

Supplementary Information

Molybdenum carbide as an efficient catalyst for low-temperature hydrogenation of dimethyl oxalate

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Experimental Section

Catalyst preparation

Silica-supported molybdenum carbide catalysts were synthesized by the hydrogen thermal treatment (HTT) method according to literature procedures.^{1,2} A typical procedure for fabricating Mo₂C/SiO₂ catalyst was as follows. Firstly, the silica-supported mixed salt precursor was prepared by impregnation of silica (Aerosil 200, Degussa) with an ammonia solution of (NH₄)₆Mo₇O₂₄·4H₂O (AHM) and hexamethylenetetramine (HMT) (the molar ratio between AHM and HMT was 1:8), which was obtained by dissolving the reagents in 25% ammonia solution. After stirring the mixture for 24 h at 298 K, the precursors dried in *vacuo* at 393 K for 12 h, yielding a white solid. The obtained solid was then heated to 973 K at a rate of 15 K min⁻¹ under a H₂ flow of 20 mL min⁻¹, and maintained for 2 h. Finally, the products were cooled to room temperature under argon and were passivated in a flow of 1% O₂/N₂ to obtain the supported carbide. The Mo₂C/SiO₂ catalysts with theoretical loadings of 5, 10, 20, 25, 30, and 40 wt % Mo₂C were prepared.

For comparison, the Cu/SiO₂ catalyst containing 20% copper was prepared by the incipient wetness impregnation process without washing. A typical procedure was as follows: alcoholic solution with 1.85 g of copper nitrate (Cu(NO₃)₂·3H₂O, 0.5 mol L⁻¹) was put into contact with 2 g of the silica with an impregnation volume of 1.5 ~ 1.8 mL g⁻¹. After thorough mixing, a blue gels

was obtained. The samples were dried in air overnight at 473 K, followed by calcinating in air for 4 h at 823 K.

Experimental procedures

The catalytic activity test was conducted using a fixed-bed reactor. Typically, 0.5 g of catalyst (40 ~ 60 meshes) sample were packed into a stainless steel tubular reactor (i.d. = 10 mm) with the thermocouple inserted into the catalyst bed for better control of the actual pretreatment and reaction temperature. Prior to the measurement, all catalyst were activated in a stream of diluted hydrogen (10% H₂ in N₂) at 623 K under atmospheric pressure for 4 h with a flow rate of 30 mL min⁻¹. After cooling to the reaction temperature, 12.5 wt% DMO (purity > 99.5%) in methanol and pure H₂ was fed into the reactor at a H₂/DMO molar ratio of 200 and a system pressure of 2.5 MPa. The liquid hour space velocity (LHSV) was set at 0.2 h⁻¹. The products were condensed and analyzed by a gas chromatograph (Shimadzu Trace GC ultra) fitted with a 30 m HP-5 capillary column and a flame ionization detector (FID).

The conversion and selectivity of products for the reactions were calculated based on the following equations:

$$\text{Conversion (\%)} = 100 - \frac{\text{Amount of feed after reaction (mol)}}{\text{Total amount of feed (mol)}} \times 100$$

$$\text{Selectivity (\%)} = \frac{\text{Amount of a product (mol)}}{\text{Total amount of feed converted (mol)}} \times 100$$

Notably, the selectivity of methanol was calculated based on the following equation:

$$\text{Selectivity}_{\text{MeOH}} (\%) = \frac{\text{Amount of methanol product from C-C bond of DMO scission (mol)}}{\text{Total amount of feed converted (mol)}} \times 100$$

Overall turnover frequencies (TOF) were calculated based on the following equation:

$$\text{TOF} = \frac{\text{product formation rate (mol g}_{\text{cat}}^{-1}\text{h}^{-1})}{\text{mole of Mo}_2\text{C (mol g}_{\text{cat}}^{-1})}$$

To obtain the intrinsic activity of catalysts, reactant conversion was kept below 10%.

