

Electronic Supplementary Information

Activated carbon supported molybdenum carbides as cheap and highly efficient catalyst in selective hydrogenation of naphthalene to tetralin

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Experimental Section

Reagents

All the reagents are purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Activated carbon (AC) was purchased from Dalian Institute of Chemical Physics. The AC is prepared by a direct chemical activation in which petroleum coke is reacted with excess KOH at 900 °C to produce the carbon materials containing potassium salts. These salts are removed by successive water washing. The surface area of the carbon materials measured by Brunauer-Emmett-Teller (BET) method is about 3234 m²/g. The pore volume is about 1.78 m³/g and the average pore size is about 2.2 nm. Argon used here was 99.995% in purity.

Synthesis of Mo₂C/AC

In a typical synthesis of (HMT)₂(NH₄)₄Mo₇O₂₄·2H₂O/AC, a desired amount of C₆H₁₂N₄ (HMT) and (NH₄)₆Mo₇O₂₄·4H₂O (AHM) with a mole ratio of 2 was dissolved in 1 mL 15 wt% NH₃H₂O. 0.2 g activated carbon was dispersed in the obtained solution and then sonicated for 2 min to get a high dispersion. After NH₃H₂O volatilized at room temperature, the black powder was dried at 80 °C for 3 h in a vacuum dryer. In the thermolysis section, the black powder was put in a quartz-tube reactor (10 mm, diameter) fixed in a domestic microwave oven. Ar was introduced into the reactor 2 hours before heating. The oven was operating at 2.45 GHz, 800 W with 30 mL/min Ar for 30 min. The products were cooled to room temperature. All the operations in this section were conducted under Ar.

Hydrogenation of naphthalene

All the reactions were carried out in a cylindrical fixed-bed stainless steel reactor (12 mm×2 mm×500 mm). Typically, 0.16 g catalyst was added into the reactor and the rest part of the reactor was filled with quartz sand. Then the reactor was heated to 400 °C at a rate of 10 °C /min under 1

MPa H₂ and kept for 2 h to get the catalyst refreshed and this is called the pre-reduction step. After the reactor was cooled to 340 °C, a desired amount of *n*-decane with 1 wt% naphthalene was introduced into the reactor under 4 MPa H₂ with the oil/hydrogen ratio of 1:600. The steady state was achieved after reacting for 3 h. The reaction time was recorded once the steady state was obtained. After the desired reaction time, a small amount of liquid product was taken out of the reactor and cooled naturally. The amounts of tetralin and decalin were determined by an Agilent 7890-□ gas chromatograph equipped with an OV-101 capillary column (5 m) and a FID detector.

Adsorption test

A certain amount of 30 wt% Mo₂C/AC was added into the reactor. Then the reactor was heated to 400 °C in a rate of 10 °C /min under 1MPa H₂ and kept for 2 h to get the catalyst refreshed. Then switch to Ar to evacuate H₂, after the reactor was cooled to 340 °C, a desired amount of *n*-decane with 0.45 wt% naphthalene and 0.55 wt% tetralin was introduced into the reactor at 0.14 mL/min under 1 MPa Ar. After 30 min, a small amount of liquid product was taken out of the reactor, cooled naturally and analyzed by GC.

Hydrogenation of tetralin with varied contents of naphthalene

0.16 g 20 wt% Mo₂C/AC catalyst was added into the reactor. Then the reactor was heated to 400 °C in a rate of 10 °C /min under 1 MPa H₂ and kept for 2 h to get the catalyst refreshed. After the reactor was cooled to 340 °C, a desired amount of *n*-decane with desired content of naphthalene and tetralin was introduced into the reactor under 4 MPa H₂ with the oil/hydrogen ratio of 1:600. LHSV was set at 14.3 h⁻¹. The steady state was achieved after reacting for 3 h. A small amount of liquid product was taken out of the reactor, cooled naturally and analyzed by GC.

Stability test

0.16 g 20 wt% Mo₂C/AC catalyst was added into the reactor. Then the reactor was heated to 400 °C in a rate of 10 °C /min under 1 MPa H₂ and kept for 2 h to get the catalyst refreshed. After the reactor was cooled to 340 °C, a desired amount of *n*-decane with 1 wt% naphthalene was introduced into the reactor under 4 MPa H₂ with the oil/hydrogen ratio of 1:600. LHSV was set at 14.3 h⁻¹. The steady state was achieved after reacting for 3 h. The reaction time was recorded once the steady state was obtained. After the desired time, a small amount of liquid product was taken out of the reactor, cooled naturally and analyzed by GC

