

Electronic Supplementary Information (ESI)

Preparation of Supported Mo₂C-Based Catalysts from Organic-Inorganic Hybrid Precursor for Hydrogen Production from Methanol Decomposition

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Experimental section:

The precursor of Mo₃O₁₀(C₆H₈N)₂·2H₂O was prepared through the co-precipitation process. 2.48 g of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) was dissolved in 40 ml of distilled water, and 3.34 g of aniline was added in the above solution. Afterwards, 1 M HCl aqueous solution was dropwise added with magnetic stirring at room temperature until white precipitate appeared (pH 4~5). After a reaction with stirring at 50 °C in oil bath for 2~6 hours, the product was filtrated and washed with ethanol, and dried at 50 °C.

The synthesis of supported Mo₂C catalysts was conducted as follow: 0.266 g of Mo₃O₁₀(C₆H₈N)₂·2H₂O was dispersed and dissolved in 40 mL H₂O and 40 mL EtOH, followed by adding of 1.9 g of CNT. After stirring for 10 hours at room temperature, this mixture was dried at 50 °C. Finally, Mo₂C/CNT catalysts can be obtained by calcining the above dried product at 725 °C for 5 hours under argon flow.

Co-Mo₂C/CNT catalysts were prepared through the same impregnation procedure as Mo₂C/CNT except that Co(NO₃)₂·2H₂O is added with Mo₃O₁₀(C₆H₈N)₂·2H₂O in the starting impregnation solutions to different Mo/Co ratios. The sum of loaded Mo₂C and

Co is fixed as 6.0%. After the same calcinations as those in Mo₂C/CNT catalysts, a series of Co-Mo₂C/CNT catalysts were obtained.

Physical measurement: XRD patterns were taken on a Bruker D8 diffractometer using Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$). TEM and SEM images were obtained on a JEOL JEM-2011 and a Philips XL 30 instrument. N₂ sorption isotherms were collected on a Micromeritics ASAP 2010 adsorption analyzer at -196 °C (77 K). BET specific surface area was calculated from adsorption data at a relative pressure range from 0.071 to 0.20. And X-ray fluorescence measurement on Bruker S4Explorer was used to measure Mo/Co ratio of each sample (after calibration using standard samples).

Catalytic activity of methanol decomposition was conducted at atmospheric pressure in a fixed-bed, continuous flow reactor consisting of a reaction tube (8 mm i.d.) with a thermocouple located in the catalyst bed. The amount of the catalyst used was 1.0 g. Methanol was injected into the reactor by a metering pump. The carrier gas was argon with a flow rate of 40 ml/min. The effluent composition was analyzed by an Agilent 6820 gas chromatograph equipped with a thermal conductivity detector (TCD) and a Porapak Q packed column. The performance of the catalysts was analyzed in terms of hydrogen production rate, methanol conversion and hydrogen selectivity in all H₂-containing products.

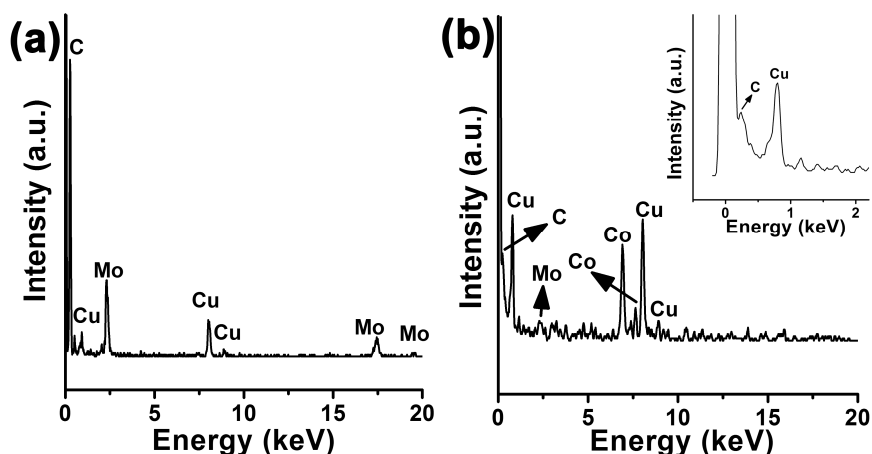


Fig. S1 EDS of (a) Mo₂C and (b) Co nanoparticles in Co-Mo₂C/CNT catalyst. The inset of b is the magnification of EDS signal in the range of 0~2 keV.