Characterization of the catalysts

XRD analysis were carried out with a Bruker AXS-D8 diffractometer, equipped with Cu K α radiation ($k = 1.54 \text{ \AA}$) in the 2θ range from 5° to 85° with a scanning rate of 4° min^{-1} . The X-ray source was operated at 40 kV and 100 mA. ASTM powder diffraction files were used to identify

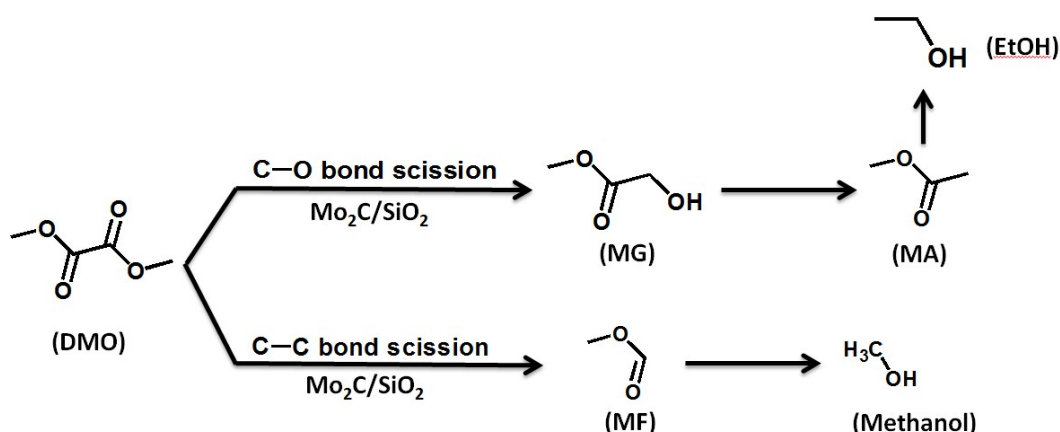
the phase of the sample.

N₂ adsorption-desorption analyses of the catalyst were carried out with Micromeritics Tristar ASAP 3000. The catalyst was degassed in He at 473 K for 4 h prior to Brunauer–Emmett–Teller (BET) analysis. After degassing, 30% N₂/He was flown over the samples, and the temperature was reduced to 77 K. Specific surface areas of the sample were calculated according to the BET method. Pore size distributions were estimated by the Barrett–Joyner–Halenda (BJH) method.

A JEM 2010 microscope operating at 200 kV equipped with an EDX unit was used for the TEM investigations. The samples were prepared by grinding and subsequent dipping the powder in ethanol and applying a drop of very dilute suspension on copper grid.

Reaction pathway for DMO hydrogenation

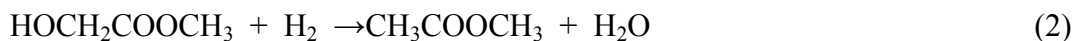
Scheme S1 gives the reaction pathway for the hydrogenation of DMO over the Mo₂C-base catalysts.



Scheme S1. Illustration for hydrogenation of DMO over Mo₂C-based catalysts.

In the DMO hydrogenation process, from DMO can be taken place of stepwise hydrogenation to form target products. On the one hand, the carbon–oxygen bonds were selectively broken, DMO first reacted with hydrogen to methyl glycolate (MG) (shown in eq 1), and then methyl acetate (MA) generated from the hydrogenation of MG (shown in eq 2). At last EtOH would be obtained by the hydrogenation of MA (shown in eq 3). On the other hand, methanol as the side product would be produced through the hydrogenolysis of carbon–carbon bonds of DMO. In this case, DMO firstly reacted with hydrogen to form methyl formate (MF) (shown in eq 4) and then hydrogenated to methanol (shown in eq 5).





To confirm the possibility that MF was an intermediate during DMO hydrogenation to methanol, the activity of MF hydrogenation over the 25Mo₂C/SiO₂ catalyst was examined and compared with that of DMO hydrogenation, as shown in Table S1. MF almost be completely converted over the 25Mo₂C/SiO₂ catalyst at 473 K, and the selectivity of methanol is 99%. This indicates that a small amount of methanol might be formed by the hydrogenation of intermediate MF, which was formed through the hydrogenolysis of carbon–carbon bonds of DMO.

