SUPPLEMENTARY INFORMATION

Thin-water-film-enhanced TiO₂-based catalyst for CO₂ hydrogenation to formic acid

Shaoqin Chen,^{a,b} Siyuan Fang,^b Zongwei Sun,^a Zhangyang Li,^a Chunling Wang^{*a} and Yun Hang Hu^{*b}

^aSchool of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

^bDepartment of Materials Science and Engineering, Michigan Technological University, Houghton, Michigan 49931-1295, United States

*Corresponding authors. Email: wangchunling@sjtu.edu.cn, yunhangh@mtu.edu

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Experimental section

Materials

Titanium (IV) oxide (P25, TiO₂, 99.5%) was purchased from Sigma-Aldrich Co., Ltd. Hydrazine sulfate (N₂H₄·H₂SO₄, 99.0%), ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 99%), and ammonium acetate (CH₃COONH₄, 99.7%) were purchased from Macklin Co., Ltd. All chemicals were used without further purification. Other metal precursors included CH₃COOH (Sinopharm), ethanol (Sinopharm), and diethyl ether (Sinopharm). The feed gas mixture (25% CO₂ + 75% H₂) was supplied by Air Liquid Co., Ltd.

Synthesis of the catalysts

 N_2H_4 · H_2SO_4 (0.8 g, 6.1 mmol) was added into a 250 mL aqueous solution containing $(NH_4)_6Mo_7O_{24}$ · $4H_2O$ (5.6 g, 4.5 mmol) and CH_3COONH_4 (12.5 g, 162.2 mmol). The solution was stirred for 10 min with the color turning to blue-green, after which 83 mL 50% CH_3COOH was added. The resulting solution, now green, was stored in a 500 mL open beaker in the fume hood at 20 °C for 4 d without further stirring, during which the slow color change to dark brown was observed. Afterwards, Mo_{132} , as crystallized on the inner wall of the beaker, was washed with ethanol and diethyl ether for several times followed by pulverization and drying in air.

2.5 wt% Mo_{132}/TiO_2 catalyst was synthesized by wet impregnation. Namely, 0.028g Mo_{132} and 0.500 g TiO₂ were added to 10 mL water, which was then stirred for 10 min, followed by in-situ hydrothermal treatment at 60 °C for 12 h to disperse Mo_{132} molecules onto TiO₂ surface (Scheme S2).

Characterizations

High resolution-transmission electron microscopy (HRTEM) images were acquired on a HT7700 Exalens transmission electron microscope with an acceleration voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) measurement was carried out with an AXIS Supra X-ray photoelectron spectrometer by Kratos Analytical Inc. using monochromatized Al K α radiation (hv = 1486.7 eV, 225 W) with a base pressure of 10^{-9} torr. X-ray diffraction (XRD) patterns of the samples were recorded on a Shimadzu XRD-6100 X-ray diffractometer. Raman spectra were taken in the range of 200-1000 cm⁻¹ using the Senterra R200-L micro-Raman spectrometer with an excitation wavelength of 785 nm by an Ar ion laser. Fourier-transform infrared spectroscopy (FT-IR) was performed using a Nicolet IS-10 infrared spectrometer in the range from 400 to 4000 cm⁻¹. The surface areas of the samples were measured and calculated using the multipoint Brunauer-Emmett-Teller (BET) technique with a BET Sorptometer (ASAP 2020 PLUS HD88) based on the adsorption isotherms. Thermolysis was studied by a SDT Q600 V20.9 Build 20 equipment. Test sample was heated at 5 °C/min in air.

