

Catalytic Decomposition of Methanol Effected by (Cu-ZnO)@C Nanoreactors

C.-I. Hong^{*}, H.-Y. Kang^{*}, C.-Y. Peng^{**}, J. Wang^{***}, and H. Paul Wang^{*}

^{*}National Cheng Kung University, Tainan 70101, Taiwan, wanghp@mail.ncku.edu.tw

^{**}Tamkang University, New Taipei City 25137, Taiwan

^{***}University of California, San Diego, CA 92037, USA

ABSTRACT

Methanol can be decomposed to yield H₂ that may be the alternative fuels for automobiles and fuel cells. The feasibility study for catalytic decomposition of methanol (DM) to CO and H₂ with (Cu-ZnO)@C core- and yolk-shell nanoreactors was, therefore, carried out. The relatively low activation energy (E_a), low reaction temperature, and high yields of H₂ with the core-shell or yolk-shell nanoreactors were found, which may be associated with the fact of high collision frequency between Cu-ZnO active species and methanol within the confined nanoreactors. The data obtained from the component fitted X-ray absorption near edge structure spectra suggest that metallic copper (Cu) in the nanoreactors can promote the formation of H₂ from the catalytic DM reaction. In addition, the reactivity of DM catalyzed by the nanoreactors increases with an increase of the ZnO fractions in the Cu-ZnO encapsulated in carbon-shell.

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

1. INTRODUCTION

Methanol which can be produced commercially from syngas with the Cu/ZnO/Al₂O₃ catalysts was used as the feedstock in fuel cells for electrical power generation. The zero-emission vehicles can also be achieved with the feed of the H₂ fuel directly. Although steam reforming of methanol provides more H₂ than DM, DM has the advantages of lower reaction temperatures and simpler processes.

Decomposition of methanol is an endothermic reaction. Methanol-fueled automobiles have more efficient and cleaner than undecomposed methanol and gasoline [1, 2]. The catalysts must be active even at low exhaust-heat temperature and endure rough operating conditions [2].

Decomposition of methanol to methoxy (CH₂OH) on the clean Cu(110) surface takes place at 270 K. Note that Cu(111) and Cu(100) are inactive to DM. It is suggestive that CH₃OH → CH₂OH → CH₂O → CHO → CO is the favorable DM reaction pathway on Cu(110). After the initial O-H bond scission of methanol, three successive C-H

breaking may occur. The rate-limiting step during DM is the dehydrogenation of CH₂OH to formaldehyde (CH₂O) which is found on the Cu(110) surface. The barrier for the C-H bond breaking of CH₂OH to CH₂O is >0.5 eV that is greater than other steps.

Cu- and ZnO-based catalysts can catalyze the DM reaction at relatively low temperatures. Compared with Ni, Pd and Pt catalysts, Cu is less aggressive in hydrogenation and dehydrogenation reactions [3]. The addition of ZnO can enhance the stability and dispersion of Cu. Recently, the DM reaction with Pt has attracted a great interest taking place on the anodes of the direct methanol fuel cells (DMFCs) which offer direct conversion of methanol to electricity with a greater efficiency than the conventional combustion-based power generation system. However, the performance of DMFCs is limited by the CO poisoning on the Pt-anodes [4].

Nano size-controllable Cu@C core-shell nanoparticles can be prepared in a very simple process [5]. A controlled etching of Cu from the Cu@C core-shell nanoparticles can create desirable space and form the so-called Cu@C yolk-shell nanoparticles [6]. In the present work, zinc was filled into the Cu@C yolk-shell nanoparticles to form the (Cu-ZnO)@C core- and yolk-shell nanoreactors wherein more H₂ can be yielded from the catalytic DM reaction.

2. EXPERIMENTAL

The DM reactions catalyzed by (Cu-ZnO)@C core- and yolk-shell nanoreactors were carried out in a micro-reactor at 473-573 K. Methanol was injected steadily using a syringe pump. The flow rate of the feed containing 21% of methanol and 5% of O₂ in N₂ regulated at 20 mL/min by a mass flow controller. About 0.1 g of the nanoreactor catalyst was used in the catalytic DM experiments.

The concentration of H₂ in the product gases was analyzed by chromatography (Bruker GC-430) equipped with a TCD detector. Molecular sieve 5A column (353 K) 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 spectroscopy (Varian, FTS-40). A 32-scan data accumulation was conducted at a resolution of 4 cm⁻¹.

The X-ray absorption spectra of copper in the 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).

3. RESULTS AND DISCUSSION

H₂ was yielded from the catalytic DM with the (Cu-ZnO)@C core- and yolk-shell nanoreactors at 473-573 K. The Arrhenius parameters such as activation energy (E_a) and pre-exponential factor (A) for the DM reaction catalyzed by the nanoreactors were derived and summarized in Table 1. The E_a for the catalytic DM are in the range of 11-14 kcal/mol. Methanol decomposition may occur in the confined spaces between the core Cu-ZnO and carbon-shell in the nanoreactors which may be associated with the relatively low E_a, high collision frequency and high yields of H₂ in the core- and yolk-shell nanoreactors.

