

Supporting Information

A Novel Approach of Reduction of CO₂ into Methanol by Water Splitting with Aluminum over Copper Catalyst

Lingyun Lyu^a, Fangming Jin^{*a}, Heng Zhong^{*b}, Hongjuan Chen^c, Guodong Yao^a

^a School of Environmental Science and Engineering, Shanghai Jiao Tong University,
800 Dongchuan Road, Shanghai 200240, China

^b Research Center for Advance Science and Technology, The University of Tokyo,
Tokyo 153-8904, Japan

^c State Key Laboratory of Pollution Control and Resources Reuse, College of
Environmental Science and Engineering, Tongji University, 1239 Siping Road,
Shanghai 200092, China

* To whom correspondence should be addressed. E-mail: fmjin@sjtu.edu.cn;
Tel/Fax: (86)21-54742283; zhongheng@hotaka.t.u-tokyo.ac.jp

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1. Experimental Methods and Materials

1.1 Test Materials. NaHCO₃ was used as the source of CO₂ to simplify the experiments. NaHCO₃, Al (200 mesh), Fe (200 mesh), Zn (200 mesh), Cu (200 mesh), CuO, hydrochloric acid (38%) and sulfuric acid (98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Mn (200 mesh) was obtained from Aladdin Chemical Reagent. For all metals and oxides, 200 powders were used. Formic acid (98%), methanol and formic acid were obtained from Sigma-Aldrich. All reagents were used as test materials without further purification. Formic acid and methanol were used for the quantitative analysis of liquid products.

1.2 Experimental Procedure. All experiments were conducted in a SUS 316 lined reactor with an internal volume of 42 mL. The desired amounts of NaHCO₃, metal reductant, catalyst and degassed deionized water (deionized water was purged with nitrogen for 20 min to removing the oxygen dissolved in the deionized water) were added to the SUS 316 reactor, and then the reactor was purged with nitrogen for 5 min to remove the air in the reactor. After that the reactor was sealed and put into an induced heating furnace and heated to a desired temperature with an increasing 15 °C /min. For experiments with the addition of HCl, to avoid the reaction between HCl and NaHCO₃, HCl was put firstly in the bottom of the reactor, and then a piece of SUS-316 mesh (the same materials as the reactor) was horizontally put in the middle of the reactor. After that, solid reagents of Cu, Al and NaHCO₃ were put on the mesh. After sealing, the reactor was reversed to make the added reagents fully mix and then was putted into the heater for the reaction. After the reaction time, the reactor was taken out of the furnace and cooled by electric fan. The water filling was defined as the ratio of the volume of the water put into the reactor to the inner volume of the reactor, and the reaction time was defined as the time during the temperature reached to the desired reaction temperature to the preset time. After the reaction, liquid samples were collected and filtered through a 0.22- μ m filter for analysis. Solid samples were washed with deionized water and ethanol for three times and then dried in air for further analysis. Gaseous samples were collected by a gas-collection for analysis.

1.3 Product Analysis. A high-performance liquid chromatography (HPLC) analyses was

performed on Agilent 1260 series equipped with a tunable ultraviolet/visible (UV-vis) detector and two Shodex RSpak KC-811 columns. The solvent in the system was 2 mmol/L HClO₄ with a flow rate of 1.0 mL·min⁻¹ and the UV absorbance detector adjusted to 210 nm. Gas chromatography/mass spectroscopy (GC-MS) was Agilent 7890A GC system and equipped with a 5975C inert mass selective detector (MSD). The samples were separated by HP-Innowax capillary column with helium as a carrier gas. GC-FID (Shimadzu GC-2010) equipped with DB-FFAP capillary column with a dimension of 30 m × 250 μm × 0.25 μm. Gaseous samples were analyzed by HP-5890 Series II GC-TCD system equipped with an HP-Innowax packing column. Solid samples were characterized by XRD on Shimadzu XRD-6100 equipment.

