

Decomposition of Methanol Catalyzed by Cu-ZnO@C

Ching-I Hong^{*}, H. Y. Kang^{*}, Fang-Chih Chang^{*}, H. Paul Wang^{*, **, ***}

^{*} Department of Environmental Engineering,

Tel.: +886 6 276 3608, fax: +886 6 275 2790, wanghp@mail.ncku.edu.tw (H. Paul Wang)

^{**} Sustainable Environmental Research Center

^{***} Center for Micro/Nano Science and Technology,

National Cheng Kung University, Tainan 70101, Taiwan

ABSTRACT

H_2 yielded from decomposition of methanol (DM) can be used in fuel cells. In the present work, DM to H_2 was catalyzed by Cu-ZnO@C core-shell nanoreactors. Yields of H_2 from DM catalyzed by the (Cu-ZnO)@C nanoreactors increase with an increase of the ZnO fractions. It is also found that a significant increase of collision frequency in the confined space in nanoreactors is also associated with the high H_2 yield. By component fitted X-ray absorption near edge structure (XANES), it is clear that Cu plays the main role in the catalytic DM reaction.

Keywords: methanol decomposition, Cu-ZnO@C, EXAFS, XANES.

1 INTRODUCTION

Fuel cells have many advantages for electrical power generation. The “zero emission vehicle” can be obtained by feeding H_2 directly. Methanol commercially produced from syngas using Cu/ZnO/Al₂O₃ as catalysts can be used as the feedstock in directly methanol fuel cells [1]. The catalytic decomposition of methanol (DM) which can be considered as the reverse of the synthesis of methanol (SM) is widely used for synthesizing syn-gas and H_2 -rich gases. Stoichiometrically, steam reforming of methanol (SRM) provides more H_2 than DM. Methanol can be stored and mixed with product H_2O from the fuel cells for the reformer. However, the neat methanol storage needs H_2O recovery and fuel mixing subsystem [2].

Methanol is regarded as an alternative fuel for automobiles in the future. Recently, methanol decomposition to H_2 and CO has attracted great interest. Decomposition of methanol is an endothermic reaction. Methanol-fueled automobiles have more efficient and cleaner than the gasoline ones [3, 4]. CO and H_2 could be formed by decomposition of formate during DM on ZnO at 580 K [5]. Cu and Cu(I) have been considered as the catalytic active centers in the DM, SM, and SRM reaction [6,7].

Experimentally, decomposition of methanol to CH₂OH on clean Cu(110) surfaces takes place at 270 K. In addition, Cu(111) and Cu(100) are inactive to DM [1]. It is suggested that DM proceeds the reaction pathway of

$CH_3OH \rightarrow CH_2OH \rightarrow CH_2O \rightarrow CHO \rightarrow CO$, to form CO on Cu(110). After the initial O-H bond scission of methanol, three successive C-H bond breaking may occur. The rate-limiting step during DM is the dehydrogenation of CH₂OH to formaldehyde (CH₂O) the surface intermediate on the Cu(110) surface. The barrier for C-H bond breaking of CH₂OH to CH₂O is >0.5 eV which is greater than other steps in the route.

Cu- and ZnO-based catalysts have a great activity for DM reaction which can be operated at relatively lower temperature. Compared with Ni, Pd and Pt catalysts, Cu are less aggressive in hydrogenation and dehydrogenation reactions [8]. The addition of ZnO can enhance the stability and dispersion of Cu. Recently, the DM reaction catalytic by Pt has attracted a great interest, especially taking place on the anodes of direct methanol fuel cells (DMFCs). A direct conversion of methanol to electricity with a greater efficiency than the conventional combustion-based power generation systems was found. However, the performance of DMFCs is limited by the CO poison on the anode surface when Pt is used [9].

The state of Cu in Cu/ZnO catalysts can be changed dynamically [10]. Partial reduction of ZnO may cause a small amount of Cu-Zn alloy formed [11]. Furthermore, Cu(I) of the Cu/Zn/Cr catalysts can be reduced to Cu by H_2 , CH₃OH or CH₃OH during DM [12]. By in situ X-ray absorption spectroscopy, it was found that CuO was reduced to Cu during DM. Size-controllable Cu@C core-shell nanoparticles were prepared in our laboratory. In the present work, a controlled etching of Cu from Cu@C core-shell nanoparticles was carried out to create desirable space within the carbon shell. The Cu@C core-shell nanoreactors were thus used in H_2 production from DM. Moreover, ZnO was also filled in the Cu@C core-shell nanoparticles for enhancing H_2 yields from DM.

