Synthesis of Dimethylformamide from CO_2, H_2 and dimethylamine over Cu/ZnO

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1. Experimental Section

Chemicals $Cu(NO_3)_2{\cdot}3H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ were purchased from Sinopharm Chemical Reagent Co. Ltd. $Al(NO_3)_3{\cdot}9H_2O$, Na_2CO_3, $Ce(NO_3)_3{\cdot}6H_2O$, $Na_2B_4O_7$, HCl (36% aqueous solution), H_2SO_4, ammonia aqueous solution (28%), DMF, n-butanol, and ethanol were provided by Beijing Chemical Reagent Company. Dimethylammonium-dimethylcarbamate (DIMCARB) was purchased from ACROS Organics. The molar ratio of dimethylamine to CO_2 in the DIMCARB was 1.6:1, as determined by standard acid base titration method.[S1] All chemicals above were analytical grade and used as received. The CO_2 (>99.99%), H_2 (>99.99%), and N_2 (>99.95%) were provided by Beijing Analytical Instrument Company.

Determination of dimethylamine content in dimethylammonium-dimethylcarbamate (DIMCARB) The content of dimethylamine in the DIMCARB was determined according to the standard acid base titration method.[S1] In the experiment, the mixture of 0.1g DIMCARB and 3mL concentrated H_2SO_4 was heated in a three-necked flask at 413 K for 2 hours. 15mL of 40% (w/v) NaOH solution was added and distillation was performed and the distillate entered a 25mL of 4% (w/v) boric acid solution. Water was injected regularly into the three-necked flask during the distillation. The distillation continued until about 100 mL of the distillate was obtained. An mixed solution of indicators (0.2% (w/v) methyl red ethanol solution and 0.1%(w/v) methylene blue ehtanol solution was added into the distillate before titrating with a standardized 0.1mol/L HCl solution for dimethylamine content. The molar ratio of dimethylamine to CO_2 in the DIMCARB was 1.6:1. The repeatability of the method was better than ±3%.

Catalyst characterization The scanning electron microscopy (SEM) examination was conducted on a Hitachi-s4800 electron microscope operated at 10 kV. The samples were spray-coated with a thin layer of platinum before observation. The transmission electron microscopy (TEM) characterization was carried out on JEM 2011 at an accelerating voltage of 100 kV. The samples were dispersed in ethanol and dropped on a carbon film supported on copper grid for TEM analysis. Powder XRD measurements were performed on a Rigaku D/max2500 diffractometer using CuKα radiation (λ=1.5406 Å). X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlKα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The ratios of the metals in the catalysts were calculated from the masses of the chemicals used to prepare the catalysts, which agreed well with the data determined in this work by ICP (ICP-OES, Optima 5300DV). This is understandable because the precursors of Cu, Zn, and Al are insoluble at the pH value to prepare the catalysts. [S2]

2. Results

SEM, TEM, and HRTEM images of the catalysts The SEM, TEM, and HRTEM images of the $Cu/ZnO/Al_2O_3$, Cu/Al_2O_3, ZnO/Al_2O_3, Cu, ZnO, Al_2O_3 catalysts used are presented in Figures S1-S6.