Characterization

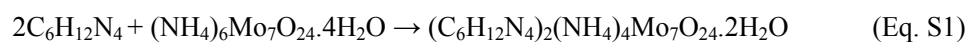
X-ray diffraction (XRD) pattern was collected on a Rigaku D/MAX2400 diffractometer with Cu Ka (40 kV, 100 mA) radiation. Transmission electron microscopy (TEM) was performed on a Philips CM200 FEG transmission electron microscope with an accelerating voltage of 200 kV. X-Ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) set-up equipped with a Gamdata-Scienta SES 2002 analyzer. The base pressure in the measurement chamber was 2 × 10⁻¹⁰ mbar. Monochromatic Al Ka (1486.6 eV; 14 kV; 55 mA) was used as incident radiation, and a pass energy of 200 eV was chosen resulting in an energy resolution better than 0.5 eV. Charging effects were compensated by a flood gun. Binding energies were calibrated using the main C 1s peak at 284.5 eV as reference.

TG-MS analysis

In a typical preparation of (HMT)₂(NH₄)₄Mo₇O₂₄·2H₂O, 0.5 g AHM was dissolved in 20 mL H₂O, then 20 mL H₂O containing 0.1 g HMT was added into AHM solution. The white precipitate was

collected by filtration, washed with H₂O, and dried at 80 °C for 6h. Thermal decomposition of (HMT)₂(NH₄)₄Mo₇O₂₄·2H₂O was performed with a Cahn TG-2131 thermobalance in pure He with a heating rate of 3 °C min⁻¹ from room temperature to 850 °C. Elemental analysis was carried out using an Elementaranalysator varioEL (Elementar Analy-sensysteme GmbH, Hanau, Germany) system. Multiple signals were monitored with $m/z=2, 16, 17, 18, 28, 44$, corresponding to H₂, CH₄, NH₃, H₂O, CO/N₂, CO₂ species.

The precursor is obtained from the reaction between HMT and AHM at a fixed stoichiometry of two. The chemical reaction equation is proposed as below:



The white precipitate with a chemical formula of $(\text{C}_6\text{H}_{12}\text{N}_4)_2(\text{NH}_4)_4\text{Mo}_7\text{O}_{24} \cdot 2\text{H}_2\text{O}$ is the precursor, which can also be $(\text{HMT})_2(\text{NH}_4)_4\text{Mo}_7\text{O}_{24} \cdot 2\text{H}_2\text{O}$ for short.

Table S1 The result of the adsorption test.

	Napthalene	Tetralin
Before Adsorption	45 wt%	55 wt%
After Adsorption	72 wt%	28 wt%

Table S2 The result of the hydrogenation of tetralin with varied contents of naphthalene.

		Naphthalene content in feed ^a					
		/ wt%					
		0	5	15	40	60	80
Content in Product / wt%	Tetralin	75.2	88.1	89.9	89.2	93.3	94.3
	Decalin	22.1	8.9	7.2	6.6	5.4	4.2

^a The feed is the mixture of naphthalene and tetralin

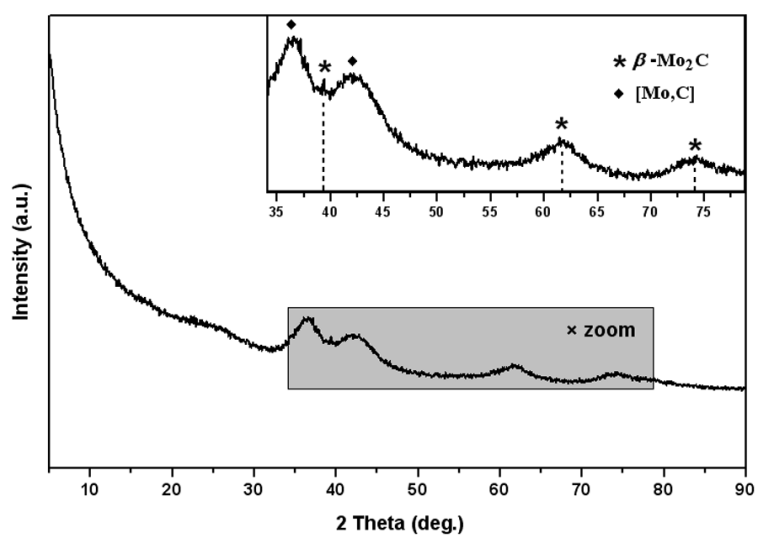


Fig. S1 Representative XRD pattern of $\text{Mo}_2\text{C}/\text{AC}$ with 20 wt% Mo loading; scanning rate: $1^\circ/\text{min}$; standard pattern of β - Mo_2C present in sticks with dot; inset is the magnified pattern of the selected part (outlined with square).

