Research Article

Highly Dispersed α - MoC_{1-x} in Porous Silica for CO Hydrogenation

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A facile method has been developed to prepare highly dispersed α - MoC_{1-x} in porous silica. By utilizing C atoms in methyl modified silica supports, α - $\text{MoC}_{1-x}/\text{SiO}_2$ was obtained via insitu carburization. The obtained samples exhibited high activity for CO hydrogenation.

1. Introduction

The development of new heterogeneous catalysts is a highly attractive topic in current chemical research [1, 2]. Molybdenum carbides have been found to show high catalytic activities as noble metals and may be an inexpensive alternative to noble metal catalysts [3, 4]. In recent years, molybdenum carbides highly dispersed in mesoporous silica molecular sieves have been synthesized [5] however, to insert molybdenum species during the synthesis of mesoporous silica supports, the routes are somewhat complicated and difficult. Molybdenum source, MoO_3 or polymolybdates, needs to be treated into low-nuclearity molybdenum peroxo complexes via the peroxo route at the initial synthesis of mesoporous silica supports [6]. Furthermore, to carburize molybdenum species into its carbides, one of the most widely used methods is the temperature-programmed reduction (TPR) of the transition metal oxide by gaseous hydrocarbons, such as CH_4 [7], C_2H_6 [8], C_3H_8 [9], and C_4H_{10} [10], as pioneered by Levy and Boudart [3]. Few studies have been carried out on the utilization of other carbon sources.

Herein, we report a facile synthesis of highly dispersed α - MoC_{1-x} in porous silica through insitu carburization of molybdenum species on methyl modified silica (Mo-M-silica) in Ar gas. Mo-M-silica was synthesized via sol-gel route using $\text{Si}(\text{OC}_2\text{H}_5)_4$ (TEOS) and polymethylhydrosiloxane (PMHS) as silica sources without using any surfactants. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (AHM) as molybdenum source

was introduced without peroxo treatment. CO hydrogenation reaction was used as a probe reaction: the obtained α - $\text{MoC}_{1-x}/\text{SiO}_2$ exhibited high catalytic activity and selectivity to alcohols in CO hydrogenation.

2. Experimental

2.1. Synthesis of Samples. The typical synthesis method is as follows. $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ was dispersed into 80 mL ethanol to obtain a white suspension. Then, 1.5 mL PMHS was added under vigorous stirring. Si-H bonds in PMHS interacted with transitionmetal (Mo), and the suspension turned from white to gray. Ethylene diamine (EDA) was added as catalyst to allow residual Si-H bonds to react with part of the $\text{C}_2\text{H}_5\text{OH}$ and release H_2 . After being stirred for 12 h at room temperature, 5 mL TEOS and determined deionized water were added under vigorous stirring. The resulting gray solid was dried at 100°C in a vacuum oven to remove the EtOH and EDA. The carburization of Mo-M-silica was carried out under atmospheric pressure in Ar gas at 700°C . Then, the sample was quenched to room temperature and gradually passivated with 1% (v/v) O_2/N_2 before exposure to air. Similarly, another sample was carburized in 10% (v/v) CH_4/H_2 gas for comparison.

2.2. Characterization Methods. X-ray patterns were measured using Ni filtered Cu $K\alpha$ radiation ($\lambda = 1.5404 \text{ \AA}$) and a Rigaku D Max III VC diffractometer equipped with

a rotating anode operated at 40 kV and 30 mA. Changes of Mo-M-SiO₂ during carburization were monitored by thermogravimetric analysis (TG, Rheometric Scientific STA 1500 equipped with a simultaneous thermal analyzer). A small quantity (approximately 30 mg) of Mo-M-SiO₂ was loaded into a small platinum crucible and placed into the balance in the instrument. N₂ adsorption isotherms were obtained at 77.3 K on a Tristar 3000 sorptometer, using static adsorption procedures. Samples were degassed at 423 K and under a vacuum of 10⁻⁶ Torr for at least 12 h prior to the measurement. BET specific surface areas were calculated using the adsorption data in a relative pressure (P/P°) range from 0.05 to 0.20. The XPS was recorded on a VG MultiLab 2000 spectrometer with Mg K α (1253.6 eV) radiation as the excitation source. The experimental setup consisted of a preparation chamber connected to a UHV system. The sample holder with the tablets was placed onto a vertical tube that could be pushed up into a quartz reactor. The bores in the sample holder stub ensured that the gases flew through the sample and exited from the setup through a valve in the lower end of the vertical tube. From time to time, the carburization process was interrupted at given temperatures, the reactor was evacuated, and the sample was transferred into the UHV system via an insertion mechanism. After spectrum acquisition, the samples were drawn back to the chamber, which was kept at the given temperature in the meantime. The chamber was flooded with the gas mixture, the flow was set, and the sample was pushed into the reactor cell. Afterwards, heating to the following temperature began and the treatment cycle was repeated until reaching the final temperature. TEM images were taken on a JEOL 100CX microscope operating at an accelerating voltage of 200 kV. Chemical analyses were carried out at the Service Central d'Analyse (CNRS-Lyon) by inductive coupling plasma atomic emission spectroscopy (ICP-AES) after alkaline fusion with Li₂B₄O₇.

