Available online at www.sciencedirect.com

ScienceDirect

Microporous and Mesoporous Materials 110 (2008) 508–516

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

The states of vanadium species in V-SBA-15 synthesized under different pH values

Fei Gao [a], Yanhua Zhang [a], Haiqin Wan [a], Yan Kong [b,*], Xingcai Wu [a],
Lin Dong [a,*], Baiqin Li [a], Yi Chen [a]

[a] Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China
[b] State Key Laboratory of Material-Oriented Chemical Engineering, Nanjing University of Technology, Nanjing 210009, PR China

Received 11 January 2007; received in revised form 25 June 2007; accepted 25 June 2007
Available online 5 July 2007

Abstract

V-SBA-15 ($n_{Si/V} \approx 10$) mesoporous molecular sieves have been synthesized in different pH-value medias and characterized by XRD, N_2 adsorption, TEM, UV–vis, Raman, FT-IR, ESR, and NH_3-absorbed in situ FT-IR techniques. Results indicated that the pH value played an important role on the states of vanadium species in the prepared materials. As the pH value increased, the amount of the crystalline vanadium oxides decreased, the incorporated vanadium species with isolated tetrahedral (V^{5+}) and square pyramidal coordination (VO^{2+}) increased accordingly. At pH = 3.0, vanadium species were mainly in the silica framework and formed stronger acid sites, it seems to suggest that the linear configuration V^{5+}–ONH_3H^+–O–V^{4+} groups have been formed after ammonia was adsorbed. However, for the samples synthesized at the low pH values, the crystalline vanadium oxides existed and the amount of the dispersed tetrahedral vanadium species decreased, which caused the weaker acid sites.

Keywords: SBA-15; State; Vanadium; In situ FT-IR; Synthesis

---

1. Introduction

Since the researchers at Mobil Research and Development Corporation reported the M41S family [1,2], many efforts have been devoted to the study of the synthesis and application of mesoporous molecular sieves in the last few decades. Among them, SBA-15 prepared using triblock copolymer as template has attracted much attention due to its larger pores, thicker walls and much higher hydrothermal stability than those of MCM-41 [3]. However, pure silica SBA-15 showed very limited catalytic activities due to the lack of lattice defect, redox properties, basicity and acidity. Hence it has become a remarkable object that introduced guests into the framework of SBA-15 to increase the active sites and thus improve the catalytic activity [4].

Vanadium oxides were the essential ingredients of many powerful redox catalysts in industrial processes, especially in the oxidation reactions for the manufacture of fine chemicals [5]. Vanadium-substituted micromolecular sieve, such as V-ZSM5, was a potential catalyst for the selective oxidations [6]. Mesoporous molecular sieves containing vanadium such as V-MCM41, V-SBA-15, and so on were also effective for the same type of reactions, especially for the oxidation of large organic compounds such as cycloalkene, cycloalkanes and branched alkanes due to their large pore sizes [7–9].

The content and state of vanadium in the catalysts have an important effect on their activity. A higher loading of vanadium with a high dispersion was helpful for many oxidation reactions [10–12]. For instance, in the reaction of partial oxidation of methane to formaldehyde, the conversion of methane increased almost linearly from 5.15% to 15.13% with the vanadium content up to loading of 3.85 wt.% (close to the monolayer capacity) and then

---

[*] Corresponding authors.
E-mail addresses: kongy36@njut.edu.cn (Y. Kong), donglin@nju.edu.cn (L. Dong).

1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.06.041

declined to 9.98% at higher vanadium loading (5.54 wt.%) attributed to a decrease in the number of accessible surface V sites as a consequence of the formation of more agglomerated V species on the SBA-15 surface [12]. Nevertheless, the incorporation of metal ions into the framework of SBA-15 was difficult because of the strongly acidic conditions [13]. Therefore, it was important to control and adjust the final loading and states of vanadium oxide in the material by exploring the new preparing methods and suitable conditions. However, most of the methods in the literatures used solely postsynthetic grafting methods or needed complex experimental conditions. Luan et al. [14] prepared V-SBA-15 by incipient-wetness impregnation inside a glovebox under flowing nitrogen. Segura et al. [15] reported the synthesis of V-SBA-15 with highly dispersed vanadium oxide by the molecular designed dispersion method using acetylacetonate complexes as vanadium sources and toluene as solvent.

