Synthesis and characterization of tungsten-incorporated mesoporous molecular sieve MCM-48 by one step

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Abstract Tungsten-substituted mesoporous MCM-48 materials are successfully synthesized at 393 K by a one-step co-condensation sol–gel method. The prepared samples with different Si/W ratios are characterized by X-ray diffraction (XRD), nitrogen adsorption, high-resolution transmission electron microscopy (HRTEM), diffuse reflectance UV–visible spectroscopy and FT-IR, and the results indicate the presence and good dispersion of tungsten species inside the silica pores, the Si/W ratio is controlled above 28. When the Si/W ratio is less than 28, though no bulk tungsten is detected outside the MCM-48 mesoporous silica, the pore structure order becomes worse.

Keywords Mesoporous materials · W-MCM-48 · Tungsten

1 Introduction

In 1992, researchers at Mobil Corporation reported a series of ordered mesoporous silicates, which were synthesized by the self-assembly of surfactants and inorganic species [1]. M41S were generally referred to MCM-41 and MCM-48, and possessed well-defined pore structures. MCM-41 possessed a large specific surface area, a hexagonal array, and uniform mesopore channels. MCM-48 had a cubic pore system indexed in the space group Ia3d, and possessed a bicontinuous structure centered on the gyroid minimal surface [2] that divided available pore space into two

nonintersecting subvolumes [3, 4] The discovery of mesoporous materials offered an opportunity for catalyst supports.

Recently, MCM-48 indexed to an Ia3d unit cell [5], had attracted much attention because of its unique three-dimensional pore structure that was more desirable than MCM-41 for industrial applications. Since it's highly interwoven and branched structure provided many places MCM-48 could avoid pore blockage caused by reactant molecules. However, pure siliceous MCM-48 limited its practical application especially in catalysis owing to be lack of active sites in the wall. Hence, it was of great importance to incorporate heteroatom into the walls of these mesoporous silica materials.

The incorporation of transition-metal elements such as Al, Ga, Mn, Cr, Zr, and V into the amorphous silica walls was mandatory for the formation of catalytic active sites in mesoporous molecular sieves. Many efforts had focused on MCM-41 [6–8] and SBA-15 [9, 10]. And a few of works had aimed at MCM-48 [11–16]. In addition, there were materials about tungsten incorporated, such as W-HMS [17], W-SBA-15 [18, 19] and W-MCM-41 [20–22], which were synthesized easily. However, little attention was paid to the synthesis and characterization of tungsten incorporated MCM-48 [23, 24], the MCM-48 phase was often an intermediate during the transformation from a hexagonal phase to a lamellar phase, other ion added destroyed easily an intermediate, so metal incorporated MCM-48 materials were more difficult to synthesize than to synthesize MCM-48. Though it was difficult to synthesize tungsten-containing MCM-48, catalytic performance of tungsten-containing MCM-48 was better than WO₃/MCM-48 because WO₃ species were highly dispersed into the lattice of the bulk. Yang et al. [23] synthesized W-MCM-48 by two steps and applied W-MCM-48 to oxidation of CPE.

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Morey et al. [25] used $W(OC_2H_5)_5$ as tungsten source to synthesize W-MCM-48 and investigated perspectives on catalytic peroxide activation. Recently, metal incorporated silica materials attract attentions in the fields, such as metathesis [26], Absorbent [27]. So formation of catalytic active sites in mesoporous molecular sieves is important work, but the methods reported in previous literatures were complicated. Firstly hydrothermal condition kept in stainless steel autoclave for 72 h and pH was adjusted by hydrochloric acid, then hydrothermal condition kept 24 h. So we take attempt to synthesize W-MCM-48 by one step without adjusting pH and short synthesizing time.

Here, this paper reports tungsten incorporated into mesoporous silica pores by one step co-condensation sol-gel method which improves dispersion of the tungsten species, alleviates aggregation of WO_3 and strengthens interactions between tungsten species and silica. Introducing tungsten into MCM-48 materials opens new opportunities for further synthesis of tungsten oxide materials. The method used in this work is a simple and new approach for the synthesis of tungsten-containing mesoporous silica materials.

2 Experimental Sections

2.1 Materials

The reagents used in this study are tetraethylorthosilicate (TEOS) as silica source, cetyltrimethylammonium bromide (CTAB) as surfactant, sodium hydroxyl (NaOH) as alkali source, ammonium metatungstate as tungsten source and deionized water.