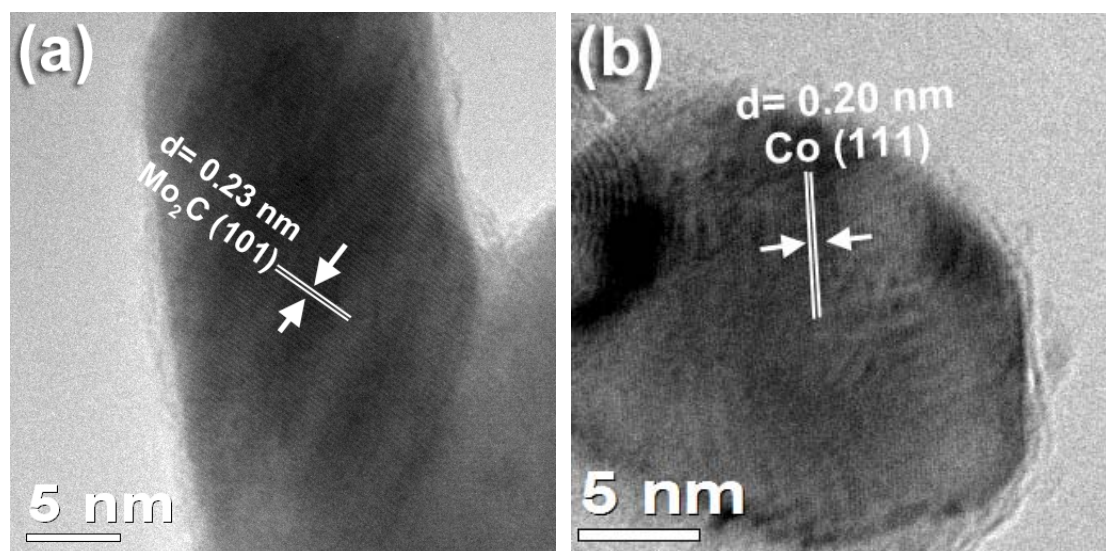


Fig. S2 Magnified TEM images of (a) Mo₂C and (b) Co nanoparticles in Co-Mo₂C/CNT catalyst, which have been shown in manuscript as Fig. 1 d and e, respectively.

Table S1 The BET surfaces of supported Mo₂C-based catalysts

Catalysts (loading amount: 6.0%)	S _{BET} (m ² /g)
CNT blank	181.8
Mo ₂ C/CNT	156.5
Co-Mo ₂ C/CNT (Mo/Co=3.0)	148.8
Co-Mo ₂ C/CNT (Mo/Co=2.0)	159.7
Co-Mo ₂ C/CNT (Mo/Co=1.0)	152.2
Co-Mo ₂ C/CNT (Mo/Co=0.5)	150.5
Co-Mo ₂ C/CNT (Mo/Co=0.3)	149.7

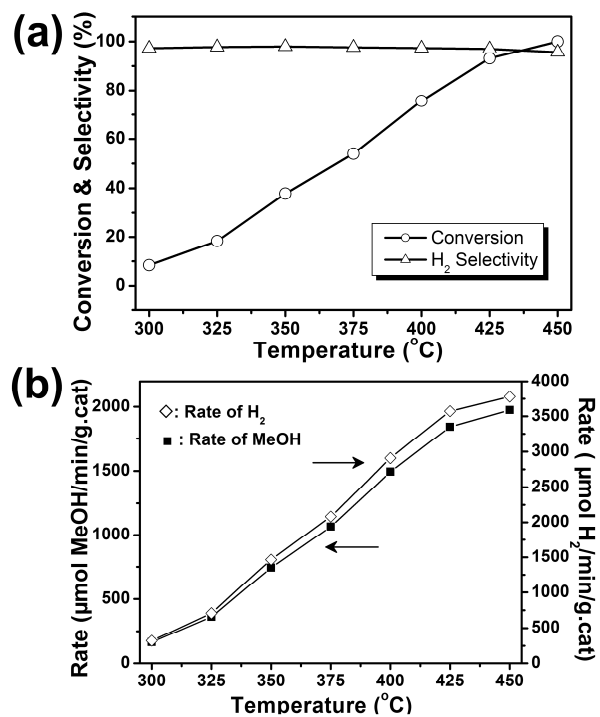


Fig. S3 (a) Producing H₂ from methanol decomposition over 6.0 wt% Co-Mo₂C/CNT (Mo/Co = 1.0) with increasing reaction temperature, and (b) the corresponding reaction rate and hydrogen production rate. Data were taken after 2 hours of reaction at given temperatures.