2.3. CO Hydrogenation. CO hydrogenation was carried out using a stainless fixed-bed reactor with 4 mL of catalyst. The effluents were analyzed by 1790-GC and among these H₂, CO, CH₄, and CO₂ were analyzed by thermal conductivity detector (TCD) equipped with a TDX-101 column; C₁–C₄ alkanes were detected by flame ionization detector (FID) with a chromosorb 101 column; C₁–C₄ alkenes were detected by FID with a packed column C-18; the water and methanol in liquids were also detected by TCD with a GDX-401 column; the alcohols and hydrocarbons were analyzed by FID with a porapak-Q column. C₅⁺ hydrocarbons were detected by FID with a capillary column. The mass balance was based on carbon, and the error of the balance of oxygen and hydrogen was within 5%. The selectivity and products distribution (alcohols and hydrocarbons) were calculated on a CO₂ free basis.

3. Results and Discussion

3.1. Structural Properties. Figure 1 shows the powder XRD patterns of the three samples. The XRD pattern of Mo-M-silica shows none-Mo-related XRD diffraction peaks, but

FIGURE 1: XRD patterns of (A) Mo-M-silica, (B) α -MoC_{1-x}/SiO₂ carburized in Ar gas, and (C) α -MoC_{1-x}/SiO₂ carburized in CH₄/H₂ gas.

a very wide diffraction peak of amorphous SiO₂ at 24–25°. It can be concluded that molybdenum species are not crystallized and highly dispersed in SiO₂. The two carburized samples, respectively, in Ar gas and in CH₄/H₂ gas, show similar XRD patterns, which are in agreement with the α -MoC_{1-x} reported by Bouchy et al. [11]. The intensity of (111) peak is higher than that of the (200) one. So, it can be concluded that the carburization of molybdenum species can be realized by only utilizing C atoms in silica supports (sample B).

Table 1 shows the surface area and pore volume of the three samples. It can be seen that, BET surface area increases after carburization, respectively, from 77 to 339 m² g⁻¹ in Ar gas and to 311 m² g⁻¹ in CH₄/H₂ gas. The large increase of micropore volume after carburization perhaps resulted from the exhaustion of methyl in silica during carburization. Table 1 also shows the content of Mo and C in the three samples. It can be seen that the content of C in uncarburized Mo-SiO₂ reaches 7.23 wt%, and the α -MoC_{1-x}/SiO₂ carburized in Ar gas decreased to 0.62 wt%, while the α -MoC_{1-x}/SiO₂ carburized in CH₄/H₂ gas only decreased to 0.78 wt%, which is little higher than that of α -MoC_{1-x}/SiO₂ carburized in Ar gas. This may be the cause of amorphous carbon formed by the CH₄ pyrolytic reaction [12], which is accumulated on molybdenum carbides.

Figure 2 shows the representative HRTEM images of α -MoC_{1-x}/SiO₂ obtained in Ar gas, taken at different magnification. Clearly, Figure 2(a) shows a 3D wormhole-like structure with a disorganized porous network. At higher magnification, it can be seen from Figure 2(b) that α -MoC_{1-x} nanoparticles with diameter of ~3 nm are highly dispersed in silica supports. The d -value of 0.21 nm matches the value determined from the XRD analysis, which is in agreement with other reports [13].

3.2. XPS Study of the Carburization Process of Mo-M-SiO₂. XPS were used to investigate the change of molybdenum species during carburization. The corresponding results are

TABLE 1: The surface area data and pore parameters of the obtained samples.