Table S1. Selective hydrogenation reactions over the 25Mo₂C/SiO₂ catalyst^a.

Reactant	Temperature (K)	Conversion (%)	Selectivity (%)					TOF (h ⁻¹)
			MA	EtOH	Methanol	DE ^b	MF	
DMO	453	100	62.4	21.5	13.7	1.3	1.1	6.3
	473	100	7.3	70.8	19.4	1.7	0.8	0.6
MG ^b	453	100	64.6	22.3	11.9	1.0	0.2	7.9
MA ^b	473	99.9	—	76.4	19.8	1.9	0.4	8.5
MF ^b	473	91.4	—	—	99.0	—	—	—

^aReaction conditions: 2.5 MPa, H₂/*x* (*x* = DMO, MG, MA and MF) = 200 (mol mol⁻¹), LHSV = 0.2 h⁻¹. ^bMG: methyl glycolate; MA: methyl acetate; MF: methyl formate; DE: diethyl ether.

Table S2. Physicochemical properties and catalytic performances^a.

Catalyst	Mo ₂ C loading (%) ^b	Conversion (%)	Selectivity (%)					S _{BET} (m ² g ⁻¹)	D _{pore} (nm)	V _{pore} (m ³ g ⁻¹)
			MA ^c	EtOH	Methanol	DE ^c	MF ^c			
SiO ₂	—	0	0	0	0	0	0	180.7	10.1	0.41
10Mo ₂ C/SiO ₂	8.9	56.2	51.1	26.3	20.3	1.2	1.1	128.9	27.1	0.78
20Mo ₂ C/SiO ₂	18.6	90.4	10.5	65.0	21.8	1.4	1.3	91.8	25.3	0.64
25Mo ₂ C/SiO ₂	23.8	100	7.3	70.8	19.4	1.7	0.8	83.8	23.9	0.59
30Mo ₂ C/SiO ₂	28.3	98.9	18.1	59.4	19.8	1.3	1.4	61.3	22.0	0.41
40Mo ₂ C/SiO ₂	37.8	96.0	27.3	50.3	19.7	1.5	1.2	49.7	20.9	0.30

^aReaction conditions: 473 K, 2.5 MPa, LHSV = 0.2 h⁻¹, H₂/DMO = 200 (mol mol⁻¹). ^bDetermined by ICP-AES analysis. ^cMA: methyl acetate; DE: diethyl ether; MF: methyl formate.

