

## Surfactant-Promoted Formation of Supported Metallic Cu Nanoclusters for Selective Dehydrogenation of Methanol

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### Introduction

Metallic nanoparticles dispersed on robust inorganic oxides are widely used in a variety of catalytic reactions, and effective ways to prepare supported nano-sized metal particles have been extensively explored as a key issue to develop new efficient catalytic systems. We have found that a surfactant CTAB (cetyltrimethylammonium bromide) promotes the reductive synthesis of metallic Cu nanoclusters on inorganic oxides from Cu<sup>2+</sup> ions without any additional reducing reagent. Hydrothermal treatments of a mixture of Cu nitrate and Mo, Zn, Al, and Si cationic precursors in the presence of CTAB produce the nano-sized metallic Cu clusters supported on crystalline Mo, Zn, and Al oxides and amorphous Si oxide. The prepared Cu nanoparticles were active and selective for catalytic dehydrogenation of methanol [1].

### Experimental

The preparation of Mo-oxide-supported metallic Cu nanoclusters is typically described as follows. An aqueous solution of a given amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was added dropwise with vigorous stirring to corresponding precursors of Mo, Zn, Al and Si in hot water. Then an aqueous solution of CTAB was added to the mixture of two metal precursors. The resultant mixture was hydrothermally treated at 448 K for 2 h in an autoclave vessel. The product was washed and dried at 373 K, followed by heating at 773 K under He.

The characterization of the supported Cu nanoparticles was performed by XRF, XRD, XPS, TEM, BET and XAFS. Cu K-edge XAFS spectra were measured at BL-10B and 12C stations in a transmission mode at 20 K. Background subtraction was conducted by the AUTOBK program, and Fourier-transformed spectra were fitted in R space by FEFFIT program.

### Results and Discussion

XRD spectra of the supported Cu nanoparticles showed that there were no peaks attributed to Cu species and highly crystalline structures of Mo or Zn oxides were formed in the presence of CTAB. TEM and BET results agreed the crystalline structures of the supports.

The curve-fitting results of Cu K-edge EXAFS spectra are summarized in Table 1. The coordination number of Cu-Cu of fresh Cu/Mo-CTAB was 4.4 at 0.254 nm, which is similar to the bond length for Cu metal. The much smaller CN of Cu-Cu than that of bulk Cu metal (CN=12) indicates the formation of nano-sized metallic Cu clusters.

Table 1 Curve-fitting results of Cu K-edge EXAFS measured at 20 K

Sample	Shell	CN	Distance /nm	$\sigma^2 / 10^{-5} \text{ nm}^2$
Cu/Mo-CTAB (fresh) <sup>a</sup>	Cu	4.4±0.8	0.254±0.001	3±1
(after reaction) <sup>b</sup>	Cu	3.9±0.7	0.254±0.001	2±1
Cu/Mo (fresh) <sup>c</sup>	O	2.4±0.3	0.190±0.002	8±2
Cu/Zn-CTAB (fresh) <sup>d</sup>	Cu	6.0±1.3	0.257±0.001	4±1
(after reaction) <sup>e</sup>	Cu	8.8±0.7	0.254±0.001	4±1
Cu/Si-CTAB (fresh) <sup>f</sup>	Cu	4.4±0.7	0.254±0.001	4±1
Cu/Al-CTAB (fresh) <sup>g</sup>	Cu	1.5±0.2	0.249±0.001	4±1

<sup>a</sup> k=30-120 nm<sup>-1</sup>, R=0.18-0.28 nm, R<sub>f</sub>=1.29%. <sup>b</sup> k=30-120 nm<sup>-1</sup>, R=0.18-0.28 nm, R<sub>f</sub>=0.95%. <sup>c</sup> k=30-114 nm<sup>-1</sup>, R=0.10-0.20 nm, R<sub>f</sub>=1.94%.

<sup>d</sup> k=30-114 nm<sup>-1</sup>, R=0.18-0.28 nm, R<sub>f</sub>=1.27%. <sup>e</sup> k=30-114 nm<sup>-1</sup>, R=0.18-0.28 nm, R<sub>f</sub>=0.17%. <sup>f</sup> k=30-140 nm<sup>-1</sup>, R=0.18-0.28 nm, R<sub>f</sub>=1.89%. <sup>g</sup> k=30-140 nm<sup>-1</sup>, R=0.16-0.27 nm, R<sub>f</sub>=0.93%.

After the selective methanol dehydrogenation, there was no significant difference in CN and Cu-Cu distance as shown in Table 1. In the absence of CTAB, no interaction of Cu-Cu was observed on Cu/Mo, and Cu oxide was formed on amorphous Mo oxide. For the Zn-supported Cu nanoparticles, CN of Cu-Cu was initially 6.0 at 0.257 nm but increased to 8.8 at 0.254 nm after the reaction. The Cu-Cu CNs of fresh Cu/Si-CTAB and Cu/Al-CTAB were 4.4 at 0.254 nm and 1.5 at 0.249 nm, respectively.

The Cu/Mo-CTAB was the most active catalyst for the selective dehydrogenation of methanol to formaldehyde: 61.2% conv. and 98.5% selectivity. H<sub>2</sub> selectivity was 100% with no dehydration products. The EXAFS result after the reaction demonstrates that the Cu/Mo-CTAB is so durable under the reaction conditions. The Cu/Zn-CTAB exhibited 26.5% conv. and 99.1% selectivity, but the increase in the Cu-Cu CN after the reaction indicates sintering the Cu particles. The metallic Cu nanocluster was created in the organized assembly of Mo and CTAB under the hydrothermal synthesis conditions, which was most active and selective for methanol dehydrogenation.

### References

[1] R. Bal, M. Tada, and Y. Iwasawa, *Chem. Commun.*, in press.

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