Journal of Catalysis 365 (2018) 440–449

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Synergy between Cu and Brønsted acid sites in carbonylation of dimethyl ether over Cu/H-MOR

Ying Li [a,1], Shouying Huang [a,1], Zaizhe Cheng [a], Shengping Wang [a], Qingfeng Ge [b,*], Xinbin Ma [a,*]

[a] Key Laboratory for Green Chemical Technology of Ministry of Education, Collaborative Innovation Center of Chemical Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, China
[b] Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, USA

ARTICLE INFO

Article history:
Received 17 September 2017
Revised 25 April 2018
Accepted 26 June 2018

Keywords:
Dimethyl ether
Carbonylation
Synergy
Cu/H-MOR zeolite
Density functional theory
Infrared spectroscopy

ABSTRACT

As a key step in ethanol synthesis from syngas, zeolite-catalyzed carbonylation of dimethyl ether (DME) to methyl acetate (MA) has attracted much attention. Loading metal, especially Cu, into zeolites improves the formation of MA dramatically. As Cu^0 has been identified as an active species in previous work, the present work is focused on the mechanism of carbonylation of DME over Cu/H-MOR based on results from *in situ* IR spectroscopic study and density functional theory (DFT) calculation. The results from the experiments and DFT calculations support a synergetic mechanism involving both the Cu and Brønsted acid sites for DME carbonylation on Cu/H-MOR. In the synergetic mechanism, the Cu^0 site and the neighboring Brønsted acid site accommodate the coexistence of CH_3— and CH_3OH from DME adsorption and dissociation. The coadsorption of CO with the Cu—CH_3 species facilitates CO insertion to form the acetyl species. This Cu bound acetyl species, Cu—$COCH_3$, reacts with the adsorbed CH_3OH to form MA.

1. Introduction

Ethanol as a bulk industrial feedstock, solvent, and fuel alternative is mainly produced from crops (e.g., corn, sugarcane) and petroleum-derived ethylene [1-3]. In recent years, the demand for fuel ethanol has been gaining momentum because of its contribution to energy security and the environment. Therefore, exploring efficient ethanol production processes from alternative resources, such as coal- and biomass- derived syngas, is of great scientific and industrial importance. Among these emerging routes, carbonylation of dimethyl ether (DME) to methyl acetate (MA) with CO followed by hydrogenation of MA has attracted much attention, owing to its high atom economy, appreciable selectivity, and potential implementation in industry [4-7].

Considerable research effort has been devoted to the development of halogen-free catalysts for carbonylation of DME. Among the catalysts tested, microporous aluminosilicate zeolite is the most competitive candidate. Iglesia and his co-workers reported that acidic zeolites, such as MOR, FER, and ZSM-5, exhibited high selectivity for the DME carbonylation reaction [8]. Among them, H-MOR shows the highest activity and selectivity (>99%). Further study showed that only the Brønsted acid sites located in the eight-membered ring (8-MR) selectively catalyzed the reaction [9,10].

Metal-loaded zeolite is usually considered a typical multisite catalyst, possessing both metal and acid sites. Many attempts have been made to determine if there is a synergy between the metal and acid sites, and further, to understand how the metal or metal oxides and the acid sites of zeolites work synergistically to catalyze the reaction on catalysts such as Ga/H-ZSM-5 [11], Cr/H-ZSM-5 [12], and Zn/H-BEA [13,14]. For the DME carbonylation reaction, it was revealed that loading a metal, such as Fe, Co, Ni, Cu, Ag, or Pt, into H-MOR resulted in better activity than with H-MOR [7,15-18]. Among the metals, Cu facilitates the formation of MA remarkably.

For Cu-promoted zeolites, much work has focused on identifying the active form of the Cu species and unraveling the promotion mechanism. For example, Corma's group proposed that the Cu^+ sites preferably activate CO and adsorb DME over methanol and water, resulting in an enhanced MA formation rate [15]. On the other hand, Wang et al. suggested that the Cu^{2+} species contributes to CO activation through its Lewis acidity [16]. In contrast, our group demonstrated that it is the Cu^0 species rather than Cu^+ or Cu^{2+} that works synergistically with the Brønsted acid sites to catalyze MA formation [19]. However, how Cu and Brønsted acid sites cooperate during the reaction is not fully understood.