At 573 K, yields of H₂ from the DM reaction catalyzed by (Cu-ZnO)@C core-shell nanoparticles have formation rate of 0.098 mol/gCu-hr. Promotion of H₂ yields in the presence of ZnO in the yolk-shell nanoreactors is also observed.

For more detailed characterization of active copper and zinc species in the nanoreactors, their X-ray absorption spectra were measured. The XANES spectra of copper in the nanoreactors are shown in Fig. 1. The absorption edges of copper and zinc species are observed at 8979 and 9659 eV, respectively. ZnO is the main zinc species in the DM reactions. To determine the copper oxidation states, XANES spectra of copper in the nanoreactors are analyzed by component fitting. After the catalytic DM reactions at 473 K, the main copper species in the nanoreactors are low-oxidation state copper.

Cu/ZnO molar ratios	A (10 ⁵ s ⁻¹)	E _a (kcal/mol)
Core-shell nanoreactors		
1.5/1.5	7.15	13.3
2.0/1.0	2.30	12.4
2.7/0.3	1.01	11.7
3.0/0.0	0.67	12.3
Yolk-shell nanoreactors		
1.5/1.5	2.10	12.4
3.0/0.0	1.78	12.2

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

Table 1: Arrhenius parameters for catalytic DM reactions with the (Cu-ZnO)@C core- and yolk-shell nanoreactors at 473-573 K.

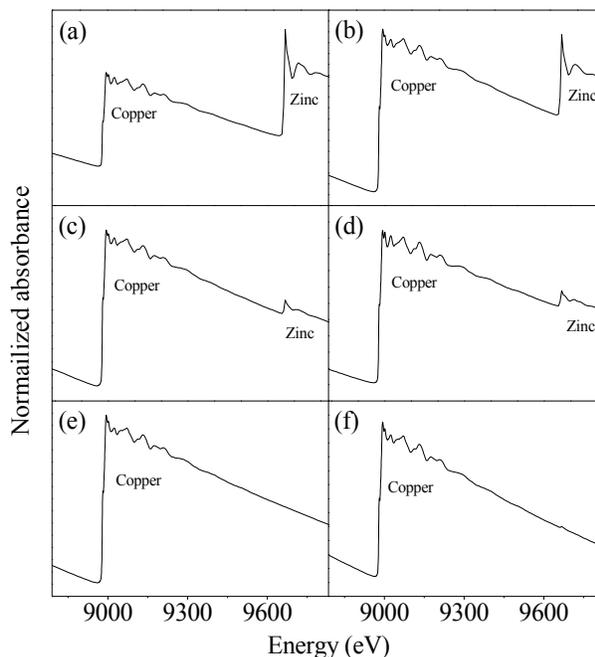


Fig. 1: XANES spectra of (Cu-ZnO)@C core-shell nanoreactors having the Cu/ZnO molar ratios of (a) 1.5/1.5, (b) 2.0/1.0, (c) 2.7/0.3, and (e) 3.0/0 and yolk-shell nanoreactors having the Cu/ZnO molar ratios of (d) 1.5/1.5 and (f) 3.0/0 (having a Cu diameter of 7 nm) after the catalytic DM at 473 K.

4. CONCLUSION

Methanol can be catalytically decomposed to form H₂ effected by the (Cu-ZnO)@C core- and yolk-shell nanoreactors at 473-573 K. By XANES, the main copper and zinc active species in the nanoreactors are Cu and ZnO, respectively. The relatively high reactivity and high yields of H₂ for the catalytic DM reaction may be associated with the fact of high collision frequency between active species (i.e., Cu and ZnO) and methanol in the confined nanoreactors.

ACKNOWLEDGEMENTS

The financial supports of Taiwan National Science Council, Bureau of Energy, and National Synchrotron Radiation Research Center are gratefully acknowledged.

REFERENCES

- [1] Y. Usami, K. Kagawa, M. Kawazoe, M. Yasuyuki, H. Sakurai and M. Haruta, Catalytic methanol decomposition at low temperatures over palladium supported on metal oxides. Applied Catalysis A: General, 171, 123-130, 1998.

- [2] W.H. Cheng, Deactivation and regeneration of Cu/Cr based methanol decomposition catalysts. *Applied Catalysis B: Environmental*, 7, 127-136, 1995.
- [3] M.V. Twigg and M.S. Spencer, Deactivation of copper metal catalysts for methanol decomposition, methanol steam reforming and methanol synthesis. *Topics in Catalysis*, 22, 191-203, 2003.
- [4] J. Greeley and M. Mavrikakis, Competitive paths for methanol decomposition on Pt(111). *Journal of the American Chemical Society*, 126, 3910-3919, 2004.
- [5] C.H. Huang, H.P. Wang, J.E. Chang and E.M. Eyring, Synthesis of nanosize-controllable copper and its alloys in carbon shells. *Chemical Communications*, 31, 4663-4665, 2009.
- [6] C.I. Hong, H.Y. Kang, H.P. Wang, W.K. Lin, U.S. Jeng and C.H. Su, Cu-ZnO@C nanoreactors studied by in-situ synchrotron SAX spectroscopy. *Journal of Electron Spectroscopy and Related Phenomena*, 184, 301-303, 2011.