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Single crystals of mesoporous tungstenosilicate W-MCM-48 molecular sieves for the conversion of methylcyclopentane (MCP)

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ABSTRACT

Highly ordered W-MCM-48 mesoporous materials containing isolated W atoms in tetrahedral framework positions were successfully synthesized following the S^+I^- pathway, up to a Si/W of 40. When tungsten content was increased up to a Si/W of 20, the ordered cubic structure was only partially maintained, and for a Si/W of 10 an amorphous phase was obtained. Highly isolated tetrahedral framework tungsten atoms in the W-MCM-48 with a Si/W of 40, have been identified by UV–vis band at 225 nm, IR-TF band at 970 cm^{-1} and XRD. The W 4f XPS results suggest that the tungsten atoms exist in two oxidation states, W^{4+} and W^{5+}. The morphology of the samples varies as a function of tungsten content. The W-MCM-48 samples with a Si/W ratio of 40 existed as crystals with a unique crystalline morphology consisting of cubes truncated rhombic dodecahedrons belonging to the cubic *Ia3d* space group, while the samples with a Si/W ratio of 20 exhibited a different morphology consisting of spheres and cubes truncated by rhombic dodecahedrons. A comparison of samples with Si/W of ∞, Si/W of 40 and Si/W of 20 was performed using the conversion of MCP carried out at 450 °C under H_2.

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1. Introduction

The discovery of the M41S family [1] of nanostructured mesoporous molecular sieves, well-defined mesostructures, has attracted a pervasive interest from academic and industrial researchers due to the huge surface area, uniform pore size distribution, large pore size, large pore volume, and large number of current and foreseen applications of these materials. Applications of these materials include catalysis, environmental chemistry, organic synthesis, adsorption, medical imaging, molecular collection and storage [2,3]. The three most important members of the M41S family are the hexagonal MCM-41 (*p6mm*) with a one-dimensional (1D) pore system, the cubic MCM-48 (*Ia3d*) with a three-dimensional (3D) pore system, and the lamellar MCM-50. These mesoporous materials are synthesized by the cooperative self-assembly of cationic surfactants and an inorganic precursor [1]. These surfactants can preferentially form hexagonal or lamellar structures, suggesting that the synthesis of high quality MCM-48 suffers from poor reproducibility. One can select between these structures, by selecting a surfactant with an appropriate surfactant packing, parameter "g" [4], which is described as $g = V/a_0 l$, where V is the total volume of the surfactant chains, a_0 is the effective head group area at the micelle surface, and l is the kinetic surfactant tail length or the curvature elastic energy [5]. The cubic phase (*Ia3d*) forms when g values are in the interval $1/2 < g < 2/3$, whereas the hexagonal phase (*p6mm*) and lamellar phase form when $g = 1/2$ and 1, respectively [6]. As demonstrated by the literature [7,8], a great deal of attention has been focused on the improving the conditions used to synthesize MCM-48. Among these fascinating structures of the M41S family, MCM-48 has attracted more attention due to its three-dimensional (3D) pore system, which transcends MCM-41 one-dimensional (1D) pore system and MCM-50 lamellar structure. The complex structure of MCM-48, which falls in the space group *Ia3d* [9], is defined by a gyroid minimal surface [10]. The gyroid infinite periodic minimal surface provides two independent tridirectional channels running along the [1 1 1] and [1 0 0] directions [11]. Consequently, MCM-48 provides favorable mass transfer to bulk molecules, which decreases diffusion limitations, and makes MCM-48 resistant to pore blockage [12] and more attractive for catalytic reactions, compared to the one-dimensional pore system of MCM-41. On the other hand, it is well known that pure-silica MCM-48 mesoporous molecular sieves show low activity due to the absence of active sites, which typically require heteroatoms. Therefore, one of the emerging trends in the area of MCM-48 mesoporous molecular sieve synthesis is the incorporation of heteroatoms, which play a role of catalytically active sites. One of the most

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elegant procedures for the incorporation of heteroatoms, which also permits the design of the catalysts with active sites located on the highly accessible internal surfaces of the pore channels, is the isomorphous substitution of Si in the framework by other elements such as Al [13], Ga [14], Fe [14], Ti [15], V [16], Mn [16], Cr [16], Cu [17], Co [18], and Zr [19]. The incorporation of tungsten atoms into MCM-48 would seem to be a challenging task, taking into account that only one research group has reported W-MCM-48 synthesis [20], but prepared in two steps by pH adjustment method. Despite its complex and attractive porosity, W-MCM-48 has received less attention in the literature than W-MCM-41 [21,22] probably due to its difficult synthesis. In order to circumvent these synthetic difficulties, we have for the first time synthesized W-MCM-48 (Si/W ratio = 40–10) by a one step method under basic conditions, which takes advantage of electrostatic interactions, and follows the S^+I^- pathway.

The catalysts prepared by this method are tested as catalysts for the ring opening of methylcyclopentane (MCP). The ring opening of MCP is a well studied reaction [23] due to its importance in the petroleum industry. As a result of environmental legislation, it is being considered as a plausible way to improve the quality of diesel fuels [24] in particular to obtain a higher cetane numbers. The ring opening of MCP can be catalyzed by metallic or acidic sites in a catalyst. Traditionally, monometallic Rh [25], Pt [26], Pd [27], and Ir [28] and bimetallic Rh–Ge [29], Rh–Sn [30], Rh–Pt [31], Rh–Ag [32], Pt–Ru [33], and Pt–Re [34] supported catalysts have attracted a great deal of interest in studies of this reaction. These studies showed that the reaction mechanism depends on the nature of the metal, the metal particles size and the nature of the support [35]. The noble metal catalysts show high activity and selectivity, but suffer from several drawbacks, including sensitivity to metal site poisoning, the requirement of a high pressure of hydrogen, the special conditions required to prepare the catalysts, the limited abundance, and the environmental impact of these metals. As a result, the tendency now is to replace the noble metal catalysts used in the ring opening reaction of MCP. In light of the ubiquitous restrictions imposed by environmental and economical legislation, use of nanostructured mesoporous molecular sieves, which can be very selective for the desired products at low temperature and are recyclable, is one alternative to the use of traditional catalysts.