* Corresponding author.
E-mail addresses: qge@chem.siu.edu (Q. Ge), xbma@tju.edu.cn (X. Ma).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.jcat.2018.06.026
0021-9517/

To clarify the catalytic mechanism for MA formation on Cu/H-MOR, we examined the elementary steps involved in the carbonylation of DME on the catalyst using *in situ* Fourier transform infrared (FTIR) spectroscopy and the density functional theory (DFT) method. We propose that the Cu^0 and Brønsted acid sites acted through a synergetic mechanism to catalyze the reaction based on combined results from experiments and DFT calculations.

2. Experimental and computational details

2.1. Catalyst preparation

Commercial NH_4-MOR powder (Si/Al = 8.2, Yangzhou Zhonghe Petroleum Chemicals Institute Co.) was calcined at 873 K for 4 h to obtain H-MOR.

The Cu-loaded catalyst was prepared using a solution-based ion-exchange process to achieve the desired Cu loading (3.5 wt%). Typically, a predetermined amount of $Cu(NO_3)_2{\cdot}3H_2O$ (AR, Sinopharm Chemical Reagent Co.) was dissolved in deionized water, followed by adding $NH_3{\cdot}H_2O$ (25%, Tianjin Kermel Chemical Co.) dropwise to adjust pH to 10 under stirring. Then,10 g commercial NH_4-MOR was added to 100 mL copper ammonia solution. The suspension was stirred for 4 h at room temperature, followed by filtering and washing with deionized water until the filtrate was neutral. After the final ion exchange, the sample was dried at 383 K for 24 h and calcined at 773 K for 4 h. The actual mass fraction of copper in the sample was determined to be 3.35% from ICP-OES analysis. The prepared catalyst was labeled as Cu/H-MOR.

For reference, we also prepared the Cu/H-MOR catalyst using the solid-state ion-exchange (SSIE) method. It has been established that the Cu species in the Cu/zeolite prepared using SSIE are isolated Cu^+ ions in a well-defined monovalent state. Dried H-MOR and purified CuCl were mixed and heated at 823 K for 7 h under flowing N_2 to allow sufficient ion exchange. After cooling to room temperature, the sample was collected and labeled as SSIE Cu/H-MOR.

2.2. Collection of Fourier transform infrared spectra

In situ FTIR experiments were performed on a Thermo Scientific Nicolet 6700 spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The spectra were recorded at a resolution of 4 cm^{-1}, with 32 scans being averaged for background and 4 scans for adsorption spectra. Catalyst powder (15 mg) was pressed into a 13-mm-diameter self-supporting pellet and placed in a cell equipped with CaF_2 windows. Prior to adsorption, all the Cu/H-MOR pellets were reduced under 10% H_2/Ar (Tianjin Sixon Gas Co.) at 673 K for 3 h. For comparison, the H-MOR pellet was dehydrated under He (99.99%, Tianjin Sixon Gas Co.) at 573 K for 3 h. In a typical experiment, the temperature was reduced to 473 K after pretreatment and the background spectrum was collected prior to introduction of DME/He (1:10 vol.: vol.) into the cell at ambient pressure. Once the steady state was reached, the stream was switched to He in order to remove DME in the gas phase as well as the weakly adsorbed species. CO was then introduced for 1 h, followed by purging with He. Then DME was flowed into the cell again. The flow rates of DME/He mixture, CO, and He were controlled by the corresponding mass flow meters. Before flowing into the *in situ* cell, the feed gas passed through a molecular sieve trap to remove water and further deoxygenate He.