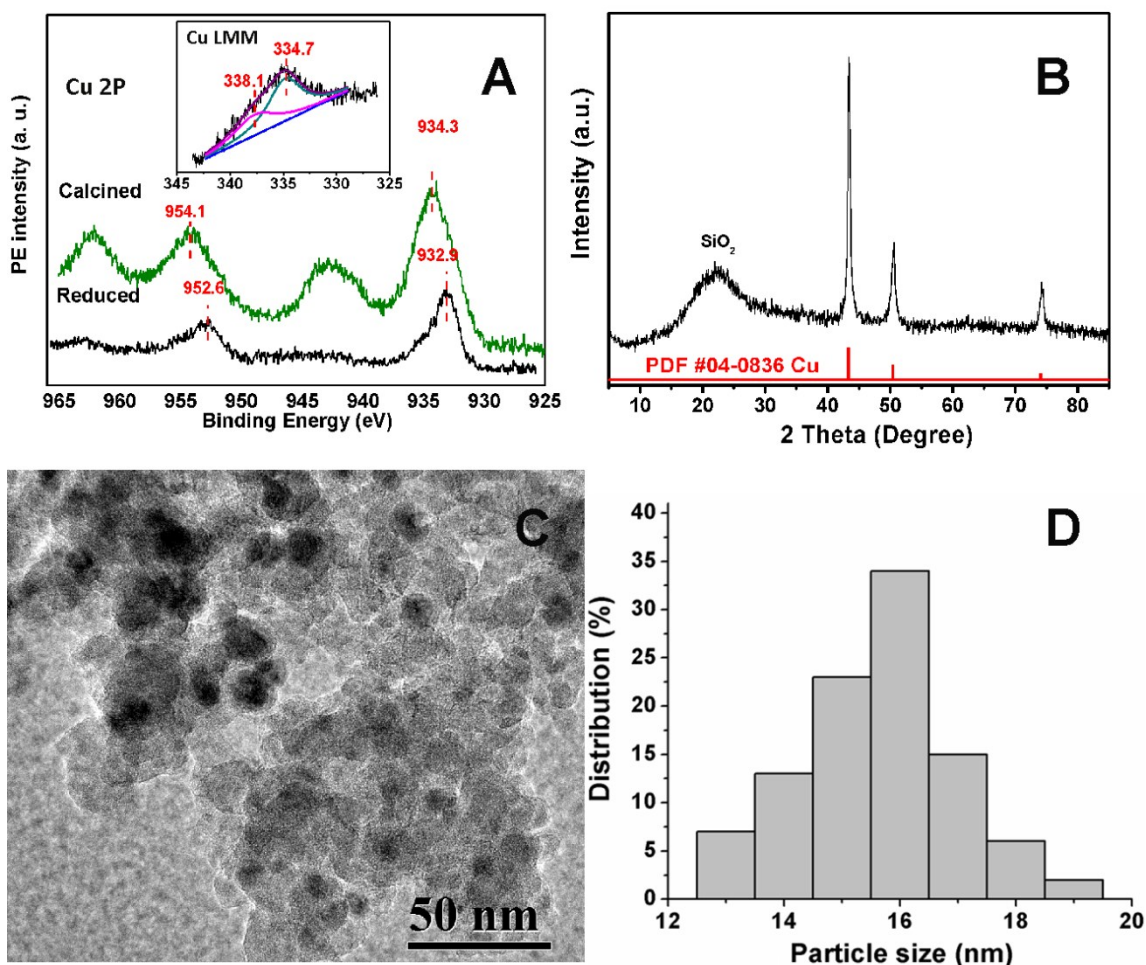


Figure S1. (A) Cu 2p XPS spectra of calcined and reduced Cu/SiO₂ samples and (inset) Cu LMM XAES spectra of reduced Cu/SiO₂ samples. (B) XRD patterns of reduced Cu/SiO₂ catalyst. (C) TEM images of reduced Cu/SiO₂. (D) Size distribution diagram of the Cu NPs.

The XPS data for the calcined samples shows that the Cu oxidation state is +2 valence with a d³ electron configuration in the calcined sample, as evidenced by the Cu 2p_{3/2} peak at ~934.3 eV, the Cu 2p_{1/2} peak at ~954.1 eV, and the 2p → 3d satellite peak between 941 and 945 eV.⁴ For the reduced samples, the binding energies of Cu 2p_{1/2} at around 952.6 eV and Cu 2p_{3/2} at 932.9 eV, respectively, can be attributed to the Cu⁰ state.⁵ This conclusion is also supported by the X-ray diffraction patterns (Figure S1B). In order to distinguish between Cu⁰ and Cu⁺ species produced in reduction, the Cu LMM X-ray excited Auger spectroscopy was recorded for the sample after reduction (inset in Figure S1A) and a significant asymmetric peak was observed and overlapped by two peaks at 334.7 and 338.1 eV respectively correspond to the Cu⁰ and Cu⁺,^{5,6} thus implying the copper particles in Cu/SiO₂ catalyst were in Cu⁰ and Cu⁺.