In this work, we report a successful one-step synthesis of W-MCM-48 mesoporous molecular sieves with Si/W ratios between 40 and 10, under basic conditions following the S^+I^- pathway. To the best of our knowledge the tungsten single crystal of W-MCM-48 has not been previously reported. The samples were characterized by various techniques, such as XRD, SEM, TEM, N_2 sorption, UV–vis, IR-TF, and XPS. A comparison of samples with a low (Si/W of 40) and a high (Si/W of 20) tungsten content was performed using the ring opening reaction of MCP carried out at 450 °C under H_2. However, this reaction has never been studied using mesoporous materials as catalysts.

2. Experimental

2.1. Catalyst synthesis

W-MCM-48 mesoporous solids with Si/W molar ratio ranging from 10 to 40 were synthesized hydrothermally using tetraethyl orthosilicate (TEOS $C_8H_{20}O_4Si$, 98% Acros) and sodium tungstate W (VI) (Na_2WO_4, 2 H_2O, Sigma–Aldrich), as precursors. Cetyltrimethylammonium bromide (CTAB, $C_{19}H_{42}N{\cdot}Br$, Sigma–Aldrich) was used as the structure-directing agent (SDA). NaOH (NaOH 98%, SDS) aqueous solution was used as the basic source. The molar gel composition was: 1 TEOS: (0.02–0.1) W: 0.48 CTAB: 0.25 Na_2O: 55 H_2O.

In a typical synthesis, the cetyltrimethylammonium bromide, doubly distilled water and sodium hydroxide have been stirred for 1 h at room temperature. Then, the tetraethylorthosilicate was added with vigorous stirring. After 0.5 h, the required amount of tungsten (VI) as sodium tungstate dihydrate was added. The gel mixtures were stirred for 2 h at room temperature. Then, the former gel mixture was transferred into an autoclave and aged for 72 h at 100 °C. The white precipitate was filtered, washed with distilled water and dried for 24 h at 60 °C. The surfactant was removed of the pores by extraction followed by the calcination. The extraction procedure was performed by the dispersion of W-MCM-48 solid in ethanol and the mixture was refluxed for 1 h. Then, the solid was filtered, washed with cold ethanol and the extraction was repeated twice. After that, the white solids were dried at 90 °C for 24 h. It was found [36] that sometimes water and ethanol in traces remained in the mesopores, which can leads to the formation of steam at high temperature. Therefore, the samples were calcined at 100 °C for 2 h and finally at 500 °C for 5 h in a muffle furnace with the heating rate of 1 °C/min. For comparison, the pure silica MCM-48 molecular sieve was synthesized following a previously reported procedure [37]. Finally, all the samples were characterized by various techniques.

2.2. Physico-chemical characterizations

The chemical composition of the MCM-48 mesoporous solid catalysts was performed by the Service Central d'Analyse of CNRS-Solaize.

The scanning electron microscopy (*SEM*) images were obtained on JEOL electron microscope 6700 scanning electron microscope operated at 200 kV from a thin film dispersed on a holly carbon grid. The calcined Si-MCM-48 and W-MCM-48 samples were used for SEM studies.

The powder X-ray diffraction patterns (*XRD*) of the MCM-48 samples were recorded on a BRUKER D8 powder diffractometer using Cu Kα radiation of wavelength 0.154 nm (40 kV and 100 mA). The diffractograms were recorded in the 2θ range of 0.5–10° (low angle) and 10–90° (wide angles). The scanning was made with a step size of 0.02 and a step time of 2 s. The unit cell parameter (a_0), $a_0 = d_{hkl} \times \sqrt{h^2 + k^2 + l^2}$, for the *Ia3d* symmetry group, was evaluated using the interplanar spacing d of the (2 1 1) XRD peak.

Transmission electron microscopy (*TEM*) images were obtained on a TopCon 2100 FCs microscope operated at 200 kV. The samples were dispersed in ethanol in an ultrasonic bath for several minutes, and then deposited on a Cu grid and dried at room temperature.*Nitrogen adsorption measurements* were performed at -196 °C on a TriStar apparatus. Prior to the sorption (adsorption–desorption) measurements, the samples were outgassed overnight at 150 °C. The specific surface area was calculated using the standard Brunauer–Emmett–Teller (BET) method. The total pores volume was estimated from the amount of nitrogen adsorbed at a relative pressure p/p_0 of 0.99, assuming complete surface saturation with nitrogen, where p and p_0 denote the equilibrium pressure and saturation vapor pressure, respectively. The pore size distribution curves were calculated from the adsorption branches of the isotherms using Barett–Joyner–Halenda (BJH) method. Additionally, the pore diameter was defined by the value at which the maximum in differential pore volume was observed. The mean thickness of the pore wall (w) of the cubic structure in the W-MCM-48 mesoporous solid was calculated according to the formula $w = (a_0/3.092) - (D_{\mathrm{BJH}}/2)$ where a_0 is the unit cell parameter, 3.092 is a constant representing the minimal surface area for MCM-48 space group [38], and D_{BJH} is the pore diameter.

UV–vis diffuse reflectance spectra were recorded on a Varian Carry 100 spectrophotometer equipped with a diffuse reflectance

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