2.3. Performance test of catalysts

Catalyst activity tests were performed using 2 mL of catalyst in a fixed-bed reactor with inner diameter 8 mm. The pressure of reaction was maintained at 1.5 MPa. Cu/H-MOR samples were reduced under 10% H_2/Ar (Tianjin Sixon Gas Co.) at a specified temperature for 3 h. For comparison, the H-MOR sample was dehydrated under He (99.99%, Tianjin Sixon Gas Co.) at 573 K for 3 h. After reduction or thermal treatment under He, the temperature was reduced to 473 K, and then the reactant gases (DME/CO = 1:49 vol.: vol.) were introduced into the reactor at a total flow rate of 150 mL/min. The products were analyzed using an Agilent 7890B GC gas chromatograph equipped with a Pora PLOT Q column connected to a flame ionization detector (FID) and two Porapack Q and one MolSieve 5 Å connected to a thermal conductivity detector (TCD). The space time yield (STY) of MA was calculated using the equations in previous work [19,20].

2.4. Computational details

Density functional theory (DFT) calculations were performed primarily using the $Dmol^3$ program package of Materials Studio [21,22]. The Perdew–Burke–Ernzerhof (PBE) functional was used to describe electron exchange and correlation [23]. A double numerical quality basis set with polarization functions (DNP) [24] was employed to locate the optimized zeolite structures. The convergence tolerance of total energy, force, and displacement were 2×10^{-5} Ha, 4×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively. The transition state (TS) was determined by complete linear synchronous transit and quadratic synchronous transit (complete LST/QST) [25]. All transition states reported here were confirmed with only one imaginary frequency. To estimate the influence of dispersion interaction, the Tkatchenko–Scheffler functional was computed during the geometry optimization and TS search [26]. Zero-point energy and vibrational entropy were calculated based on the calculated harmonic frequencies of adsorbed intermediates and transition states. Reaction Gibbs free energy and activation Gibbs free energy at 473 K were determined for several elementary steps based on the calculated vibrational entropies.

The cluster models of MOR zeolite were built from mordenite. Mordenite has an orthorhombic lattice structure with parameters a = 18.094 Å, b = 20.515 Å, c = 7.524 Å and a *Cmcm* space group [27]. The dangling bonds of the cluster were saturated with H at 1.1 Å from the O atoms and oriented toward the position occupied by the Si atoms in the next coordination sphere. A proton or extra-framework metallic species (cation or cluster) was used to compensate for the negative charge created by replacing Si with Al. The catalyst model with a Brønsted acid site and Cu species in the MOR cluster was denoted as Cu/H-MOR, while the model with a negative charge and absence of a Cu cation was labeled as H-MOR^-.

The adsorption energy (E_{ads}) was defined as

$$E_{ads} = E_{(adsorbate/Cu/H\text{-}MOR)} - E_{(adsorbate)} - E_{(Cu/H\text{-}MOR)}, \quad (1)$$

where $E_{(adsorbate/Cu/H\text{-}MOR)}$, $E_{(adsorbate)}$, and $E_{(Cu/H\text{-}MOR)}$ represent the total energies of the adsorption complex, the isolated adsorbate molecule, and the Cu/H-MOR model, respectively. The activation energy (E_a) of an elementary step was calculated as

$$E_a = E_{(TS)} - E_{(reactant/Cu/H-MOR)}, \quad (2)$$

where $E_{(TS)}$ and $E_{(reactant/Cu/H\text{-}MOR)}$ represent the energy of the transition state and reactant absorbed onto Cu/H-MOR zeolite in each elementary step, respectively.

The binding energy of the Cu cluster (E_{bind}) in the MOR zeolite was calculated as

$$E_{bind} = E_{(Cu/H-MOR)} - E_{(Cu^+)} - E_{(H-MOR^-)}, \quad (3)$$

where $E_{(Cu^+)}$ represents the energy of the Cu_6^+ cluster, and $E_{(H\text{-}MOR^-)}$ and $E_{(Cu/H\text{-}MOR)}$ are the energies of H-MOR^- and Cu/H-MOR systems, respectively. The lower E_{bind} corresponds to a more stable model of Cu/H-MOR.