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Insight into the formation mechanism and kinetics for the oxidative carbonylation of methanol to dimethyl carbonate over CuO catalyst: Effects of Cu valence state and solvent environment

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ABSTRACT

The formation mechanism and kinetics of dimethyl carbonate (DMC) via the oxidative carbonylation of methanol over Cu(II) catalyst have been investigated using density functional theory calculations under gas phase and solvent conditions. The results show that the preferred pathway of DMC formation in the gas phase is that via CO insertion into $(CH_3O)_2$ species, which is more favorable in kinetics than that via CO insertion into CH_3O; the rate-limiting step of DMC formation is CO insertion into $(CH_3O)_2$. Meanwhile, the kinetic results of DMC formation in the liquid phase show that the solvent can improve the catalytic activity of Cu(II) catalyst towards DMC formation in a liquid-phase slurry, especially in water. Moreover, the comparisons among different valence state Cu catalysts for the most favorable pathway of DMC formation indicate that Cu valence state has a significant effect on the formation mechanism of DMC. The calculated results can provide a clue to finely tune the catalytic activity of DMC formation over Cu-based catalyst using the valence state and solvent environments under the realistic conditions.

1. Introduction

Dimethyl carbonate (DMC) has been considered as a green chemical due to its high oxygen content, high dielectric constant, high solvency power, low viscosity and mild toxic [1–3]. For the synthesis of DMC, the various methods, the phosgenation of methanol, transesterification of urea, transesterification of EC and methanol, direct synthesis, oxidative carbonylation of methanol and so on, are proposed [4–10]. Among them, the oxidative carbonylation of methanol has been developed [11–22]; moreover, compared to other methods, the raw materials for the oxidative carbonylation of methanol are easily obtained from coal and natural gas [12,17,23,24]; further, the oxidative carbonylation of methanol is a thermodynamically favorable reaction [11,21,23], both the gas-phase [18,24–27] and liquid-phase methods [15,20] exist.

Up to now, the oxidative carbonylation of methanol is mainly carried out over CuCl catalyst. However, CuCl easily leads to the equipment corrosion and the catalyst deactivation due to Cl^- loss. Consequently, King et al. [19] discovered that chlorine was not necessary for Cu to catalyze the oxidative carbonylation of methanol. Thus, in order to avoid these problems, the free-chlorine Cu catalysts have been widely used, especially, Cu-exchanged zeolites is considered as one of the most potential catalysts [21,22,25,26,28–34], King [33] found that CuY zeolite exhibits good activity and selectivity for DMC formation without catalyst deactivation; moreover, Cu^+ ions are postulated to be the active species. Meanwhile, the mechanism for the oxidative carbonylation of methanol to DMC over Cu^+ species has been illustrated [11,22,31–34], for example, density functional theory (DFT) studies by Zheng and Bell [11] found that the molecularly adsorbed CH_3OH is oxidized by oxygen to either mono-methoxide or dimethoxide species; then DMC is formed from two distinct pathways: one is CO insertion into mono-methoxide to CH_3OCO, followed by its interaction with CH_3O to DMC; the other is CO insertion into dimethoxide to DMC. In addition, the mechanism and kinetics of oxidative carbonylation of methanol are also investigated employing DFT calculations over Cu_2O [31], $CuCl_2$–$PdCl_2$ bimetallic catalyst [35] and Cu(I)/β catalysts [36].

On the other hand, Wang et al. [16] prepared CuO–La_2O_3/activate carbon (AC) catalyst, which contained CuO and Cu_2O to provide Cu^+ and Cu^{2+} simultaneously; the results show CuO/Cu_2O could improve the stability and activity of the catalyst. Zhang et al. [37] found that CuO/AC performs a good catalytic activity for the oxidative carbonylation of methanol. Wang et al. [38] found that $PdCl_2$-$CuCl_2$ catalysts are more favorable than the single metal chloride catalysts. Tomishige et al. [39] suggested that $CuCl_2$/AC catalyst can promote the selectivity and activity of DMC formation through Cu-Cl-OH compounds. Sato

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et al. [40] showed that Cu(II)-polymer complexes exhibits considerable catalytic activity and stability for DMC synthesis. Unfortunately, up to now, to the best of our knowledge, the detailed mechanism for the oxidative carbonylation of methanol to DMC over Cu(II) catalyst is still unclear, and therefore the effects of Cu valence state on the reaction mechanism and kinetics are also unknown.

Further, the reaction environments might change the chemical characteristics and reaction kinetics, in which the solvent environment plays an important role [41–47]. When the liquid-phase method is used for the oxidative carbonylation of methanol in liquid phase slurry, the chemical characteristics of catalyst and its catalytic performance may be different from those in the gas-phase method. Yet, a detailed understanding about the effects of solvent environments on the mechanism and kinetics of DMC formation is seldom considered.

This study was designed to understand the mechanism and kinetics for the oxidative carbonylation of methanol to DMC over Cu(II) catalyst, as well as the effects of Cu valence state and solvent environment. Here, the results are obtained by DFT calculations with the periodic slab model. Firstly, the mechanism and kinetics of DMC formation is examined over CuO catalyst, which is used to model Cu(II) catalyst. Then, the kinetic results of DMC formation in gas phase are compared with that in the liquid phase to probe into the effect of solvent environment on the catalytic activity of Cu catalyst. Further, the comparisons of the mechanism among Cu(0), Cu(I) and Cu(II) catalysts are carried out to illustrate the effect of Cu valence state. The results are expected to provide a guide for the rational design of efficient Cu-based catalysts by tuning the catalyst valence state and solvent environments in the oxidative carbonylation of methanol.