Sample	Mo (wt%)	C (wt%)	BET surface area (m^2g^{-1})	Micropore surface area (m^2g^{-1})	Total pore volume (cm^3g^{-1})	Micropore volume (cm^3g^{-1})
Mo-SiO ₂	8.02	7.23	77	0	0.34	0
α -MoC _{1-x} /SiO ₂ (Ar)	9.43	0.62	339	190	0.45	0.088
α -MoC _{1-x} /SiO ₂ (CH ₄ /H ₂)	9.31	0.78	311	172	0.42	0.079

FIGURE 2: TEM micrographs of α -MoC_{1-x}/SiO₂ carburized in Ar gas: (a) region of wormhole-like structure and (b) highly dispersed α -MoC_{1-x} nanoparticles.

shown in Figure 3. The $3d_{5/2}$ and $3d_{3/2}$ binding energies are 232.4 and 235.5 eV for Mo⁶⁺, 230.9 and 234.0 eV for Mo⁵⁺, 229.1 and 232.2 eV for Mo⁴⁺, 228.4 and 231.6 eV for Mo²⁺, and 227.6 and 230.8 eV for Mo⁰. The values for Mo⁶⁺-Mo⁴⁺ ions are almost the same as those used by Ward et al. [14] for Mo/SiO₂. The values for Mo²⁺ and Mo⁰ are taken from the work of Yamada et al. [15]. C 1s binding energy is located at 284.6 eV and used as an energy reference (Figure 3(d)). It can be seen that before carburization Mo⁶⁺ species exist in a simple chemical characteristic in SiO₂ from the high resolution of Mo 3d doublet in XP spectrum for the unheated, according to the explanation by Liu et al. [16]. Heating this sample in Ar gas causes practically no alteration in the spectral shape with respect to the starting state up to 400~600 K, indicating no appreciable reduction of Mo⁶⁺. Dramatic changes take place after heating above this temperature range, when a three-peak structure appears on the spectrum with peak maxima at 228.6, 232.6 and 236.2 eV at 623 K. By further heating to 823 K, the three peaks all shift to lower energy, indicating a further reduction of molybdenum species. The deconvolution of Mo 3d for the resultant at 623 and 823 K is, respectively, presented in Figures 3(b) and 3(c). It clearly shows that the carburization of molybdenum species proceeds through several states of Mo. At 623 K a series of reduced Mo ions comes forth expert Mo⁰, which is reduced with temperature further getting high to 823 K. At 973 K, the Mo three peaks are converted into two peaks with maxima at 227.8 and 231.2 eV. The two-peak position has not changed but the lower-energy peak becomes stronger at higher temperature, indicating the further reduction of

Mo and the formation of carbides. At 973 K, the C 1s peak shifts to 283.1 eV, corresponding to the energy of the carbon 1s orbital measured earlier in α -MoC_{1-x} containing samples [17]. Finally, it can be concluded that molybdenum species are almost carburized at heating temperature above 973 K. Meanwhile, a minor C 1s peak at 284.9 eV indicates the existence of a little coke.

Changes of Si 2p and O 1s peaks during the carburization are similar. Both peaks shift to higher energy upon heating to 823 K and have no more shifts but become stronger at higher heating temperature. The shift of Si 2p peaks below 823 K reflects the gradual pyrogenation of Si-C bonds. And the change of O 1s peaks below 823 K is mainly caused by the gradual reduction of Mo species. Above 823 K, Si 2p and O 1s peaks are fixed, respectively, at 103.3 and 532.6 eV and reflected to complete pyrogenation of Si-C bonds leaving unhybrid SiO₂ [16].

3.3. Changes in the Mo-M-SiO₂ during Carburization. Figure 4 shows TG-DTA-DTG studies during the course of the carburization of Mo-M-SiO₂ to α -MoC_{1-x}/SiO₂. The weight-loss stages of Mo-M-SiO₂ in this carburization reaction are caused by two aspects: changes of molybdenum species and pyrogenation of methyl groups in SiO₂. The main five weight-loss stages are observed. The first weight-loss stage occurs below 388 K, and the weight loss of 1.88% is the physical absorbed water leaving. From 388 to 504 K, a weight loss of 3.01% is observed, corresponding to chemical absorbed water and en leaving. The weight loss from 504 to 694 K is about 4.61%, which can be attributed to the

FIGURE 3: Changes in the XP spectra of Mo-M-SiO₂ in the (a) Mo 3d, (b) deconvoluted spectrum for Mo 3d obtained after treatment at 623 K and (c) at 823 K, (d) C 1s, (e) Si 2p, and (f) O 1s region during carburization in Ar gas; room temperature refers to the untreated sample.