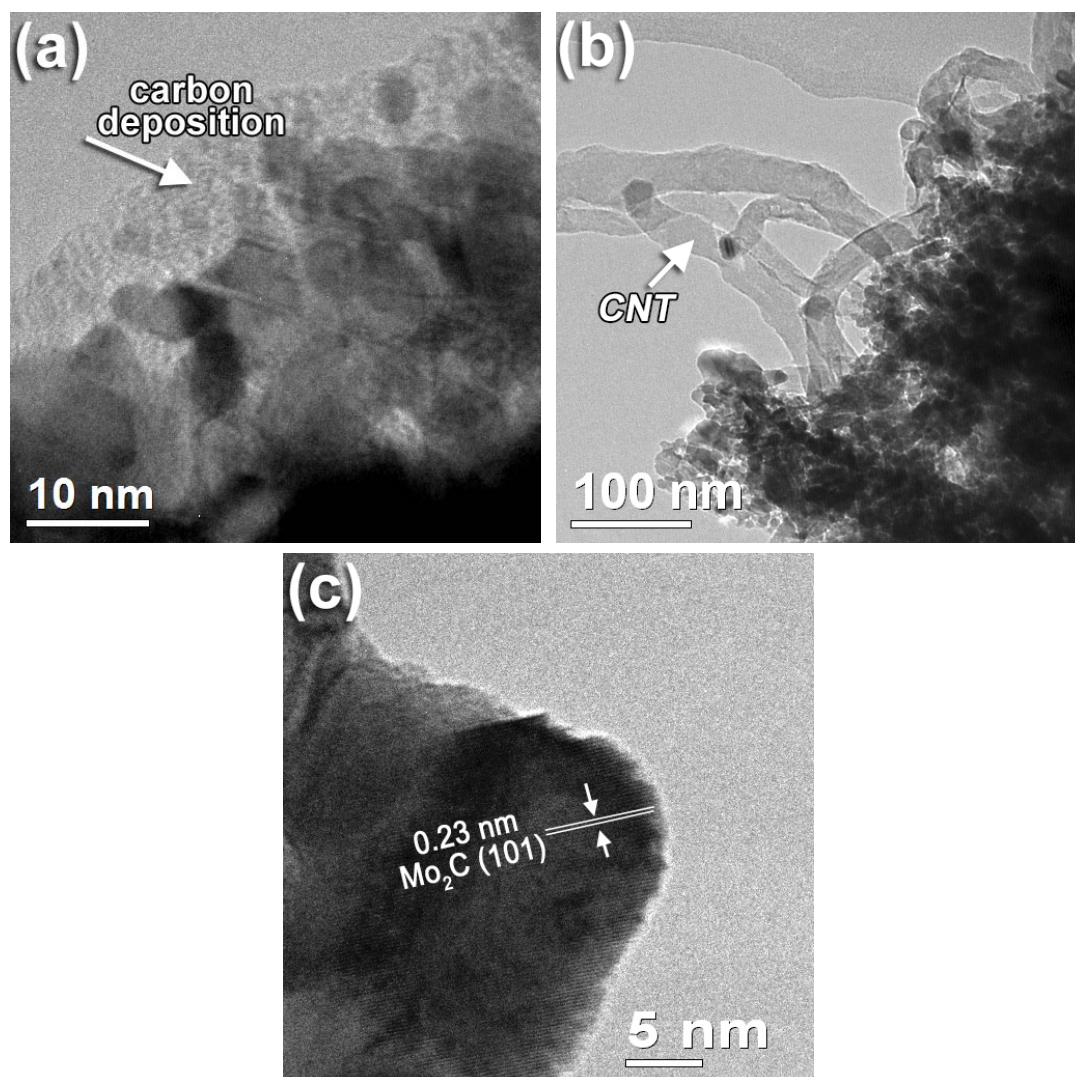


Fig. S4 Magnified TEM images of the carbon deposition on the (a) Mo₂C and (b) Co-Mo₂C catalysts after treated under CH₃OH/Ar at 450 °C in tubular reactor for 8 h. (c) is the HRTEM of Mo₂C surface in Co-Mo₂C after methanol treatment. These images have been shown in manuscript as Fig. 3.