In this paper, we reported a simple and effective route of directly incorporating large quantities of vanadium ($n_{\mathrm{Si/V}} \approx 10$) into the SBA-15 framework by adjustment of the pH value of the gel mixtures. The states of vanadium species have been characterized by using UV–vis, Raman, FT-IR, and ESR techniques. The surface acidity of the materials was also detected by using the in situ NH_3-absorbed FT-IR.

2. Experimental

2.1. Synthesis

The V-SBA-15 materials were prepared as follows: 4.0 g triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123, molecular weight = 5800, $EO_{20}PO_{70}EO_{20}$) was dissolved in 30.0 g of water and stirred for 4 h. Nine grams of tetraethyl orthosilicate (TEOS) and the appropriate amount of ammonium metavanadate (NH_4VO_3) were added directly to the homogeneous solution ($n_{\mathrm{Si/V}} \approx 10$, mol ratio). Then proper quantities of 0.30 M HCl were added to adjust the pH values of mixture to 1.3, 1.8, 2.2 and 3.0, respectively. The gel was stirred for 24 h and then maintained at 373 K for another 48 h. The resultant atrovirens precipitate was collected, washed thoroughly with distilled water, absolute ethanol for several times and dried at 343 K for 12 h. The as-prepared product was then calcined in air at 823 K for 6 h with a heating rate of 1 K min^{-1} to remove the template. The samples were labeled as V-SBA-15(x) where x denotes the pH value of the starting solution. For comparison, pure SBA-15 was synthesized at pH = 2.2 using the same procedure in the absence of vanadium precursor.

2.2. Characterization

The power X-ray diffraction patterns were collected on a Philips X'pert X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15418$ nm).

Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 instrument. The samples were degassed for 160 min at 573 K in the degas port of the adsorption analyzer. The pore size distributions were calculated from the analysis of the adsorption branch of the isotherm using the Barrett–Joyner–Halenda (BJH) algorithm.

Chemical compositions were determined using a Jarrell-Ash 1100 inductively coupling plasma (ICP) spectrometer. The samples were completely dissolved in suitable hot acid before analysis.

TEM images were taken on a FEI Tecnai G^2 20 S-TWIN instrument at an acceleration voltage of 200 kV. The samples were crushed in A.R. grade ethanol and the resulting suspension was allowed to dry on carbon film supported on copper grids.

UV–vis diffuse reflectance spectra (UV–vis) profiles were recorded in the range of 190–700 nm by a Shimadzu UV-2401 spectrophotometer with $BaSO_4$ as reference.

ESR spectra were recorded on a Bruker EMX-10/12 ESR spectrometer with X-band at 110 K.

Laser Raman spectra (LRS) were recorded using a Renishaw In-via microscopy Raman spectrometer, and an Ar^+ laser with an excitation wavelength of 514.5 nm in a macromode. A laser power of 20 mW at the sample was applied. No sample preparation was required and one accumulation of 10 s was used in each sample.

Fourier-transform infrared spectroscopy (FT-IR) was carried out on a Nicolet 5700 FT-IR instrument running at 2 cm^{-1} resolution. Samples were mixed and ground with KBr followed by pressing into pellets for IR measurement in the range of 4000–400 cm^{-1}.

In situ FT-IR spectroscopy of adsorbed ammonia (NH_3) was carried out on a Nicolet 5700 FT-IR instrument. Thin, but intact, self-supporting wafers of the adsorbents were placed inside a commercial controlled environment chamber (HTC-3). Before measure, samples were pretreated in a high-purity N_2 stream at 673 K for 1 h. After cooling to room temperature (RT), NH_3 (9.91%) and He (balance) were introduced into the cell and the temperature was increased at a rate of 10 K min^{-1}, the spectra were recorded from RT to 673 K (for every 25 K) under high-purity N_2 stream.

3. Results and discussion

3.1. Mesoporous structure of V-SBA-15

The XRD patterns of the V-SBA-15 samples synthesized at different pH values and pure SBA-15 are shown in Fig. 1. All the samples exhibited three well-resolved reflections, *i.e.*, (1 0 0), (1 1 0), and (2 0 0), and could be indexed in the hexagonal space group *p6mm*, except for sample V-SBA-15(3.0) (Fig. 1e) [3]. The (2 1 0) peak of all samples was too weak to be recognized probably due to the incorporation of high content heteroatoms into the framework of mesoporous silicate and the increase of the synthesis pH values, which caused the disorder of the structure