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Supporting Information

A novel supported Cu catalyst with highly dispersed copper nanoparticles and its remarkable catalytic performance in methanol decomposition

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I. Supports preparation

Powder SiO_2, starch and deionized water were mixed by the kneader, and then the mixture was extruded as a strip. The obtained strip was dried in air for 10h at 100℃. This starch modified SiO_2 was denoted as SiO_2-S, and the mass fraction of SiO_2 and starch was 85.0% and 15.0%, respectively. The SiO_2-S support calcined at 500℃ was denoted as SiO_2-S-500.

Using the powder SiO_2 and deionized water as materials, the obtained strip was denoted as SiO_2.

II. Catalysts preparation

The catalyst samples, with the same 22.5% Cu loading, were prepared by impregnating the supports with an aqueous solution of $Cu(NO_3)_2$. The samples were dried in air for 12h at 120℃ and named as $Cu(NO_3)_2/SiO_2$, $Cu(NO_3)_2/SiO_2$-S and $Cu(NO_3)_2/SiO_2$-S-500. Then the dried samples were calcined in air or nitrogen at 300℃ for 2h and reduced in pure H_2 at 300℃ for 2h, and the obtained samples were denoted as Cu/SiO_2[300-Air], Cu/SiO_2-S[300-Air], Cu/SiO_2-S[300-N_2] , Cu/SiO_2-S-500[300-Air].

III. Catalysts characterization

Temperature Programmed Reduction (TPR) was carried out on a FINESORB-3010C muti-function adsorption instrument using 0.03g sample for each run. The catalyst was loaded into a quartz tube and pretreated in Ar at 300 for 30min, then cooled to room temperature(RT). After that H_2-TPR was started from RT to 500℃ at a heating rate of 10℃/min in 10ml/min of 10%H_2/Ar. A thermal conductivity detector(TCD) was used to monitor the consumption of H_2.

The surface area of metallic copper and copper dispersion was determined by the method of dissociative N_2O adsorption[1]. Firstly, Catalysts were reduced at 300℃ for

30min by the H_2-TPR procedure described above. In this step the amount of hydrogen consumption was denoted as X. Second, the temperature was cooled to 50℃ in 10%H_2/Ar, then switch to 5%N_2O/He(10ml/min) for 30min. After that, decreased the temperature to RT, and the He was used to purge the catalyst for 30min. At last, the catalyst was reduced by the same H_2-TPR procedure of first step, and the amount of hydrogen consumption was denoted as Y. Based on above results, the dispersion(D) and surface area(S) of Cu were calculated as follows:

First step: $CuO+H_2 \rightarrow Cu+H_2O$ X=hydrogen consumption
Second step: $2Cu+N_2O \rightarrow Cu_2O+N_2$
Third step: $Cu_2O+H_2 \rightarrow 2Cu+H_2O$ Y= hydrogen consumption

$$D = \frac{2Y}{X} * 100\%$$

$$S = \frac{1353 * Y * Cu\%}{X} \quad (m^2\text{-Cu/g-Cat.})$$

Cu%: the content of Cu in the catalyst

The X-ray diffraction patterns (XRD) were recorded on a Rigaku MiniFlexⅡdesktop X-ray diffractometer (30 KV, 15 mA) in a 2θ range of 10-80°with Cu Kα radiation to identify the crystalline phases and estimate the relative crystallinities of samples. The particle sizes of CuO were calculated by using Scherrer equation.

X-ray photoelectron spectroscopy(XPS) was carried out on a AXIS ULTRA DLD(Kratos) with Al Kα radiation(hv=1486.6eV). The binding energies were reference to C 1s(284.8eV).

The high resolution transmission electron microscopy (HRTEM) images of catalysts were obtained by a JEM 2010 microscope operating at 200kV. The samples were dispersed in ethanol by ultrasonic for 30min. The obtained suspension liquid was deposited on copper grids coated with amorphous carbon films.

Thermo Gravimetric-Differential Thermal Analyzer (TG-DTA) of supports and dried catalyst samples were carried out on a TG-60 thermal analyzer(Shimadzu) at a heating rate of 5℃/min from 40℃ to 500℃ under the atmosphere of Air or N_2.

IV. Catalysts test

Methanol decomposition was carried out in a 10ml fixed-bed down-flow reactor. The catalyst (8-14 mesh) was loaded into the constant temperature section of the reactor. Prior to catalytic reaction, the catalyst was reduced in pure H_2 at 300℃ for 2h. After that, methanol was fed into the reaction. The reaction conditions were 300℃, atmospheric pressure, weight hourly space velocity(WHSV) of $1.56h^{-1}$. The products were analyzed by using an on-line gas chromatograph.

