

A Density Functional Theory Study of CO Adsorption on Cu-ZSM5 and Cu-Y

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Introduction

Dimethyl carbonate (DMC) and dimethoxy methane (DMM) are of commercial interest because they are good fuel additives and building blocks for organic synthesis. Both products can be produced using Cu-exchanged ZSM-5 and Y from a mixture containing O₂, CO, and CH₃OH. Experimental studies done in our research group [1,2] have shown that at identical reaction conditions, very different product selectivity, catalytic properties, and adsorption modes are observed for Cu-exchanged ZSM-5 and Y. Thus, for example, high DMC selectivity is observed for Cu-Y and high DMM selectivity is observed using Cu-ZSM-5. To understand the origins of these differences, we have carried out a theoretical analysis of density functional theory (DFT) of CO adsorption on Cu⁺ site in Cu-ZSM-5 and Cu-Y. The goal of this work is to establish how changes in the local structure of the Cu⁺ exchange center affects the electronic properties of isolated Cu⁺ cations and the strength of interaction of Cu⁺ with adsorbed CO.

Results and Discussions

Cluster method is used in this work to study CO adsorption. In order to distinguish the influence of difference zeolite structures, the terminal Si atoms were fixed in their crystallographic positions reported from experimental studies. Dangling bonds were saturated with H atoms located 1.5 Å from each Si atom oriented in the direction of the next T (tetrahedral) site. The geometry and energy calculations were performed using Beck's 3-parameter exchange functional and correlation of functional of Lee, Yang, and Parr (B3LYP), a hybrid DFT functional.

For CuZSM-5, various Cu⁺ sites including, I2, M5, M6, M7, Z5, and Z6, and different Al positions are explored. It is found that CO adsorption on CuZSM-5 is site-specific and depends on Al positions. When Cu⁺ is at the edge of the main and sinusoidal channels (I2 site), Cu⁺ is coordinated to two oxygen atoms of the Al tetrahedron before and after CO adsorption. CO binds strongly on I2 site and the calculated CO adsorption energy is in the range of 30 to 33 kcal/mol. When Cu⁺ sites in the center of a five- or six-membered ring of the main and sinusoidal channels (M5, M6, Z5, and Z6), significant Cu⁺ migration with Cu-O coordination number change before and after CO adsorption is observed. The calculated CO adsorption energy is in the range of 26 to 28 kcal/mol, less than I2 site. When Cu⁺ locates in the basket structures formed by two fused five-membered rings (M7), CO binds weakly with Cu⁺ and the calculated adsorption is 20.4 kcal/mol. In order to investigate Si/Al ratio effect on CO adsorption energy of CuZSM-5, two Si atoms are replaced by two Al atoms in M6, M7, and Z6 clusters. The calculated CO adsorption energy is found to decrease with decreasing Al/Si ratio

and between 18 to 25 kcal/mol.

For CuY, two types of Cu⁺ sites, II and III, are investigated. It is found that CO adsorbs strongly on site III, which located in the supercage near the four membered-rings. The calculated adsorption energy is 30.6 kcal/mol. CO binds weakly on site II, which is on top of the six-membered ring that connects the sodalite cage and supercage, and the calculated CO adsorption energy is 18.7 kcal/mol. Also, it is found that CO adsorption energy decreases with decreasing Al/Si ratio and a linear relationship between CO adsorption energy and Cu charge is found.

The geometries of the adsorption complex, the adsorption energies and CO stretching frequencies are calculated and compared with the available experimental studies of our research group and others as well. The agreement between the calculation results and experiments proved our choice of cluster models and computation methods. CO is found to adsorb less strongly on CuY than on CuZSM-5. DMC synthesis has been found to be first order on CO pressure, i.e., lower CO adsorption energy favors DMC production. Our calculation results explain the fact that the selectivity of DMC is higher on CuY than on CuZSM-5. This work sets the stage for the thorough understanding of Cu⁺ as the active site for DMC and DMM synthesis.

Reference

- [1] I.J. Drake, Y.H. Zhang, D. Briggs, B. Lim, T. Chau, A.T. Bell, *Journal of Physical Chemistry B* 110 (2006) 11654.
- [2] Y.H. Zhang, I.J. Drake, A.T. Bell, *Chemistry of Materials* 18 (2006) 2347.

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