2.2 Synthesis

The ordered mesoporous W-MCM-48 was synthesized by assembly of surfactant micelle with silicate precursors in alkali media as described in the literature [14]. The synthesis of W-MCM-48 was as follows: The molar composition of the reaction mixture is SiO_2 : CTAB: Na_2O : H_2O : WO_3 =1: 0.55: 0.025: 60: (0–0.05). 10.0 g of CTAB is added into 50.0 g of 0.5 M NaOH aqueous solution, and the solution is stirred at 318 K for 1 h. Then, 10.7 g of TEOS and 4.0 g of 84 wt% ammonium metatungstate solution were added to the solution under vigorous stirring at 318 K. The resulting gel is stirred for 3 h at 318 K and transferred into Teflon-lined stainless steel autoclave with polytetrafluorethylene and kept in an air oven at 393 K for another 24 h. Finally, the mixture is cooled down, and the solid products are collected after filtration, washed with water, dried and calcined at 823 K in flowing air for 5 h.

2.3 Characterization

X-ray powder diffraction patterns were recorded on a Bruker D8 ADVANCE diffract meter with $CuK\alpha$ radiation of wavelength 1.5406 Å in the 2θ range of 1.5–80° with scanning rate of 1° min⁻¹. N_2 adsorption–desorption isotherms at 77 K was recorded with a Micromeritics ASAP 2010 automatic adsorption analyzer after the catalyst samples were degassed at 523 K for 3 h. The BET surface area was calculated from the desorption isotherm in the relative pressure range of $P/P_0 = 0.01$ –1.0. The high-resolution transition electron microscope (HRTEM) images were obtained with a Tecnai G2 F20 Super-twin. The UV–Vis DRS of the catalyst samples were recorded, in the range of 200–800 nm against the support as reference, on a Hitachi U-4100 spectrophotometer equipped with an integration sphere diffuse reflectance attachment. The mid-infrared spectra had been collected on the Digilab FTS-3000 FT-IR spectrometer using KBr pellet technique. About 15 mg of the sample was pressed (under a pressure of 10 MPa) into a self-supported wafer of 13 mm diameter. This pellet was used to record the infrared spectra in the range 1,300–400 cm⁻¹.

3 Results and Discussion

3.1 XRD analysis

The quality and structural ordering of W-MCM-48 materials were evaluated by powder small angle XRD (1.5°–6°). Figure 1 showed the small angle XRD patterns of W-MCM-48 and MCM-48. Except for Si/W=20, the two XRD reflection peaks (211) and (220) at 1.5°–6°, which were indexed to Ia3d cubic structure [1], were all well-defined and in good agreement with the reported patterns of MCM-48 material in literature [28]. When the ratio of Si/W decreased from 93 to 28, the two diffraction peaks were still clearly observed. No significant changes were observed in the small angle XRD patterns of the W-MCM-48 with different the amount of tungsten oxide, except for the change in XRD peak intensity. The intensity of small angle XRD peaks and the well resolved peaks indicated the long-range ordering of the mesoporous silica materials prepared. When ratio of Si/W was 28, the intensity of peaks (211) and (220) became weaker obviously than that of the MCM-48, indicating the long-range ordering of the material to be worse. When ratio of Si/W was 20, one peak was well-resolved, which indicated that the ordering of the synthesized materials became worse. The reason might be that a large amount of ammonium tungsten caused the pH value of resulting gel to decrease.

Fig. 1 Small-angle XRD patterns of MCM-48 with different Si/W ratios

The normal XRD (10° – 80°) patterns of W-MCM-48 with different Si/W ratios were shown in Fig. 2 in order to detect the bulk WO_3 . No diffraction peaks of WO_3 were found, the WO_3 species were well dispersed into the MCM-48.

3.2 N_2 adsorption analysis

Figure 3 presents the N_2 adsorption isotherm of the W-MCM-48 materials with various ratios of Si/W. Textural characteristics of W-MCM-48 samples are presented in Table 1. The isotherms of in all samples show type IV adsorption isotherms (IUPAC) belonging to typical mesoporous materials [5]. The steep increase of the N_2 adsorption/desorption isotherm is observed in the relative pressures (P/P_0) from 0.0 to 0.3 and 0.3 to 0.7, which is due

Fig. 2 XRD patterns of MCM-48 with different Si/W ratios

to the reversible capillary with the mesopores of materials. In general, for mesoporous molecular sieves, the steepness of the capillary condensation in the isotherms indicates the narrow pore size of distribution. There are two separate well-defined hysteresis loops. One of the hysteresis loops is in the region of $P/P_0 = 0.0$ – 0.3 and related to the diameter of mesopores, and the other is at $P/P_0 > 0.3$, which corresponds to the capillary condensation in the interparticle pores [29]. The sharp inflection point shifted toward higher relative pressure (P/P_0) with increasing tungsten content, as observed in Fig. 3, the pore size distribution takes significant change due to the tungsten substitution.