2. Computational details

2.1. Surface models

In the case of CuO unit cell, each atom has four nearest neighbors of another species; oxygen atom is surrounded by a distorted tetrahedron of Cu atoms while each Cu atom is surrounded by a square of oxygen atoms [48]. The structure, stability and adsorption properties of CuO (111) surface have been investigated using DFT calculations [48–52], suggesting that the (111) surface is the most stable under the realistic conditions, which is also confirmed by the X-ray diffraction [53–55].

As shown in Fig. 1, a six-layer $p(3 \times 2)$ CuO(111) surface is used to model Cu(II) catalyst, which corresponds to the coverage of 1/6 ML. The vacuum space of 10 Å is added perpendicular to the surface to avoid the interactions between the slabs. In all calculations, the top three layers and the adsorbed species are allow to relax, while the bottom three layers are fixed to maintain the bulk crystal structure. CuO(111) surface includes eight adsorption sites: Cu_{SUF}(I), Cu_{SUB}(II), O_{SUF}(III), O_{SUB}(IV), Cu_{SUB}–Cu_{SUB} bridge(V), O_{SUB}–O_{SUB} bridge(VI), O_{SUF}–O_{SUF} bridge(VII) and Cu_{SUF}–Cu_{SUF} bridge sites(VIII). Cu_{SUF}(I) and O_{SUF}(III) sites are the surface Cu and O atoms, respectively; Cu_{SUB}(II) and O_{SUB}(IV) sites are the subsurface Cu and O atoms, respectively [56].

2.2. Calculation methods

All DFT calculations are performed with Dmol^3 program in Materials Studio 8.0 [57,58]. The exchange-correlation functional was constructed by the GGA of Perdew and Wang (PW91) [59–61]. Spin-unrestricted is used. In the computation, the inner electrons of Cu atoms are kept frozen and replaced by a DFT Semi-core Pseudopots (DSPP) [62,63]; other atoms are treated with an all-electron basis set. The valence electrons functions are expanded into a set of numerical atomic orbital by a double-numerical basis with polarization functions (DNP) [62–64]. Brillouin-zone integrations have been performed using $3 \times 3 \times 1$ Monkhorst-Pack grid and a Methfessel–Paxton smearing of 0.005 Ha [50]. The convergence criteria of SCF was 1×10^{-5} Ha; the converge criterion of geometry optimization and judged by the energy, force, displacement were 2×10^{-5} Ha, 4×10^{-3} Ha/Å, 5×10^{-3} Å, respectively; the convergence tolerance of TS search was obtained using the medium quality of 1×10^{-2} Ha/Å.

The conductor-like screening model (COSMO) implemented into the Dmol^3 has been used to simulate the solvent effect [65–69]. In this model, the solute is put in the continuous medium where the dielectric constant is ε, the methanol and water solvent environments are replaced with the permittivity $\varepsilon = 32.63$ and 78.54. The transition states (TS) of elementary reactions are searched by complete linear synchronous transit and quadratic synchronous transit (LST/QST) method [70,71]. Meanwhile, a vibrational frequency analysis is calculated to validate the true nature of the saddle point by identifying only one imaginary frequency along the reaction coordinate, and TS confirmation is performed on every transition state to confirm that they lead to the desired reactants and products.

3. Results and discussion

3.1. Evaluation of the method and model

In order to verify the credibility of calculation method and model, the bulk lattice parameters of CuO is firstly calculated, a = 4.684 Å, b = 3.423 Å, c = 5.129 Å and β = 99.54°, which agree with the experimental values [72] of a = 4.653 Å, b = 3.410 Å, c = 5.108 Å and β = 99.50°. Then, the calculated C—O bond length of gas phase CO is 1.141 Å, which is close to the experimental value of 1.128 Å [73]. Above test results show that the method and model employed in this study are reliable to describe the mechanism and kinetics of DMC formation on CuO catalyst.

3.2. The adsorption of the species involved in DMC formation

The adsorption energy (E_{ads}) is used to measure the interaction strength between the adsorbate and the substrate, which is obtained by

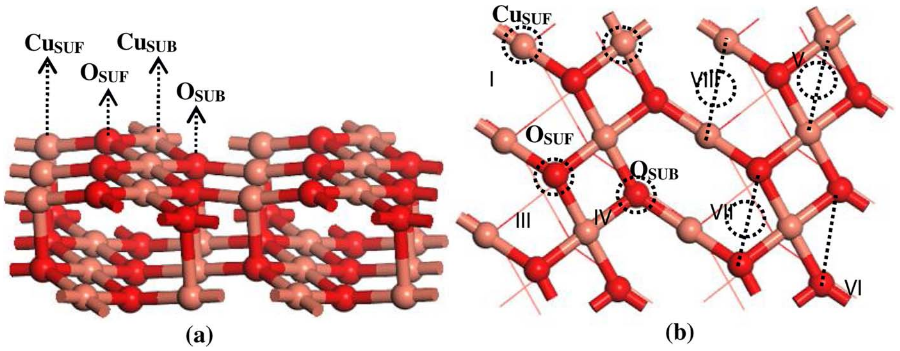

Fig. 1. The slab model of a $p(3 \times 2)$ CuO(111) surface. (a) Side view, (b) Top view. Orange and red balls stand for Cu and O atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)