The yield of methanol is defined as the percentage of methanol to the initial NaHCO₃ on the carbon basis as follows. The yields were the mean value of three times experiments and relative errors were less than 5%.

$$Yield, \text{ mmol } \% = \frac{C \text{ in methanol, mmol}}{C \text{ in the initial NaHCO}_3, \text{ mmol}} \times 100 \% \quad (1)$$

2. Some of analytic results for solid and liquid samples by XRD, GC-MS, GC-TCD, GC-FID and HPLC

2.1 XRD patterns of the solid samples

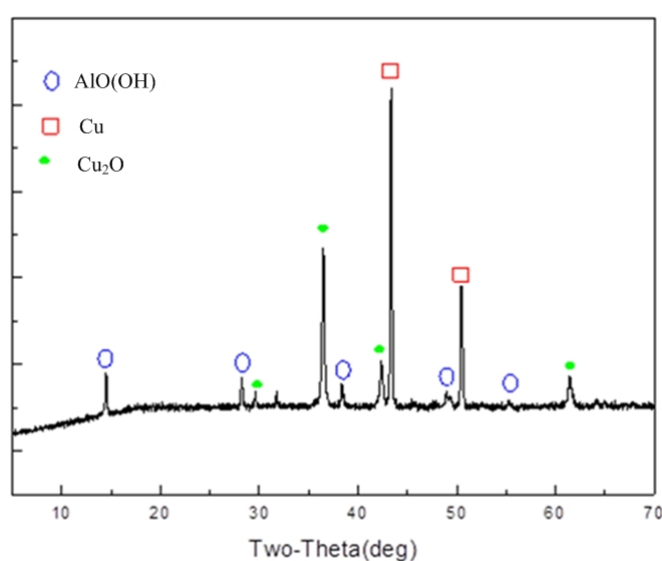


Figure SI-1. XRD patterns of the solid samples (temperature, 350 °C; time, 2 h; NaHCO₃, 40 mmol; Al, 40 mmol; Cu, 50 mmol; water filling, 50%; hydrochloric acid, 1.2 mol/L).

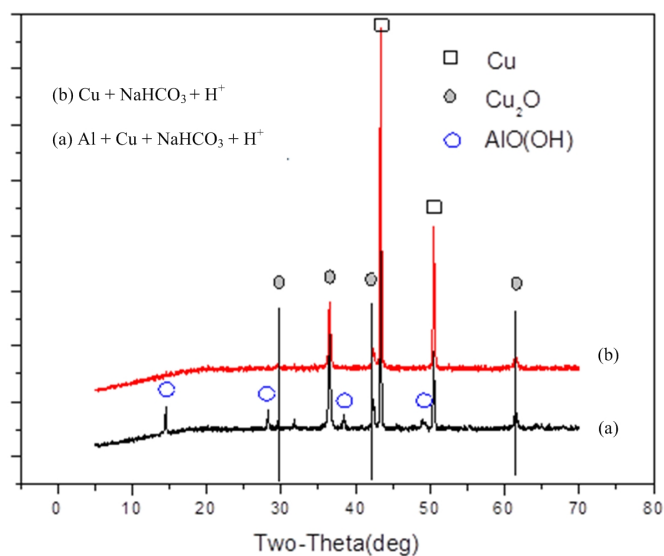


Figure SI-2. XRD patterns of the solid samples (Al, 40 mmol; temperature, 350 °C; time, 2 h; NaHCO₃, 40 mmol; Cu, 50 mmol; water filling, 50%; hydrochloric acid, 1.2 mol/L).

2.2 GC-MS, GC-TCD, GC-FID and HPLC chromatograms of liquid products

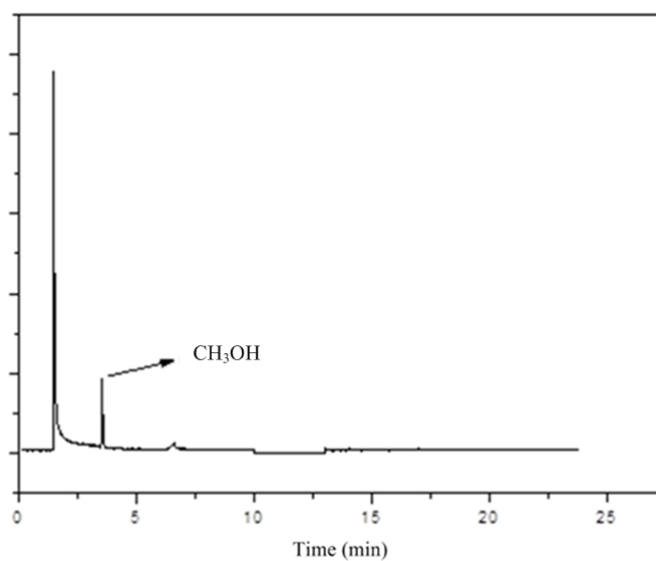


Figure SI-3. GC-MS chromatogram of the liquid sample after reaction (temperature, 350 °C; time, 2 h; NaHCO₃, 40 mmol; Al, 40 mmol; Cu, 50 mmol; water filling 50%; hydrochloric acid, 1.2 mol/L).