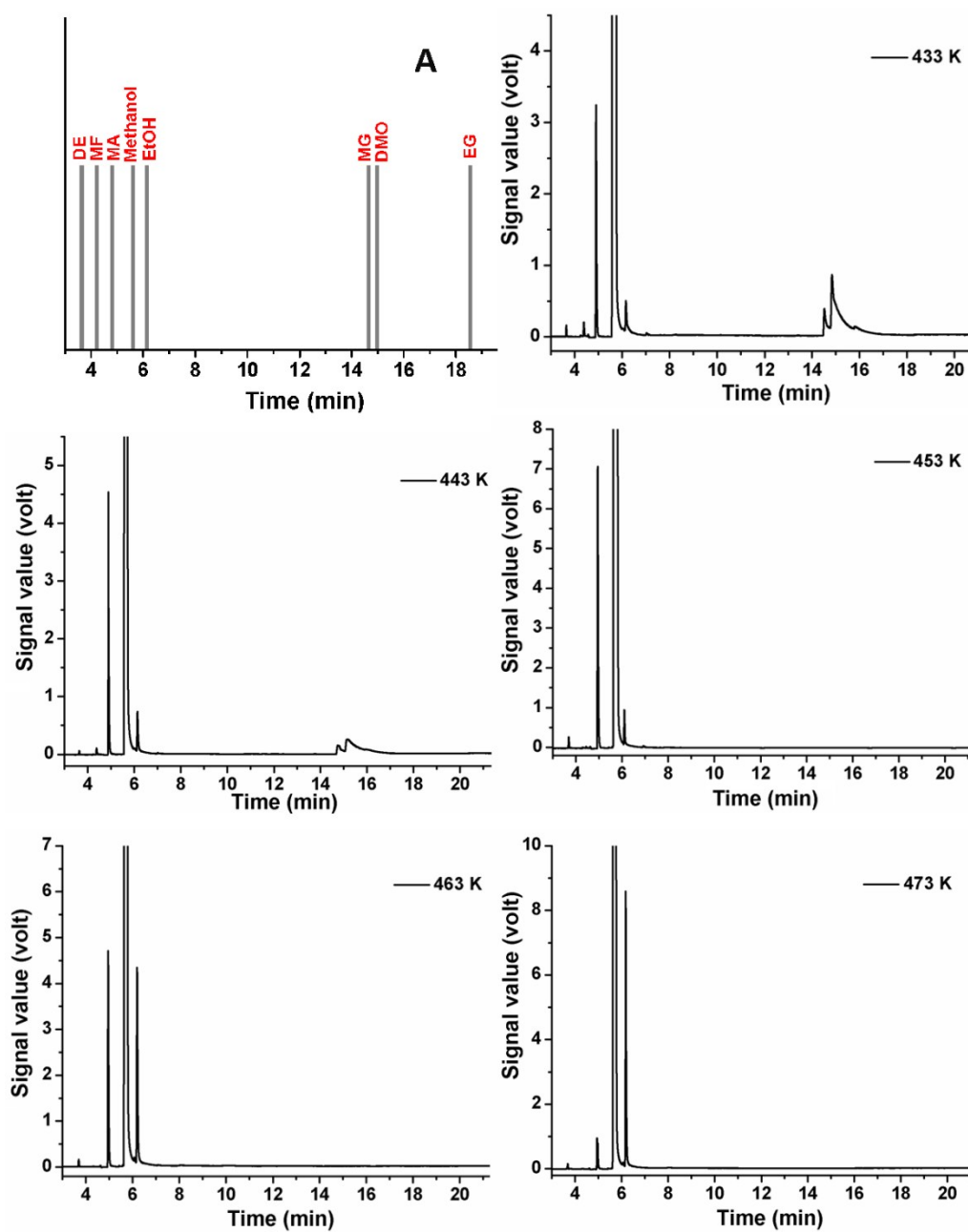


Figure S2. Gas chromatogram of the liquid products obtained from the hydrogenation of DMO over the $25\text{Mo}_2\text{C}/\text{SiO}_2$ catalyst under different reaction temperatures ((A) the peak position of the liquid products). DE: diethyl ether; MF: methyl formate; MA: methyl acetate; MG: methyl glycolate; DMO: dimethyl oxalate; EG: ethylene glycol.

