Catalytic mechanism of Cu-based catalyst in methanol dehydrogenation

Weibin Fan[a,*]

[a]*State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, P. R. China*

**Corresponding author: Fax number: 0351-4050320, E-mail: fanwb@sxicc.ac.cn*

Abstract: It remains an open question for Cu-based catalysts to understand comprehensively the catalytic roles of Cu^0 and Cu^+ due to the high mobility of Cu. Herein, an unprecedentedly stable Cu-based catalyst was fabricated by uniformly embedding Cu nanoparticles in mesoporous silica shell for clarifying the catalytic roles of Cu^0 and Cu^+ with dehydrogenation of methanol to methyl formate. It is shown that Cu^0 catalyzes the cleavage of O–H bond in CH_3OH to CH_3O and C–H bond in CH_3O to HCHO that reacts with another CH_3O species to form $HCOOCH_3$, while Cu^+ converts the HCHO into CO and H_2.

Keywords: Cu-based core-shell catalyst, methanol dehydrogenation, reaction mechanism.

1. Introduction

Cu-based catalysts have been widely used in large numbers of industrially important reactions, including synthesis of alcohols from syngas, steam reforming of methanol, oxidation of CO, water-gas shift reaction, hydrogenation of carbonyl compounds and dehydrogenation of alcohols.[1] However, the identification of active copper species, and further illustration of catalytic mechanism of Cu-based catalysts is still a challenge because of the mobility and evolution of Cu^0 and Cu^+ species in the reaction.[2,3]

Dehydrogenation of methanol (DOM) to methyl formate (MeF) could be considered as a prototype C1 chemical reaction as it generates CH_3O and HCHO intermediates and CO_x byproducts.[4] A clear understanding of the catalytic roles of Cu^0 and Cu^+ in this reaction would be highly useful for unraveling the catalytic mechanism of Cu-based catalysts in C1 chemical reactions. In this work, we develop a method to prepare a Cu-based core-shell catalyst ($Cu@mSiO_2$) that shows high catalytic stability in the DOM into MeF. In particular, the catalytic roles of Cu^0 and Cu^+ species are clarified with such a catalyst.

2. Experimental

$Cu@mSiO_2$ catalyst was prepared by a modified Stöber method with $Cu(NH_3)_4^{2+}$ as copper precursor and PVP as dispersant (Cu loading was 7 wt.%). For comparison, $Cu/mSiO_2$ and Cu/SiO_2 catalysts were prepared by the impregnation method with copper nitrate as copper precursor and mesoporous silica ($mSiO_2$, $S_{BET} = 858$ m^2/g, $d_p = 2.5$ nm) and fumed silica (SiO_2, $S_{BET} = 208$ m^2/g, $d_p = 26.2$ nm) as supports.

The reaction of DOM was carried out in a fixed-bed reactor, and the reaction conditions are as follows: 230 ^oC, 1 atm, $n(Ar)/n(CH_3OH) = 3.7$, WHSV = 4 h^{-1}. TEM, XRD, N_2O titration, CO-TPD, XPS, N_2 physisorption, in situ DRIFT spectroscopy and isotope-labeling experiments were used to characterize the samples and study the catalytic mechanism.

3. Results and discussion

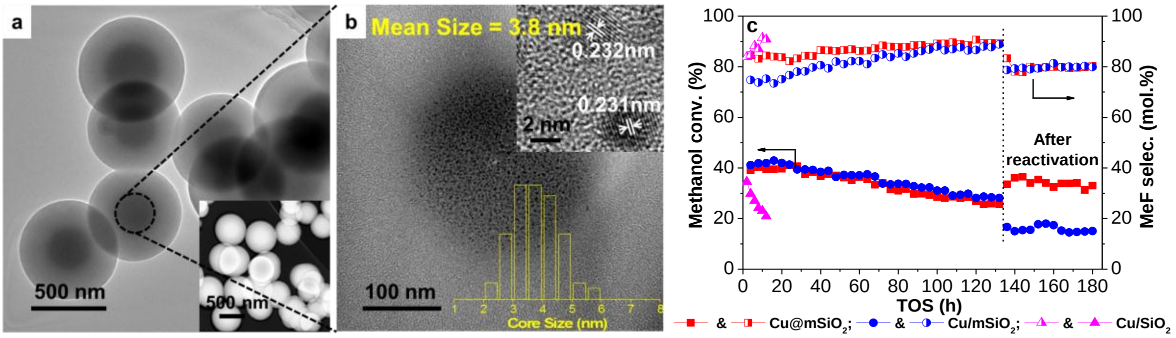

Figure 1. (**a**,**b**) TEM images of $Cu@mSiO_2$; (**c**) Catalytic results of Cu/SiO_2, $Cu/mSiO_2$ and $Cu@mSiO_2$ for DOM to MeF.

