH_2O$ compared with **1**. It is thus quite remarkable to see that, when the individual changes in chemical composition between **1** and **2**−**4** are combined together to give **5**, this catalyst not only significantly lowers $E_a$ for the hydrogenation of $CO_2$ but also significantly lowers $E_a(HCO_2H)$ and $E_a(CH_2O)$. The lowering of $E_a$ (compared with **1**) is more prominent for the hydrogenation of $CO_2$ ($-78$ kJ $mol^{-1}$) than for the hydrogenation of $HCO_2H$ ($-51$ kJ $mol^{-1}$) and $CH_2O$ ($-43$ kJ $mol^{-1}$), but all are substantial. Importantly, both the $E_a$ and $E_a'$ values for the hydrogenation reactions catalyzed by **5** are all quite low, making a zeolite of this type an attractive target for an experimental investigation of the catalysis of $CO_2$ hydrogenation.

In conclusion, ab initio calculations on microscopic zeolite models present strong evidence that appropriate chemical modifications to ZSM-5 can lead to significantly lower energy barriers for catalytic hydrogenation reactions of $CO_2$, $HCO_2H$, and $CH_2O$. Zeolites incorporating $Na^+$ and Ge are more effective catalysts than conventional acidic zeolites for the hydrogenation of $CO_2$, but they do not enhance the hydrogenations of $HCO_2H$ and $CH_2O$. Amine-based zeolites, on their own, do not lead to significantly lower barriers for any of the three hydrogenation reactions. However, when combined with $Na^+$ and Ge incorporation, a dramatic improvement in catalytic activity is achieved. Although a zeolite based on −Ge−NH−Al− linkages is currently unknown, both zeolites with amine linkages and those with Ge incorporation have recently been synthesized.[15] This opens up the possibility of a new class of zeolite catalyst for hydrogenation reactions.

We are currently investigating the behavior of a wider range of zeolites and also are further probing the rationale behind the high catalytic activity of zeolites, such as **5**. We are also examining the effectiveness of our most promising catalyst **5** for a wide range of reactions.

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**Supporting Information Available:** GAUSSIAN 03 archive entries for B3-LYP/6-31+G(d,p)-optimized geometries of relevant equilibrium structures and transition structures, calculated MP2/G3MP2Large total energies, and the full citation for refs 1 and 9. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Frisch, M. J.; et al. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(10) Geometries were obtained at the B3-LYP/6-31+G(d,p) level of theory. Improved relative energies were obtained at the MP2/G3MP2Large level, with the incorporation of scaled (by 0.9806) zero-point vibrational energies (ZPVEs) derived from B3-LYP/6-31+G(d,p) frequencies.

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