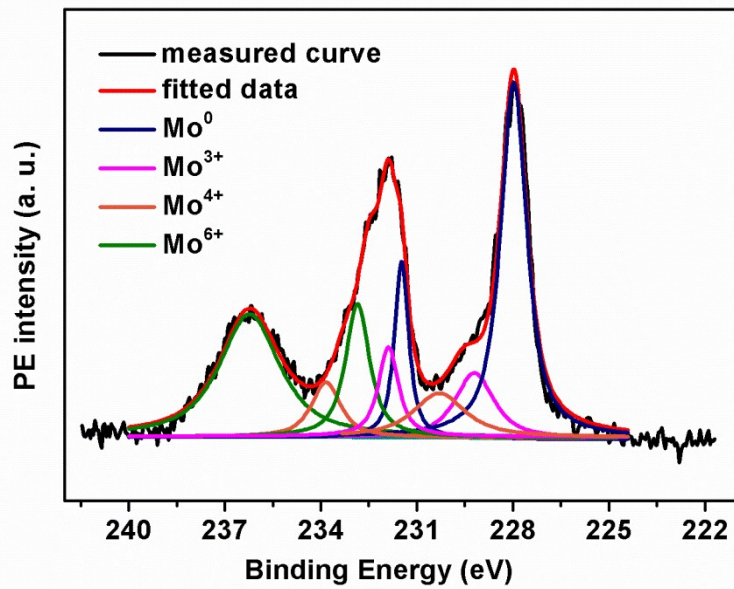


Figure S3. Mo 3d core level XPS spectrum of 25Mo₂C/SiO₂ catalyst.

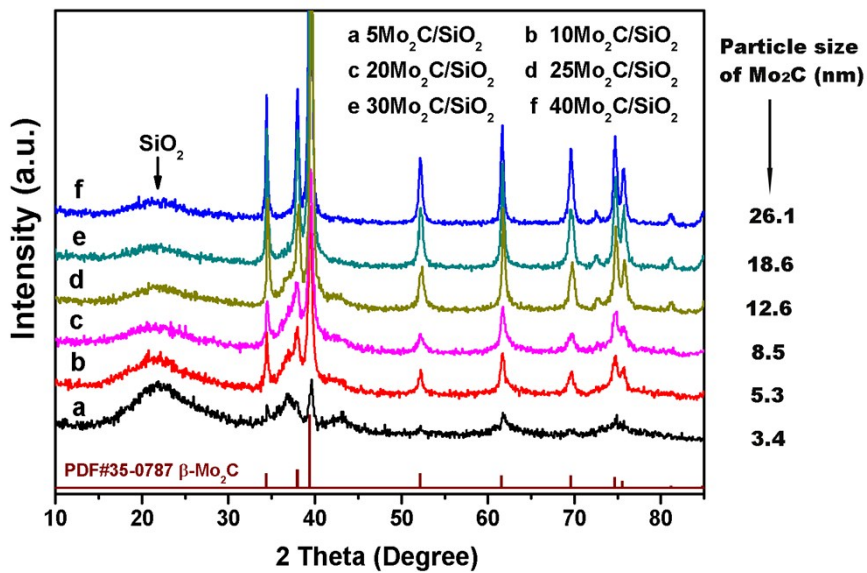


Figure S4. XRD pattern of different molybdenum carbide catalysts. Size of Mo₂C particles calculated from the XRD data of the (101) peak broadening of β -Mo₂C by Scherrer equation.