FIGURE 4: TGA-DTA-DTG curves during carburization process of Mo-M-SiO₂. FIGURE 5: Schematic presentation of the formation of highly dispersed $\alpha\text{-MoC}_{1-x}$ in porous SiO_2 .

formation of MoO_2 . At 921 K, a further weight loss of 4.32% is found, suggesting the formation of an immediate phase, molybdenum oxycarbide [MoO_xC_y , $(x + y) < 1$], between MoO_2 and the final carbides. The final weight-loss stage occurs above 921 K, in which molybdenum oxycarbide is converted to the molybdenum carbide $\alpha\text{-MoC}_{1-x}$.

3.4. Catalytic Properties. The results of CO hydrogenation over the three samples, one uncarburized and two carburized, are listed in Table 2. It can be seen that the uncarburized sample shows the lowest activity and alcohol selectivity among the three samples. It is notable that both the catalytic activity and selectivity to alcohols remarkably increase in

TABLE 2: Catalytic performances of the samples in CO hydrogenation (593 K, 6.0 MPa, H₂/CO = 1.0, 1000 h⁻¹).

Sample	CO Conv. (mol%)	STY (g/(L.h))		Selectivity (mol%) ^b	
		ROH	C ₂ + OH	Alcohol	Hydrocarbon
Mo-SiO ₂	9.7	2.3	1.2	2.7	97.3
α -MoC _{1-x} /SiO ₂ (Ar)	38.9	60.7	33.1	22.6	77.4
α -MoC _{1-x} /SiO ₂ (CH ₄ /H ₂)	33.5	32.3	17.5	13.8	86.2

^bFree of CO₂.

α -MoC_{1-x}/SiO₂ than those of uncarburized Mo-SiO₂ sample, however, the Mo-SiO₂ carburized in Ar gas showed highest activity and alcohol selectivity. Thus, it can be concluded that the higher the surface area and pore volume, the higher activity and alcohol selectivity. the amorphous carbon formed by the CH₄ pyrolytic reaction may reduce the activity and alcohol selectivity.

3.5. Formation Mechanism. We propose a formation mechanism as shown in Figure 5 to explain the α -MoC_{1-x}/SiO₂ formation. Si-H bonds are easy to be activated through interaction with transition-metal (tM), which makes activated H atoms transferred from Si to tM. In EtOH, Si-OC₂H₅ bonds are formed [18]. In our experiment, AHM is hard to dissolve in EtOH, just forming a white suspension, but still a little dissolved AHM exists. The dissolved Mo complexes interact with Si-H bonds in PMHS, which make PMHS alkyloxidized and Mo-H bonds form. Mo-H bonds react with EtOH to form Mo-OC₂H₅ bonds and release H₂, and further transform to Mo-O-Si bonds through hydrocondensation with alkyloxidized PMHS, which make Mo species connected with C long chains of PMHS (Mo-PMHS). With dissolved AHM reacting with PMHS, more AHM dissolve into EtOH and further react with PMHS. EDA as catalyst is added to activate residual Si-H bonds to form Si-OC₂H₅ bonds and release H₂. Finally, porous Mo-M-silica is obtained from hydrocondensation of alkyl oxidized Mo-PMHS and TEOS. By utilizing C atoms of methyl in SiO₂ supports as carbon sources, α -MoC_{1-x}/SiO₂ can be obtained just by heating in Ar gas.

4. Conclusion

In summary, we facilely fabricated highly dispersed α -MoC_{1-x} with an even diameter of 3 nm in micro/mesoporous silica by insitu carburization. The porous methyl modified silica supports were obtained using mixed TEOS and PMHS without additional introduction of any surfactants. AHM as molybdenum source was introduced into silica supports, and obtained high dispersion without peroxo treatment. Furthermore, the sample exhibited obvious high catalytic activity and alcohol selectivity in CO hydrogenation reaction.

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