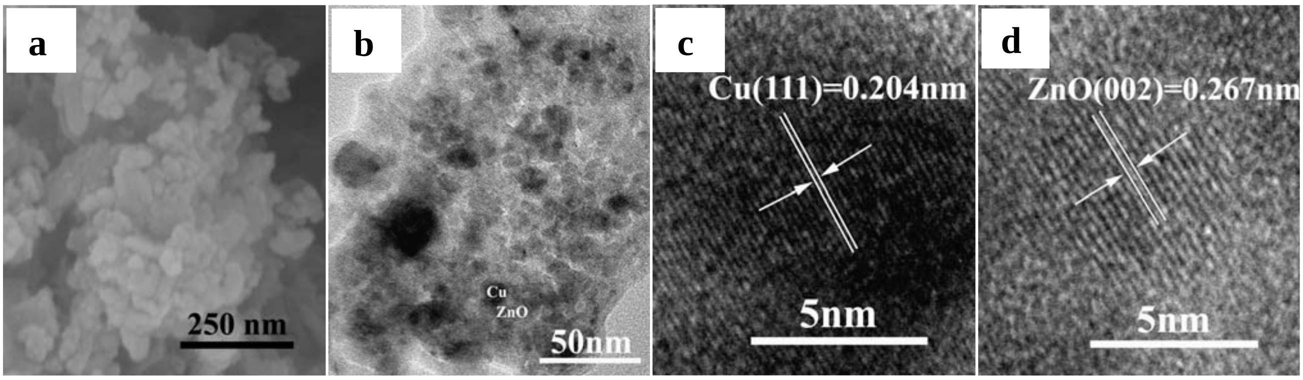

Figure S1. The SEM, TEM, HRTEM images of $Cu/ZnO/Al_2O_3$ (3:2:2)

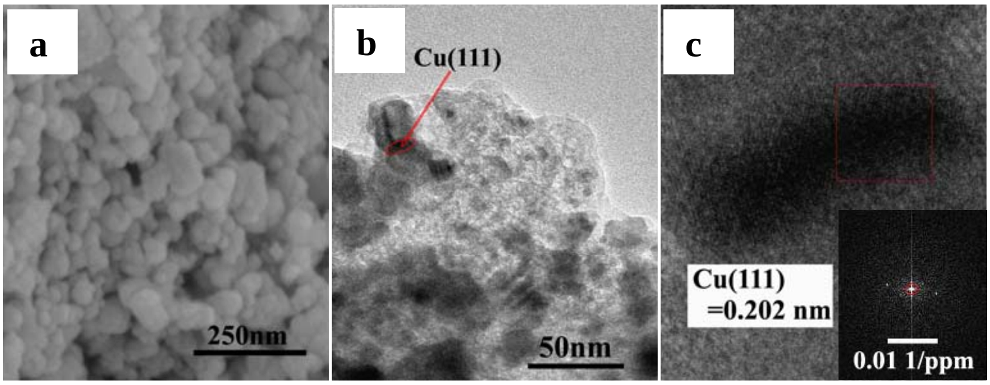

Figure S2. The SEM, TEM, HRTEM images of Cu/Al_2O_3 (3:2)

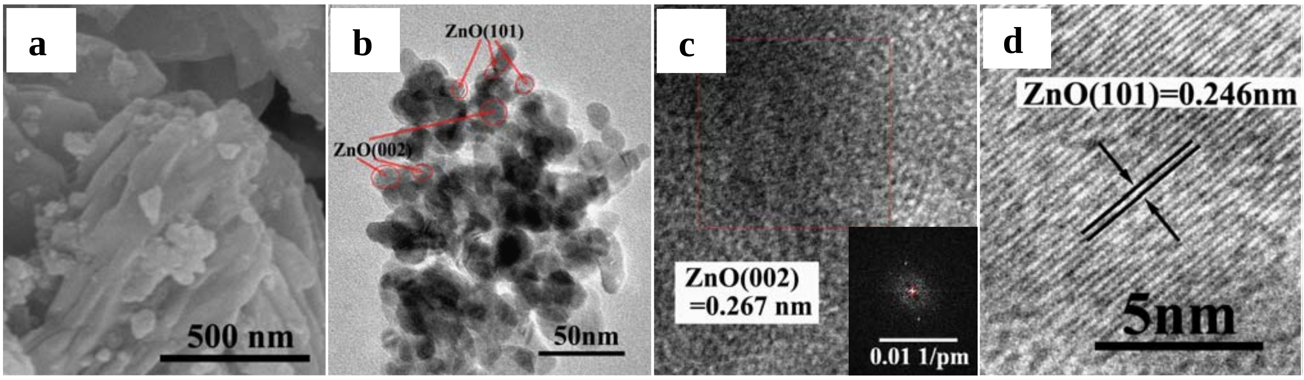

Figure S3. The SEM, TEM, HRTEM images of ZnO/Al_2O_3(1:1)