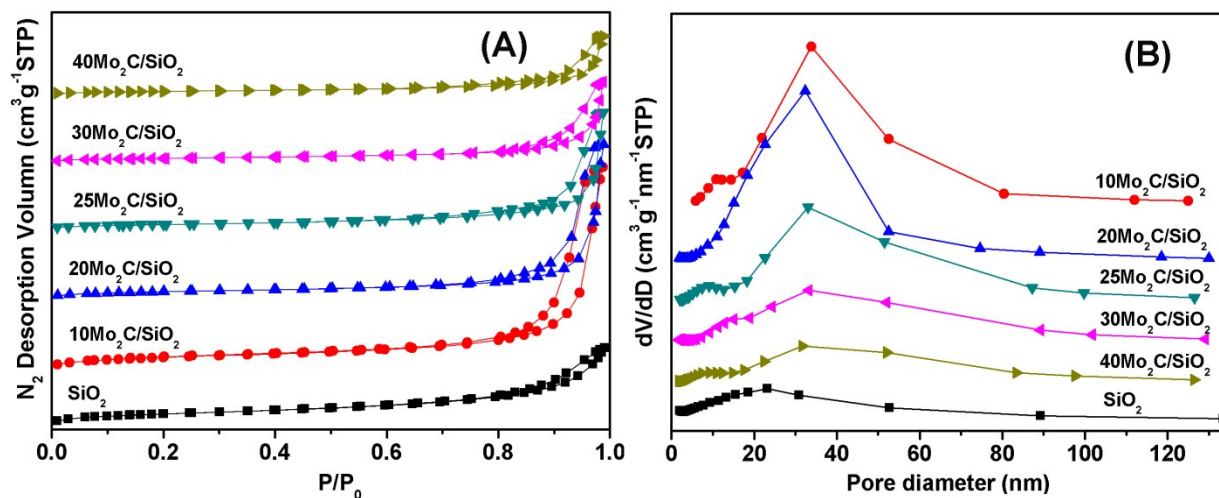


Figure S5. N_2 adsorption-desorption isotherm for (A) and BJH pore size distribution for (B) of different molybdenum carbide catalysts.

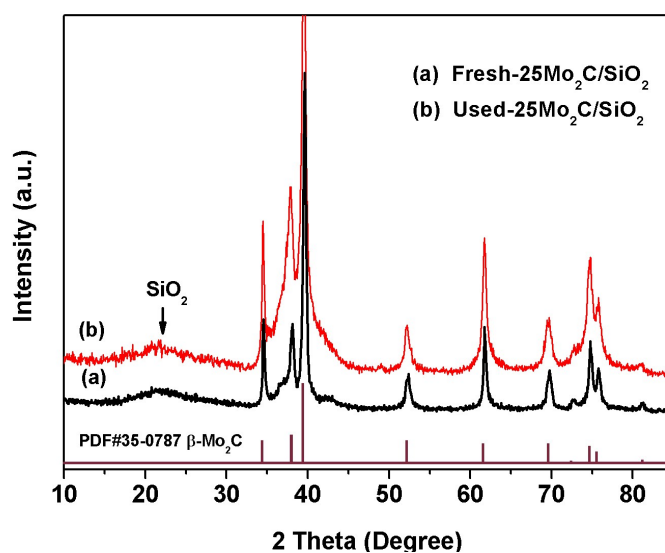


Figure S6. XRD patterns of (a) fresh 25Mo₂C/SiO₂ catalyst and (b) spent catalyst of (a) after running for 350 h at 473 K.