2 EXPERIMENTAL

The (Cu-ZnO)@C core-shell nanoparticles were prepared by carbonization of Cu²⁺- and Zn²⁺-cyclodextrin (CD) complexes having the Cu/Zn and (Cu+Zn)/CD ratios of 1-9 and 3, respectively at 573 K for 2 h [13]. Methanol was injected into a fixed-bed reactor ($V = 100$ mL) steadily using a syringe pump. The flow rate of the feed containing 21% of methanol and 5% of O₂ in N₂ was regulated at 20

mL/min by a mass flow controller. About 0.1 g of the (Cu-ZnO)@C core-shell nanoreactor catalysts were used in the catalytic DM experiments at the temperatures of 473-573 K.

The composition of the product gas was determined by gas chromatography (GC) and on-line Fourier transform infrared (FT-IR) spectroscopy (Varian, FTS-40). The concentration of H₂ in the product gases was analyzed by GC (Bruker, GC-430) equipped with a TCD detector. Molecular sieve 5A column was used for separation of H₂ from other gases. Nitrogen at a flow rate of 30 mL/min was used as the carrier gas. CO and CO₂ were analyzed by on-line FT-IR. A 32-scan data accumulation was conducted at a resolution of 4 cm⁻¹.

The X-ray absorption spectra of copper in the (Cu-ZnO)@C core-shell nanoreactors were collected on the Wiggler BL17C beam line at the Taiwan National Synchrotron Radiation Research Center (NSRRC). The energy storage ring was operated under the energy of 1.5 GeV at top-up ring current model (300 mA). EXAFS data were analyzed by the UWEXAFS 3.0 and FEFF 8.0 simulation programs.

3 RESULTS AND DISCUSSION

Figure 1 shows that H₂ are formed from the catalytic DM at 473-573 K effected by (Cu-ZnO)@C and Cu@C core-shell nanoreactors. Yields of H₂ from the catalytic DM increase as the reaction temperatures increase. At 573 K, yields of H₂ from the catalytic DM reaction effected by the (Cu-ZnO)@C core-shell nanoreactor at the Cu/ZnO ratio of 1.5/1.5 are 0.12 mol/gCu-hr. It seems that the H₂ is yielded from the catalytic DM by Cu with the help of ZnO which seems to promote the DM reaction at 473-573 K.

The Arrhenius parameters such as activation energy (Ea) and pre-exponential factor (A) for the DM reaction catalyzed by the core-shell nanoreactors at 473-573 K have been calculated and analyzed

(Rate = $\gamma_{H_2} = k[CH_3OH]$, $k = A \exp(-E_a/RT)$). Table 1 provides the Arrhenius parameters of the catalytic DM reaction effected by the (Cu-ZnO)@C and Cu@C core-shell nanoreactors. The Ea for the DM catalyzed by (Cu-ZnO)@C and Cu@C core-shell nanoparticles are in the range of 11-14 kcal/mol. The Ea obtained from Cu-ZnO@C core-shell nanoreactors are much less than that on Cu-based catalysts (18.39-24.12 kcal/mol) [14].

Methanol decomposition may occur in the confined spaces between the core (Cu-ZnO) and carbon-shell in the nanoreactors which have advantages of the low Ea, high collision frequency, and high yields of H₂.

For more detailed characterization of active copper and zinc species in the nanoreactors, their X-ray absorption spectra have been measured. The XANES spectra of copper in the nanoreactors are shown in Fig. 2. The absorption edges of copper and zinc species are observed at 8979 and 9659 eV, respectively. Cu and ZnO are the main copper and zinc species, respectively in the DM reactions.

XANES spectra of copper in the (Cu-ZnO)@C nanoreactors are analyzed by component fitting. Figure 3 shows the least-square fitted Cu-Kedge XANES spectra. After the catalytic DM reactions at 473 K, mainly Cu is observed.

The EXAFS spectra of the nanoreactors are also analyzed in the k range of 3.5-12 Å⁻¹. An over 99% reliability of the EXAFS data fitting for copper species is found. The Cu-Cu bond distances in the (Cu-ZnO)@C are in the range of 2.335-2.379 Å (as shown in Table 2). It seems that the Cu-Cu bond distance increase significantly when a small amount of ZnO is added in (Cu-ZnO)@C nanoparticles.

4 CONCLUSION

Methanol can be catalytically decomposed to form H₂ at 473-573 K in (Cu-ZnO)@C nanoreactors. By XANES and EXAFS spectra, the main copper species is Cu during DM reactions. The relatively low Ea, low reaction temperature, and high yields of H₂ in the core-shell nanoreactors may be associated with the fact of high collision frequency between Cu-ZnO active species and methanol in the confined nanoreactors.

