Supporting information

Heat treatment method-induced product selectivity switch for CO₂ reduction over Ni/MoO₂

Jie Zhao*, Tao Zhang, Xiaolong Zhang, Ruixue Bao, Ruru Sun, Chuanyi Wang

School of Environmental Sciences and Engineering, Shaanxi University of Science & Technology, Xian, Shaanxi 710021, China

*Corresponding authors. Tel.: +86 18792620657.

E-mail addresses: zhaojiehj@sust.edu.cn

Experimental Section

Catalyst preparation

Materials and chemicals. The following chemical reagents were used without further purification: Molybdenum trioxide (MoO₃ 99.9% Macklin), Nickel acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O 99.9% Macklin), Aluminium oxide (α -Al₂O₃, 99.99%, Guangzhou Metal Metallurgy Co., LTD), absolute alcohol (C₂H₅OH, 99.7%;Tianjin Fuyu Fine Chemical Co., LTD).

Preparation of Ni/MoO₂ **by wet impregnation.** The Ni/MoO₂ catalysts were prepared by using an impregnation method. Typically, a certain amount of Ni(CH₃COO)₂·4H₂O was dissolved in 30 mL of deionized water and then the solution was impregnated into 0.5 g of MoO₃ and stirred for 1 h. After being placed at room temperature for 12 h, the suspension was stirred in a 60 °C water bath until no water was visible, then dried at 80 °C overnight. The obtained powder was calcined through "single-step" or "two-step", where two-step refers to heat treatment at 400 °C for 2 h in air and then for 2 h in hydrogen flow; single-step is at 400 °C in hydrogen flow only. The Ni/MoO₂ catalysts with different Ni loadings were obtained by varying the amounts of Ni(CH₃COO)₂·4H₂O added. The prepared catalysts were denoted as xNi/MoO₂-T(S), where x is an Arabic numeral, representing the mass percent of metallic Ni in the catalysts; T and S are indicated as two-step and single-step calcination, respectively.

For comparison, Al₂O₃-supported Ni was also prepared. Except for the starting materials, their preparation processes are similar to those of the Ni/MoO₂-S sample.

Catalyst Characterizations. The crystallographic information of the samples was analyzed by XRD (Bruker D8 Advance) operated at 30 mA and 40 kV using Cu K α radiation. The scanning rate was 10° min⁻¹, spanning the 2 θ range from 20° to 80°. The N₂ adsorption/desorption analysis was executed on a Micromeritics ASAP 2460 automatic adsorption at 77 K. Before measurements, the samples were degassed at 150 °C for 6 h under vacuum. Transmission electron microscopy (TEM) images were taken on a JEOLJEM 2100 electron microscope operated at 200 kV. The elemental mapping

was collected in the HAADF mode. The chemical state and binding energy of surface elements were studied by XPS (Thermo Scientific K-Alpha) with an X-ray source of Mg-Ka radiator, and the elements were calibrated by carbon C1s binding energy of 284.8 eV as a reference. The Raman spectra in the range 50-1500 cm⁻¹ were measured on bulk and powder samples at room temperature using a Horiba-Jobin Yvon LaBRam HR spectrometer. The spectra were recorded in back-scattering geometry under excitation with Nd:YAG laser radiation (532 nm) at a power of 12 mW on the sample. H₂ temperature-programmed reduction profiles (H₂-TPR) were acquired by using a homemade instrument equipped with a thermal conductivity detector (TCD). In general, 50 mg of sample was pretreated at 100 °C with Ar flow (30 mL min⁻¹) for 1 h and then tested in the temperature range of 30-800 °C, with a heating rate of 10 °C min⁻¹ under 10%H₂/Ar flow (30 mL min⁻¹). The CO₂, CO, and H₂ temperatureprogrammed desorption (CO2-TPD, CO-TPD, and H2-TPD) tests were performed using helium or argon as the carrier gas. 100 mg of the precursor was reduced in a quartz Utube under an H₂ atmosphere at 400°C for 2 h and purged with helium (or argon) at the same temperatures for 0.5 h to remove the adsorbed gases. The CO_2 (CO or H_2) adsorption was carried out at 25 °C. The temperature-programmed desorption was carried out under a He (or Ar) flow with temperature increasing at 10 °C min⁻¹ up to 700 °C. The Bruker VERTE 70 V spectrometer was used to record the Fourier transform infrared (FTIR) spectra in the range of 400–4000 cm⁻¹ at a resolution of 4 cm⁻¹, which were obtained using a mercury-cadmium-telluride (MCT) detector. To investigate the characteristics of the CO₂ reduction process study, the IR spectra were collected with time at 80 °C in the presence of CO_2 and H_2 (25% CO_2/H_2).

Catalytic activity tests

Catalyst evaluation was performed in a quartz fixed-bed reactor (20 mm in diameter) at different reaction temperatures. 0.1 g of the catalysts were *in situ* reduced in the reactor. After that, CO_2/H_2 mixed gas (20% v/v CO_2/H_2) was introduced to the reactor at a flow rate of 20 ml/min. The reaction products were detected by an online gas chromatograph (SP-3420A, BFRL) equipped with a methanation furnace and a flame ionization detector (FID). CO selectivity was calculated according to Eq. 1,

where n_i is the yield of detected products, S_i is the selectivity of detected products.

$$\mathbf{S}_{i} = \mathbf{n}_{i} / \sum \mathbf{n}_{i} \tag{1}$$

The activation energy over the catalyst is calculated using the Arrhenius formula as follows :

$$k = Ae^{-E_a/RT}$$
(2)

where k is the rate constant, R is the gas constant, and T is the absolute temperature

(K).



Figure S1. The Raman spectra of MoO_3 (a), $10Ni/MoO_2$ -S (b), and nickel acetate $/MoO_3$ (c) after calcination at 400°C in air.



Figure S2. XRD patterns of MoO₂-S, 5Ni/MoO₂-S, 10Ni/MoO₂-S, and 10Ni/MoO₂-T at 2θ =40°~60°



Fig. S3 TEM images of 10Ni/MoO₂-S (a) and 10Ni/MoO₂-T(b), EDS mapping of 10Ni/MoO₂-S (c)



Figure S4. TPR profile of Ni/Al₂O₃



Figure S5. XPS spectra of (a) Ni 2p and (b) Mo 3d



Figure S6. H₂-TPD profile of Ni/Al₂O₃

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Catalyst	Temperature (°C)	RWGS Rate	References	
		$(\mu molCO/g_{cat}/s)$		
Ni/MoO ₂ -S	573 K	5.4	Our work	
	673 K	11.9		
Pt/MnO ₂	666 K	8.4	1	
Pt/CeO ₂	648 K	2.1	1	
Ni/a-TiO ₂	633 K	1.8	2	
Ru-Mo-Ox-spent	573 K	2.1	3	
$Ru/a-TiO_2$	573 K	2.3	4	
Pt-TiO ₂	673 K	50	5	

 Table S1. RWGS rate of the Ni/MoO2-S compared with reported conventional Catalyst.

Table S2. Estimated from the XPS results for reduced samples.

Sample	Ni(%)	Ni ²⁺ (%)	Weight ratio of Ni/Mo
Ni/MoO ₂ -S	13.60	86.40	4.31
Ni/MoO ₂ -T	12.13	87.87	6.12

Notes and references

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