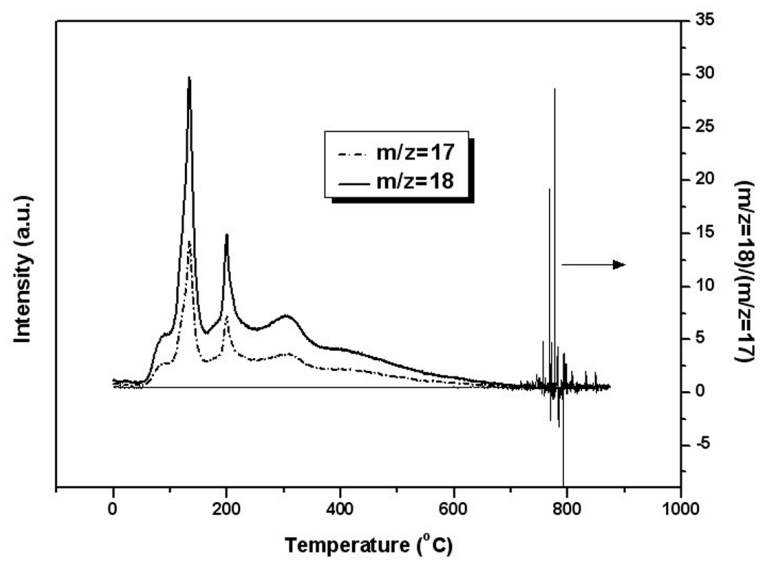


Fig. S2 Division on the intensities of signals with m/z values of 17,18.

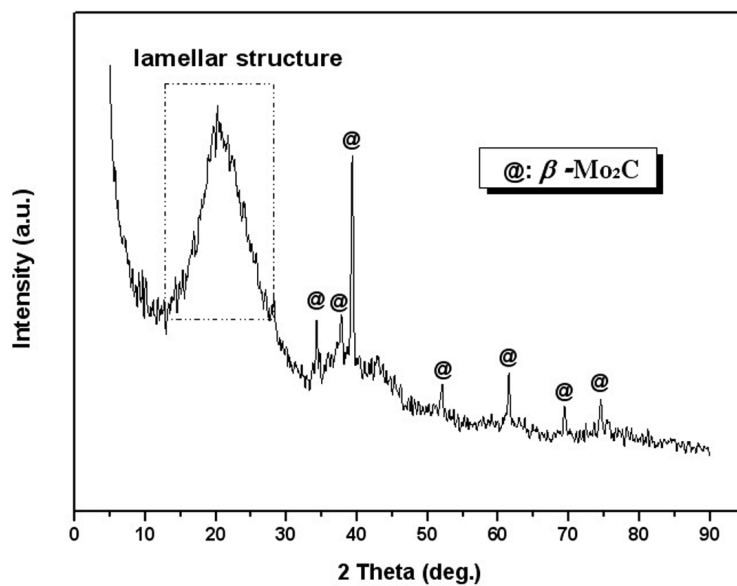


Fig. S3 XRD pattern of the spent Mo₂C/AC with 20 wt% Mo loading; the enhancement of peak intensity after use mainly contributes to the perfection of the Mo₂C crystalline due to the newly formed Mo₂C during the hydrogenation and the enlargement of the particle size mainly due to the surface graphitization.

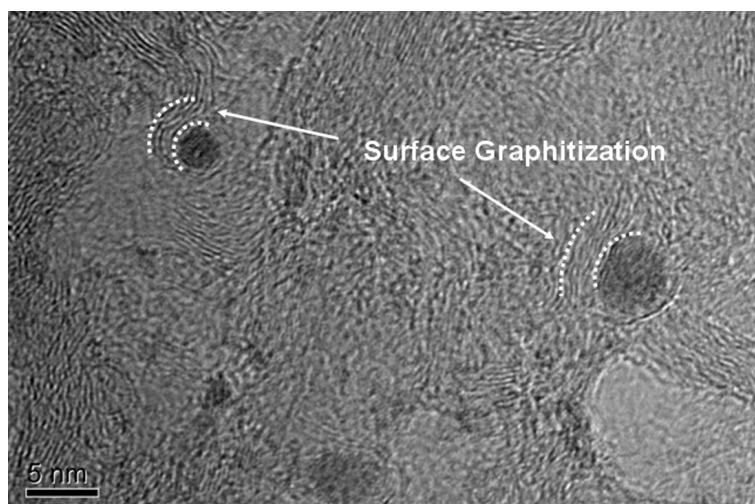


Fig. S4 TEM image of the spent Mo₂C/AC with 20 wt% Mo loading.