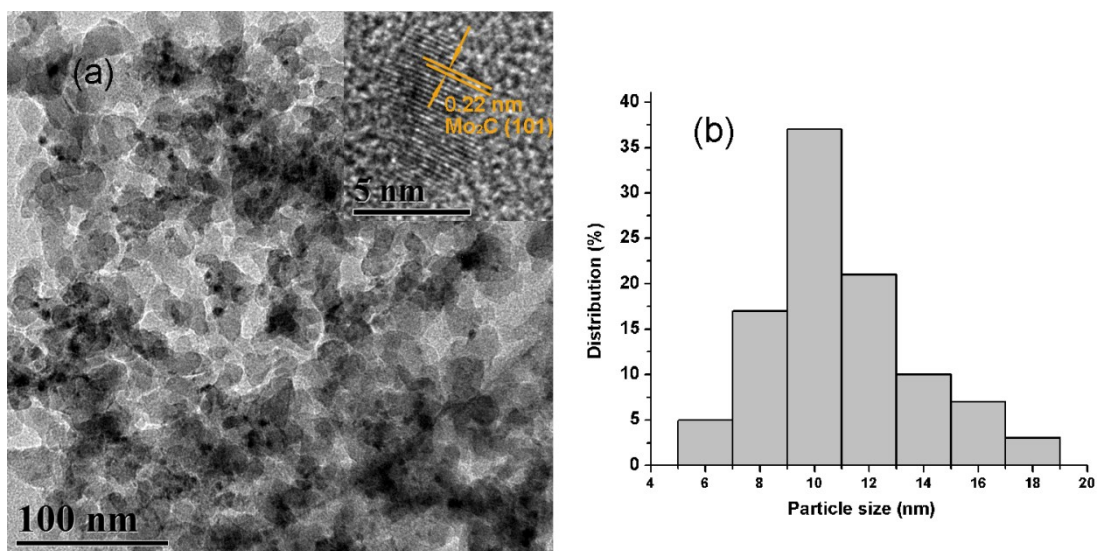


Figure S7. (a) TEM images of post-reacted 25Mo₂C/SiO₂ catalyst after running for 350 h at 473 K and high-resolution TEM images of one isolated Mo₂C nanoparticle (inset); (b) Size distribution diagram of the Mo₂C nanoparticles.

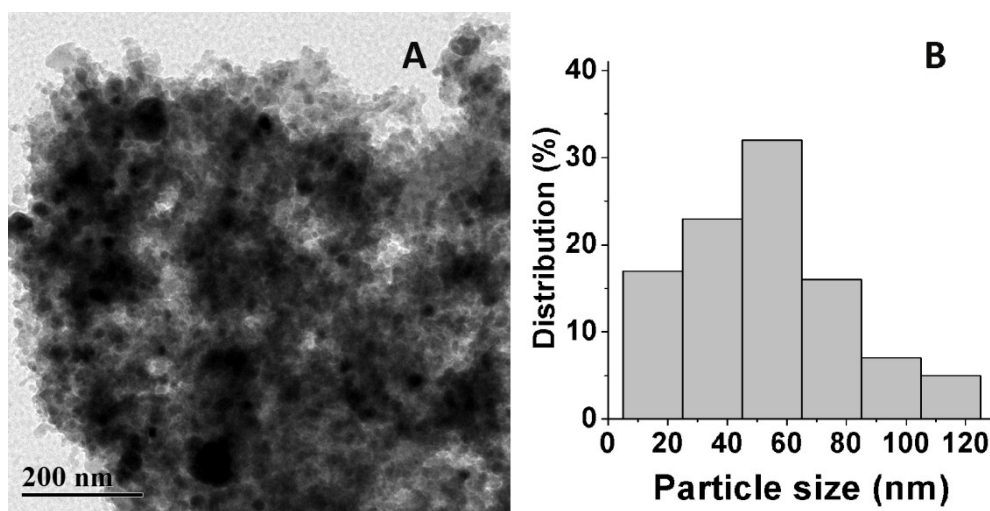


Figure S8. (A) TEM images of post-reacted Cu/SiO₂ catalyst after running for 175 h at 543 K; (B) Size distribution diagram of the Cu nanoparticles.

Reference:

1. H. Wang, X. Wang, M. Zhang, X. Du, W. Li and K. Tao, *Chem. Mater.*, 2007, **19**, 1801-1807.
2. Z. Wang, Z. Zhang and M. Zhang, *Dalton Trans.*, 2011, **40**, 1098-1104.
3. G. W. Huber, J. W. Shabaker, and J. A. Dumesic, *Science* 2003, **300**, 2075.
4. L. Chen, P. Guo, M. Qiao, S. Yan, H. Li, W. Shen, H. Xu, and K. Fan, *J. Catal.* 2008, **257**, 172.
5. C. D. Wagner, W. M. Riggs, L. E. Davis, J. E. Moulder and G. E. Muilenberg, *Handbook of X-ray Photoelectron spectroscopy*, Perkin-Elmer Corporation Physical Electronics Division, USA, 1979.
6. (a) A. Yin, X. Guo, W. Dai and K. Fan, *J. Phys. Chem. C*, 2009, **113**, 11003–11013. (b) J. Gong, H. Yue, Y. Zhao, S. Zhao, L. Zhao, J. Lv, S. Wang and X. Ma, *J. Am. Chem. Soc.*, 2012, **134**, 13922-13925.