V. Tables and Figures

Table S1. The properties of catalysts

catalyst	Cu dispersion (%)[a]	$S_{Cu}{}^0$ (m^2/g-cat.)[a]	d_{CuO} (nm)[b]	d_{Cu} (nm)[c]	d_{Cu} (nm)[d]	$R_{Cu/Si}{}^e$
Cu/SiO_2[300-Air]	4.3	6.5	15.3	20	25.1	0.008
Cu/SiO_2-S[300-Air]	21.3	31.5	8.6	8.0	8.7	0.061
Cu/SiO_2-S-500[300-Air]	8.4	12.3	16.3	-	-	-

a. Cu dispersion and surface area of Cu^0($S_{Cu}{}^0$) were determined by method of dissociative N_2O adsorption. b. Diameter of CuO particles calculated from the XRD data (Figure 1) of the (111) peak broading of CuO by Scherrer equation. c. Diameter of Cu particles (after reduced) calculated from the XRD data (Figure S5) of the (111) peak broadening of Cu by Scherrer equation. d. Diameter of Cu particles (after used) calculated from the XRD data (Figure S5) of the (111) peak broadening of Cu by Scherrer equation. e. Mole ratio of Cu to Si of the catalysts determined by XPS(Figure S3).

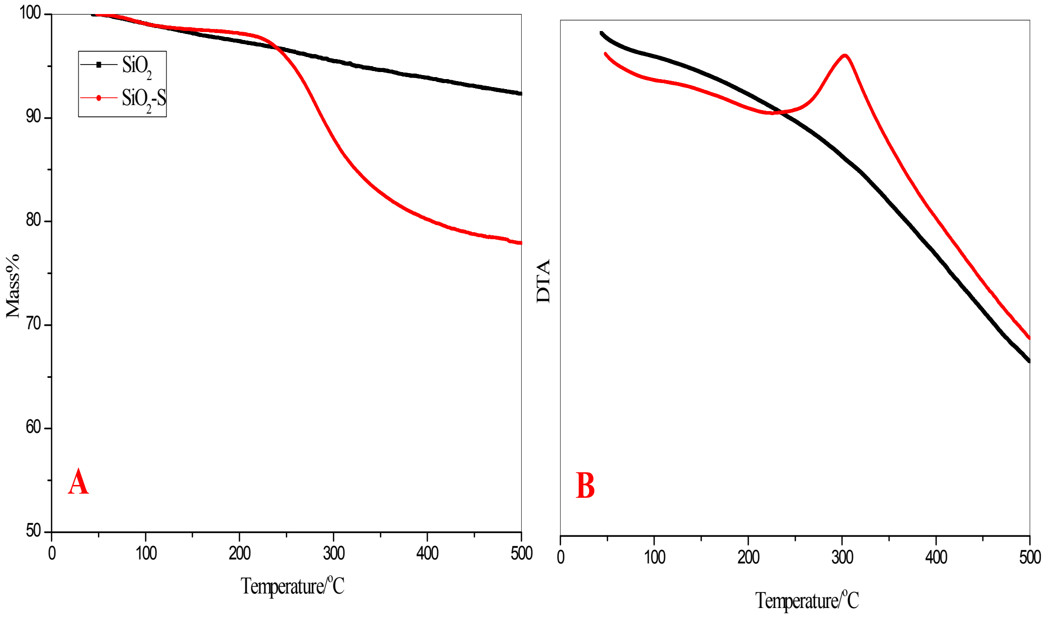


Figure S1 TG-DTA curves of SiO_2 and SiO_2-S in air

A: TG B: DTA

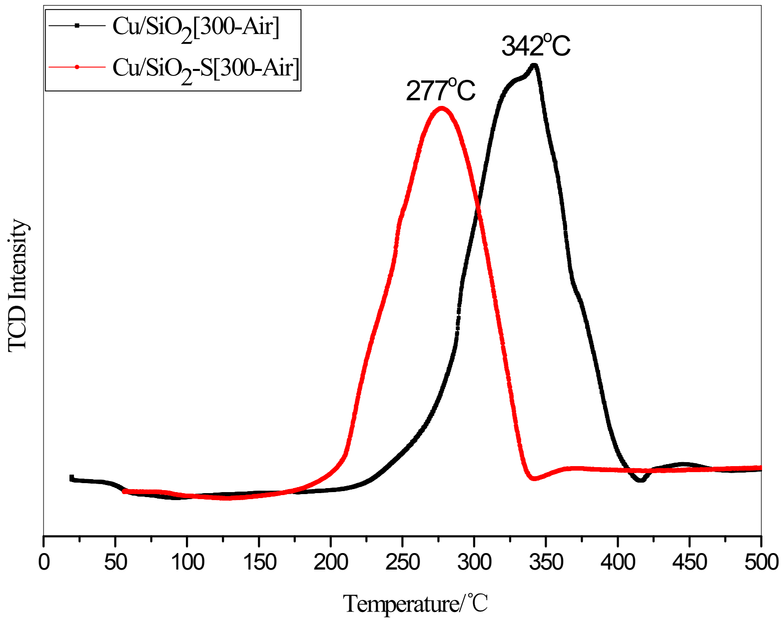
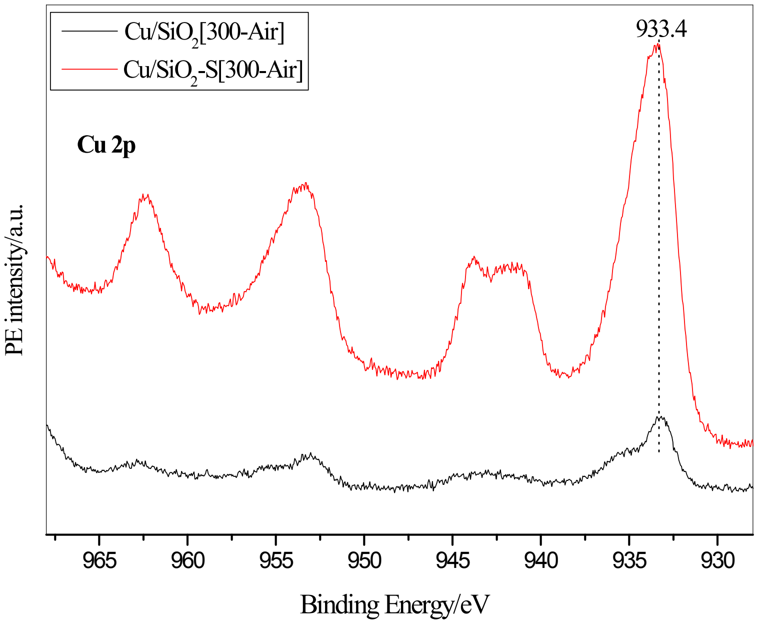


Figure S2 TPR profiles of fresh samples(after calcination)



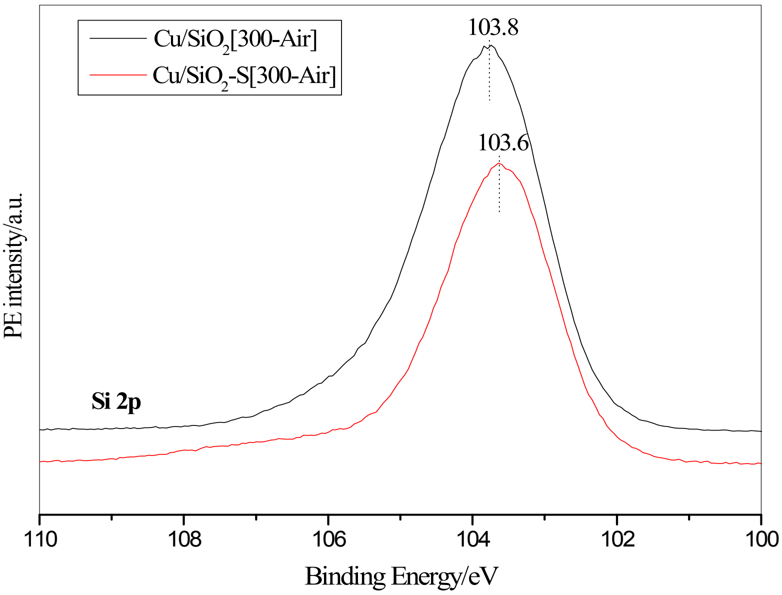


Figure S3 Cu2p and Si2p XPS photoemission peaks of fresh samples (after calcination)