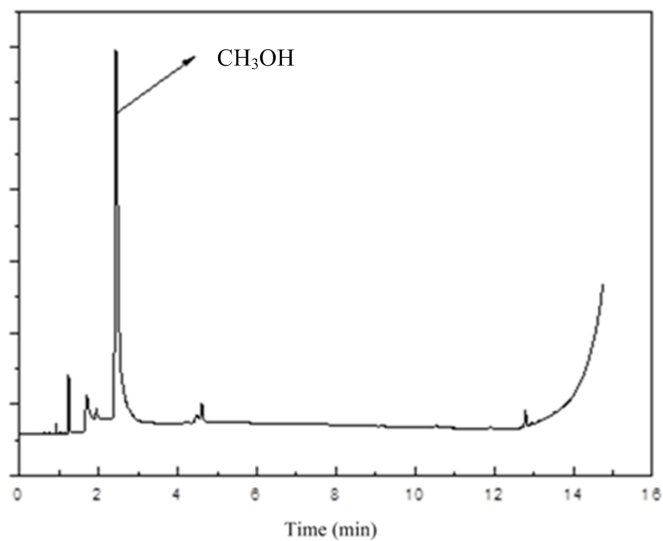


Figure SI-4. GC-FID chromatogram of the liquid sample after reaction (temperature, 350 °C; time, 2 h; NaHCO₃, 40 mmol; Al, 40 mmol; Cu, 50 mmol; water filling, 50%; hydrochloric acid, 1.2 mol/L).

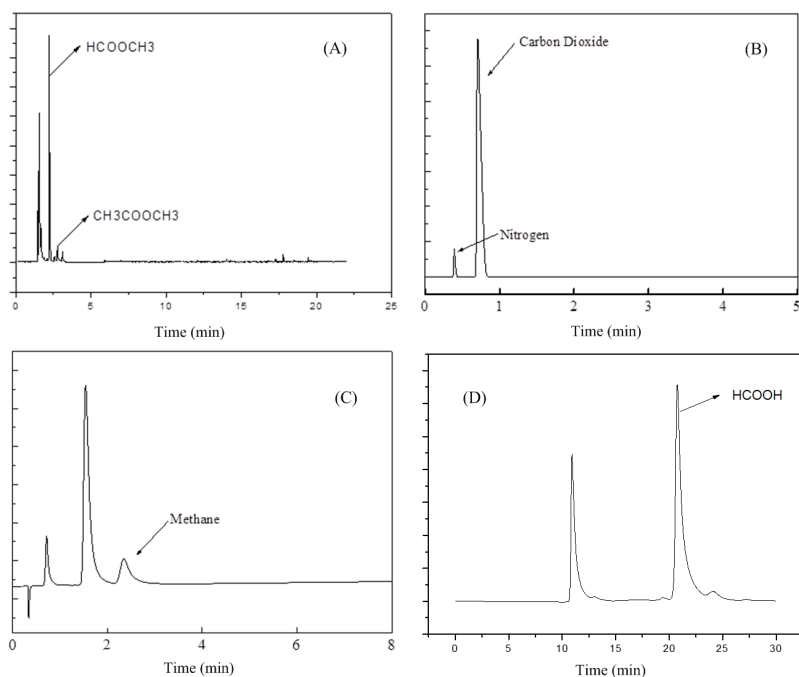


Figure SI-5. GC-MS (A), GC-TCD (B and C) and HPLC (D) chromatogram of the liquid sample after reaction (temperature, 350 °C; time, 2 h; NaHCO₃, 40 mmol; Al, 40 mmol; Cu, 50 mmol; water filling, 50%; hydrochloric acid, 1.2 mol/L. (A), liquid sample was esterified pre-treatment for GC-MS analyzing).