Catalytic activity measurement

A 2 mL suspension containing 15 mg catalyst was dropwise added onto a piece of frosted glass (5.2 cm × 2.5 cm), which was then heated at 60 °C for 30 min. The accurate catalyst amount was calculated from the difference in the mass of the pristine glass and catalyst-coated glass. 20 mL water was added into the reactor, and then the catalystcoated glass was inset into the container right above water (5 cm away) (Scheme S3). Afterwards, the reactor was sealed and purged with the gas mixture of CO₂ and H₂ for several times to remove the remaining air, and then pressurized to 2.0 MPa. The reactor was then heated to a preset temperature in the range of 50-200 °C by an electrical furnace. After 2 h reaction, the reactor was cooled down to room temperature. CH₄ and CO were analyzed by gas chromatography (GC, Kechuang GC-9800) with a TDX packed column and a thermal conductivity detector (TCD). The liquid on the glass was mixed with that in the container for analysis. CH₃OH and CH₃CHO were quantified by GC with a Propak Q packed column and a flame ionization detector (FID). HCOOH and CH₃COOH were analyzed by liquid chromatography (Shimadzu LC16) with a C18 column. In the cycling experiment, the catalyst was dried at 60 °C for 6 h after each test to remove the absorbed reactants and products. The CO₂ conversion rate was calculated by the following equation:

$$CO_2 \text{ conversion rate} = [n(CH_3OH) + n(HCOOH) + 2*n(CH_3CHO) + 2*n(CH_3COOH)] / m(catalyst)$$

where n(chemical) stands for the yield of product and m(catalyst) represents the mass of catalyst.

Isotope tracer experiments

Isotope tracer experiments were conducted by replacing 20 mL H₂O with 5 mL D₂O or H₂¹⁸O or replacing 0.5 MPa CO₂ with 0.1 MPa ¹³CO₂ while other experimental procedures were just the same as above-described. Products were analyzed by an online gas chromatography-mass spectrometry (GC-MS, PerkinElmer, PE680-SQ8T) with a DB-FFAP column (30 m). The inlet temperature was 200 °C and the split ratio was 1:10. The temperature was maintained at 60 °C for 3 min, and then elevated to 240 °C at 10 °C/min. The ion source of the mass spectrometer was electron impact ionization (70 eV), and the scan range was m/z = 8-180.



Scheme S1. Structure of Mo₁₃₂.



Scheme S2. Schematic illustration of the method to prepare Mo_{132}/TiO_2 .



Scheme S3. Scheme of the reactor.



Fig. S1. XRD patterns of TiO₂, Mo_{132}/TiO_2 and Mo_{132} (A for anatase and R for rutile

peaks).



Fig. S2. TEM image of bulk Mo₁₃₂.



Fig. S3. N_2 adsorption-desorption isotherms of (a) TiO₂ and (b) Mo₁₃₂/TiO₂.



Fig. S4. Characterization of Mo_{132}/TiO_2 after reaction. (a) Raman spectrum, (b) FT-IR spectrum in comparison with those of fresh Mo_{132}/TiO_2 .



Fig. S5. Thermogravimetric curve of Mo₁₃₂.



Fig. S6. Time-dependent catalytic activity over Mo_{132}/TiO_2 .



Fig. S7. Mass spectra of HCOOH obtained from the isotope tracer experiments with $^{13}CO_2$ over Mo_{132}/TiO_2 and background.



Fig. S8. Mass spectra of CH_3COOH obtained from the isotope tracer experiments with $^{13}CO_2$ over Mo_{132}/TiO_2 and standard spectrum of CH_3COOH (bottom).



Fig. S9. Catalytic activity of Mo_{132}/TiO_2 with different loadings.

Calibration of the thickness of the liquid film:

The method of calibration is demonstrated as following. The calibration is based on one assumption: the amount of liquid covered on the glass after the reaction is equal to the amount of liquid at the time of the reaction, plus the amount of liquid condensed above the glass sheet. Consequently, we need to subtract the vapor part to obtain the in-situ water amount. The top diameter of the container is 60 mm, bottom diameter is 28 mm, and height is 80 mm. The size of the glass is 52 mm × 25 mm. Via a geometric calculation, we get the distance from the glass sheet to the top of the chamber. We subsequently get the volume above the glass sheet in the reactor. The saturated vapor pressure of water at 150 °C is 475.72 kPa. Through the ideal gas state equation: pV=nRT, we can calculate the amount of water and the mass of water vapor, which is 0.0189 g.

Reaction time (h)	Mass difference (g)	In-situ water mass (g)	Mean thickness (µm)
0.5	0.0247	0.0058	4.5
1.0	0.0745	0.0556	42.8
2.0	0.0845	0.0656	50.5