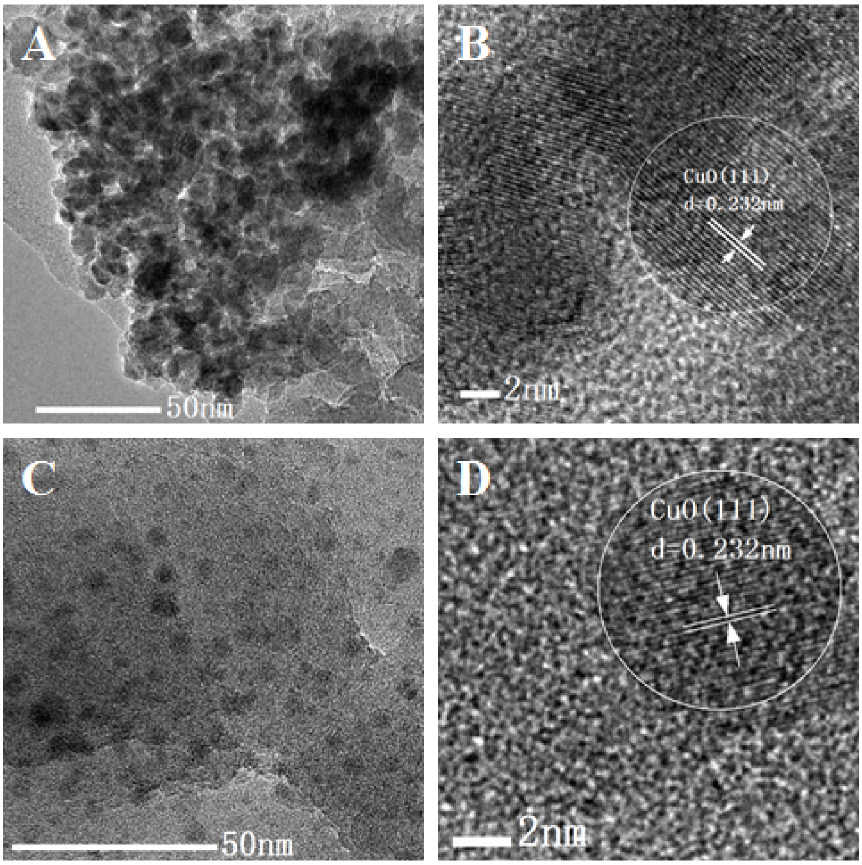


Figure S4 TEM and HRTEM images of fresh Catalysts (after calcination)
A-B: Cu/SiO$_2$[300-Air], C-D: Cu/SiO$_2$-S[300-Air]

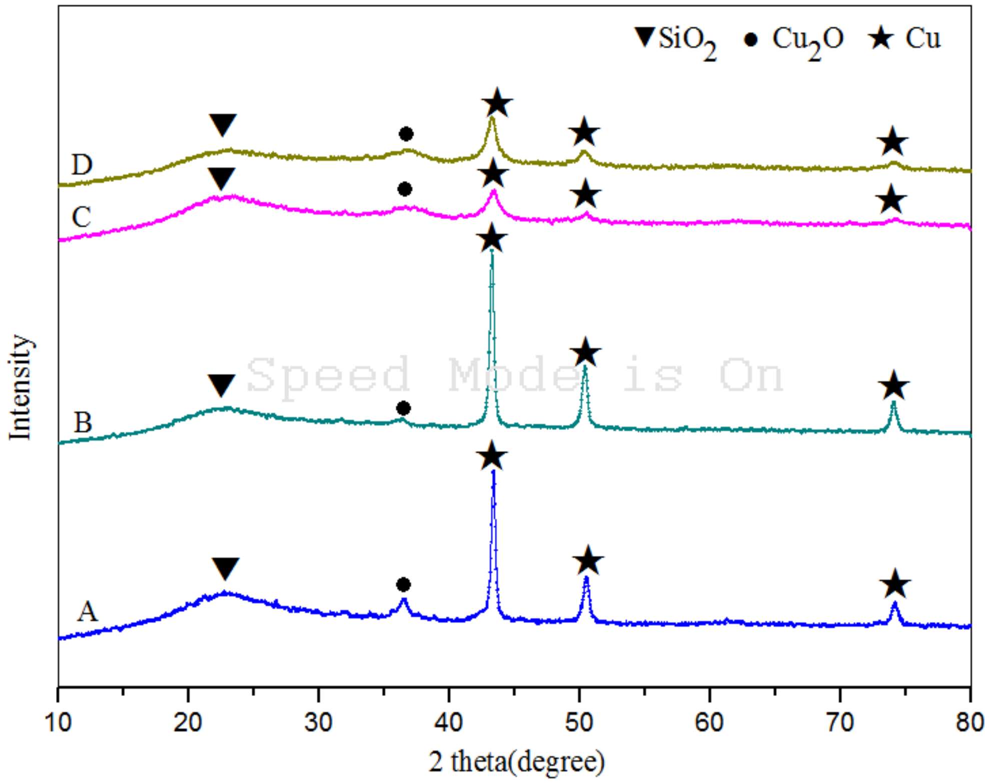


Figure S5 The X-Ray diffraction patterns of catalysts
Cu/SiO_2[300-Air]:A-reduced, B-used
Cu/SiO_2-S[300-Air]:C-reduced, D-used

VI Reference

[1] (a) J.L. Gong, H.R. Yue, Y.J. Zhao, S. Zhao, L. Zhao, J. Lv, S.P. Wang, X.B. Ma, J. Am. Chem. Soc. 2012, 134, 13922-13925. (b) Z.L. Yuan, L.N. Wang, J.H. Wang, S.X. Xia, P. Chen, Z.Y. Hou, X.M. Zheng, Appl. Catal. B: Environ. 2011, 101, 431-440.