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Table 1 Arrhenius parameters for DM catalyzed by the (Cu-ZnO)@C core-shell nanoreactors at 473-573 K for 100 min.

Cu/ZnO ratio	A (10 ⁵ s ⁻¹)	E _a (kcal/mol)
1.5/1.5	7.15	13.4
2.0/1.0	2.30	12.4
2.7/0.3	1.01	11.7
3.0/0	0.67	12.3

$$\text{Rate} = \gamma_{\text{H}_2} = k[\text{CH}_3\text{OH}], \quad k = A \exp(-E_a/RT)$$

Table 2 Speciation of copper in the first shell of Cu-Cu in the (Cu-ZnO)@C core-shell nanoreactors after the catalytic DM at 473 K for 100 min.

Cu/ZnO ratio	R (Å)	CN	σ ²
1.5/1.5	2.340	5.3	0.0108
2.0/1.0	2.352	5.6	0.0098
2.7/0.3	2.379	5.5	0.0134
3.0/0	2.335	6.6	0.0014

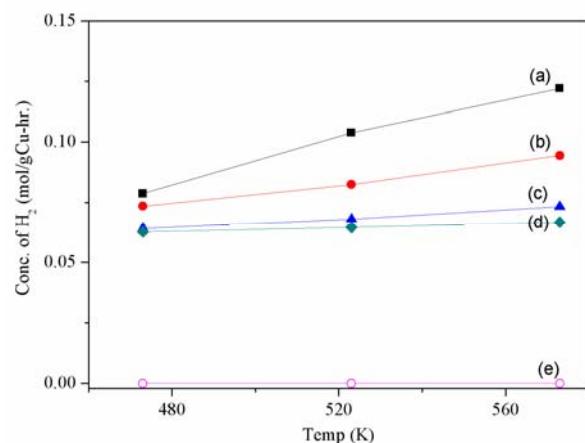


Fig. 1 Yields of H₂ from catalytic DM at the temperatures of 473-573 K in the (Cu-ZnO)@C nanoreactors at the Cu/ZnO ratios of (a) 1.5/1.5, (b) 2.0/1.0, (c) 2.7/0.3, (d) 3.0/0 and (e) without a catalyst.

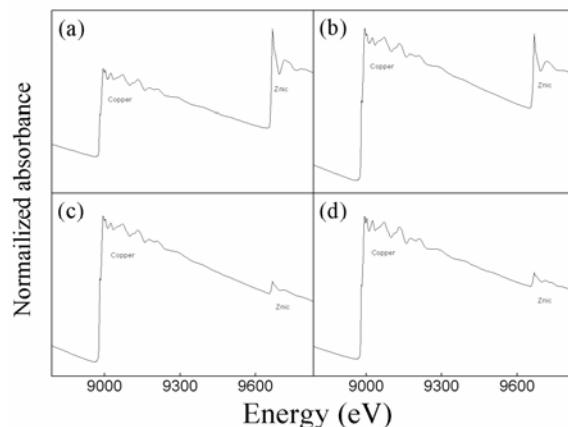


Fig. 2 XANES spectra of the (Cu-ZnO)@C nanoreactors at the Cu/ZnO ratios of (a) 1.5/1.5, (b) 2.0/1.0, (c) 2.7/0.3, and (d) 3.0/0 after catalytic DM at 473 K for 100 min.

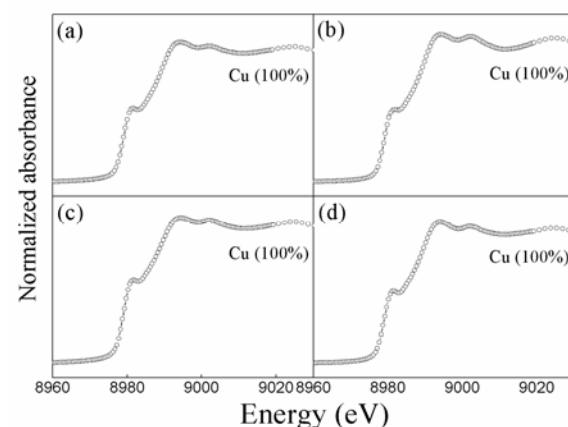


Fig. 3 Component-fitted XANES spectra of copper in the (Cu-ZnO)@C nanoreactors at the Cu/ZnO ratios of (a) 1.5/1.5, (b) 2.0/1.0, (c) 2.7/0.3, and (d) 3.0/0 after DM at 473 K for 100 min.