The introduction of tungsten oxide caused the decrease of surface area and the increase of pore volume and pore diameter with increasing tungsten oxide content.

3.3 HRTEM analysis

To investigate the pore structure of W-MCM-48, The HRTEM of the prepared samples are obtained and shown in Fig. 4. Electron micrographs have been recorded along direction [111] (the [111] direction image is similar to that reported previously by Monnier et al. [3]). As Si/W is 93 and 45, the order of pore is distinguished well. The ratio of Si/W decreases, definition becomes worse. As Si/W is 20, the quality of the images becomes disorderly and unsystematic. The reason results from more tungsten incorporated, the results are in good agreement with the XRD result.

3.4 UV–Vis DRS

UV–Visible diffuse reflection spectroscopy is a direct and effective method for determining local molecular

Fig. 3 N_2 adsorption/desorption isotherm

Table 1 Structural parameters of the MCM-48 with different ratio of Si/W

Samples	BET			
	Specific surface area		Pore volume (cm ³ /g)	Pore diameter (nm)
	Si/W	(m ² /g)		
W-MCM-48(93)	93	1,328	0.69	1.97
W-MCM-48(45)	45	1,264	0.75	2.21
W-MCM-48(28)	28	1,092	0.85	2.48
W-MCM-48(20)	20	969	1.05	2.76

coordination and bonding information for inorganic compounds such as simple mixed oxides [30–35].

To obtain the chemical nature and coordination state of tungsten oxide species, the diffuse reflectance spectra in the UV–Visible region of W-MCM-48 samples with different Si/W ratios are recorded and shown in Fig. 5. Diffuse-

reflectance UV–Vis spectrum is a sensitive tool that is widely used to detect the presence of framework and extra framework tungsten species [8, 36]. Two characteristic bands have been resolved for W-containing materials in the UV–Vis spectrum; two intense bands are centered at 225 and 270 nm. The band at 225 nm was attributed to an isolated [WO₄] tetrahedral species [37, 38] depending on the ligand field symmetry surrounding the W center [26, 39], which is generally regarded as the direct proof that transition metal atoms have been incorporated into the framework of a molecular sieve [40]. Therefore, it should be considered as the direct proof for the presence of the framework tungsten species in tetrahedral coordination. The band at 270 nm may be attributed to a distorted tetrahedral coordination environment or the existence of some tungsten species in an octahedral coordination environment [8]. The intensity of the two bands is found to increase with the increase of tungsten content, which suggests that the amount of framework tungsten oxide species increased.

Fig. 4 HRTEM image of W-MCM-48 with different Si/W ratios (a=93, b=45, c=28, d=20)

Fig. 5 UV-Vis diffuse reflectance spectra of W-MCM-48

3.5 FT-IR

The FT-IR spectra of the W-MCM-48 samples in the region $1,300\text{--}400\text{ cm}^{-1}$ is shown in Fig. 6. All samples exhibit the infrared absorption bands at 460, 560, 800, 880, 960, 1,086 and $1,220\text{ cm}^{-1}$. The IR spectra present a vibration band at 560 cm^{-1} , which is assigned to the asymmetric stretching mode of double five rings in the MFI framework [41, 42]. On the basis of previous literature assignments for silicate materials, the IR spectra for W-MCM-48 samples show characteristics absorption bands at 460, 800, 1,086 and $1,220\text{ cm}^{-1}$ that assigned to symmetric and asymmetric stretching of Si–O–Si vibrations for the tetrahedral SiO_4 structure units. These bands are usually assigned to δ (Si–O–Si), V_s (Si–O–Si) and V_{as} (Si–O–Si), respectively [43–46]. An absorption band in the $945\text{--}980\text{ cm}^{-1}$ region that characterizes the vibrational

Fig. 6 FT-IR spectra of W-MCM-48

spectrum of transition-metal elements incorporated in silicate may be considered the fingerprint of framework transition-metal [47–49]. Then the vibration at 960 cm^{-1} may be attributable to the W–O–Si linkage in the W-MCM-48. Furthermore, the intensity of the 960 cm^{-1} band enhanced with the increase in the tungsten content in the W-MCM-48 samples, which suggest the incorporation of tungsten in the mesoporous matrix.

4 Conclusions

In conclusion, the tungsten is effectively introduced into ordered mesoporous MCM-48 in strong alkaline medium in a facile way by using CTAB as template by one step. These materials have high surface area ($>900\text{ m}^2/\text{g}$), uniform pore channels, the TEM picture allows to estimate the pore size (30). The tungsten species are highly dispersed in the silica-based framework structure. As $\text{Si/W} > 28$, the characterization results indicate that the framework structure of the synthesized W-MCM-48 is long-range order.

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