Figure 1a,b shows that the uniform spherical particles of as-synthesized Cu@mSiO_2 have a core-shell structure with highly dispersed 3.8 nm CuO nano-cores and mesoporous structure silica shell. Compared with Cu/mSiO_2 and Cu/SiO_2 prepared by the impregnation method, Cu@mSiO_2 gave higher MeF yield, stablility and regenerated activity for DOM (Figure 1c). Interestingly, the average sizes of Cu NPs in the fresh, spent and regenerated Cu@mSiO_2 were almost the same. This unexpectedly high stability of Cu@mSiO_2 results from not only encapsulation of Cu NPs in mesoporous silica shell but also formation of Si–O–Cu structure.

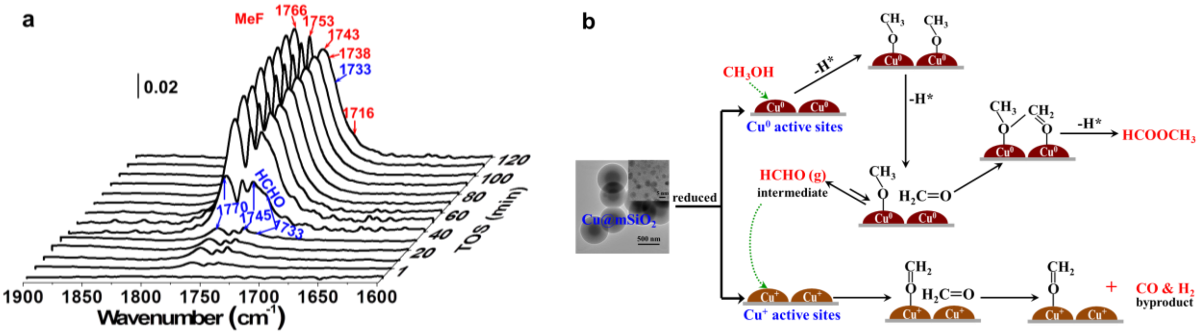

Figure 2. (**a**) In situ DRIFT spectra of Cu@mSiO_2 reduced at 300 °C for DOM at 230 °C; (**b**) Reaction pathways over different copper sites in DOM.

Figure 2a shows the in situ DRIFT spectra of Cu@mSiO_2 reduced at 300 °C for DOM into MeF at 230 °C. The bands for HCHO species and MeF appeared, implying that HCHO is one of the key intermediates in DOM. In addition, the bands characteristic of Si–OCH_3 and Cu–OCH_3 were observed over the samples. This indicates that the O–H bond of methanol splits into H and CH_3O that further converts into HCHO through breaking of C–H bond. The bands for HCHO and MeF were also observed over Cu@mSiO_2 reduced at 450 °C with abundant Cu^0 species, while they were not detected over the sample reduced at 200 °C dominated by Cu^+ species. These confirm that Cu^0 is responsible for the formation of MeF.

Cu^0 and Cu^+ species generally coexist in the Cu-based catalysts. HCHO intermediate formed on and subsequently desorbed from the Cu^0 species possibly contact with Cu^+ sites. It was found that HCHO was completely converted over metallic Cu (model for Cu^0 sites) with MeF selectivity of 62% – 70%. Whereas, no MeF was generated over Cu_2O (model for Cu^+ sites), and HCHO was mainly converted into CO with a selectivity of ≈ 85%. For CH_3OH was simultaneously generated over metallic Cu, we employed an isotope-labeling experiment, and evidenced that MeF is formed via the hemi-acetal route (reaction of HCHO and CH_3O), not via HCHO dimerization (Tishchenko mechanism) (Figure 2b).

4. Conclusions

Cu NPs encapsulated in mesoporous silica shell shows unexpectedly high stability in the DOM to MeF. Cu^0 sites enable the cleavage of O–H in methanol to CH_3O, and further to HCHO by breaking C–H bond, while Cu^+ species are unable to catalyze these steps, but immediately decompose HCHO generated on Cu^0 into CO and H_2. The MeF is formed through the reaction of CH_3O and HCHO over the Cu^0 sites, not via the Tishchenko mechanism.

References

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