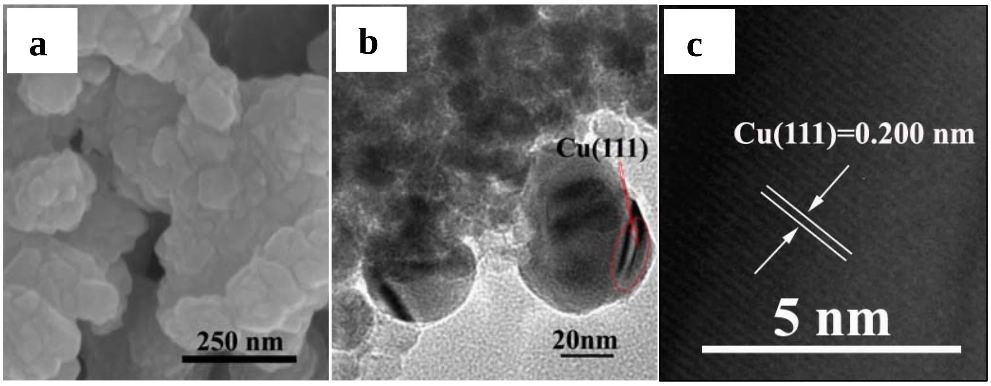

Figure S4.The SEM, TEM, HRTEM images of Cu

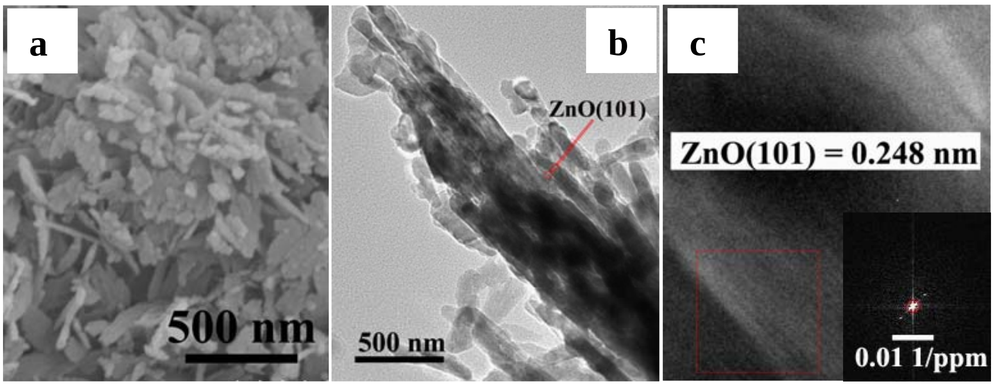

Figure S5.The SEM, TEM, HRTEM images of ZnO

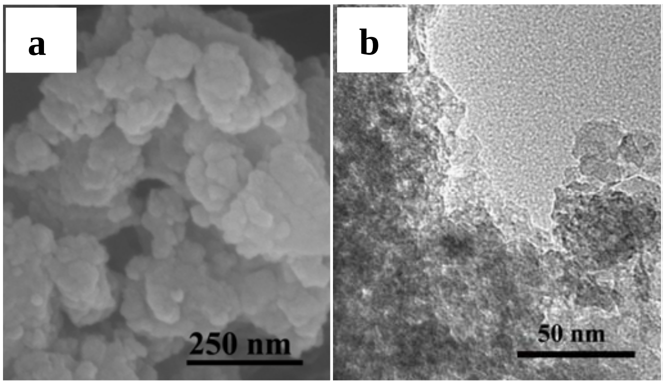

Figure S6 The SEM, TEM, HRTEM images of Al_2O_3

References

(S1) (a) HG/T 2971- 1999, Ultimate analysis of coal. (b) GB/T 476-2001, Solutions of methylamines for industrial use-Standard test method.

(S2) K. Nishida, I. Atake, D. Li, T. Shishido, Y. Oumi, T. Sano and K. Takehira. *Appl. Catal. A: General* 2008**,** **337**, 48–57.