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Synthesis, Characterization and Catalytic Activity of Nano-Spherical MCM-41 Modified with Vanadium

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Vanadium modified MCM-41 nanospheres were synthesized by the impregnation and sol–gel supermolecular method respectively. Structure and morphology of the obtained materials were characterized using X-ray diffraction (XRD), inductively coupling plasma (ICP), Fourier transform infrared (FT-IR), scanning electron microscopy (SEM) and N₂-adsorption–desorption techniques. The influence of particle sizes on their catalytic activities in styrene oxidation and benzene hydroxylation was investigated. Results revealed that all the samples had regular sphere shape and adjustable particle size within 40–160 nm, and exhibited high catalytic activities in the oxidation of styrene and hydroxylation of benzene. The smaller the particle size is, the higher the activity becomes. Meanwhile, the catalysts synthesized by the sol–gel method are more effective than that synthesized via impregnation method, indicating the vanadium species in the mesoporous framework are probably the catalytic active sites.

Keywords: Vanadium, MCM-41, Nanosphere, Catalytic Activity.

1. INTRODUCTION

Since first reported by Mobil company in 1992,¹ mesoporous molecular sieves have become one of the focuses of chemistry and material science because of their high specific surface area, large pore volume, well-ordered pore structure with uniform pore size distribution from 2 to 50 nm, etc.² However, pure mesoporous silica materials show poor catalytic activity due to their neutral skeleton structure and limited surface lattice defects and acidic sites.

Catalytic performance of a catalyst depends not only on the nature of its active sites, but also on its physical properties such as diffusion factor, particle morphology and size, etc. One of the strategies to improve the catalytic activities of mesoporous silica materials is to introduce active heteroatoms to their surface or framework via impregnation or direct hydrothermal method.^{3–9} In the later case, in order to incorporate heteroatoms into the framework, the synthetic conditions must be finely controlled, and these conditions also greatly influence the particle morphology and size. In general, it is a big challenge to synthesize mesoporous molecular sieves with both regular morphology and incorporated heteroatoms in the framework. The products of styrene oxidation are widely used in many industrial processes. However, the traditional production methods have some drawbacks, e.g., serious pollution and low productivity. Using H_2O_2 as oxidant is the preferred process because of its mild reaction conditions and environmentally benign nature.^{10–12} Catalysts with Mo,¹³ V,¹⁴ Ti^{15, 16} as the active elements have been studied in the reaction and exhibited satisfactory performance. So far, how to realize the one-step process for direct hydroxylation of benzene to phenol is still a big challenge.^{17–19} A number of catalysts have been tested for the hydroxylation of benzene by H_2O_2 ,^{20, 21} including titanium silicalite,²² supported catalysts,^{23, 24} metallic oxides,^{25, 26} and vanadium containing catalysts.^{27–30}

In the present work, vanadium incorporated MCM-41 nanospheres with different diameters were synthesized by the impregnation (V/MCM-41) and sol–gel (V-MCM-41) methods respectively. Their catalyst activities in styrene oxidation and hydroxylation of benzene by H_2O_2 were investigated.

2. MATERIALS AND METHODS

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2.1. Synthesis of V/MCM-41 and V-MCM-41

Pure MCM-41 nanospheres with various sizes of 40, 60, 80, and 120 nm were first prepared following our previous

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method by controlling the NaOH/TEOS ratio at 0.2, 0.3, 0.4 and 0.5 respectively.³¹ The synthesis of V/MCM-41 nanospheres was carried out as follows: 0.5 g spherical MCM-41 with various particle sizes was stirred in an aqueous solution containing certain amount of ammonium metavanadate at room temperature for 45 minutes, then dried at 100 °C. The amount of NH₄VO₃ added to the solution was well controlled to ensure that the unit surface area has sufficient active sites. With the spherical diameter of the support at 40, 60, 80, and 120 nm, the corresponding samples were marked as a1, a2, a3 and a4 respectively.

The synthesis of V-MCM-41 nanospheres with different diameters was carried out as follows: CTAB (0.4 g) was dissolved in the solution containing H₂O (192 ml) and certain amount of NaOH with a stirring rate of 300 rpm at 80 °C. When CTAB was dissolved completely, certain amount of ammonium metavanadate was added. Half an hour later, TEOS (2.68 ml) was added into the solution and the reaction mixture was stirred for 2 h. Both the temperature and the stirring rate were remained constant during the reaction. The resulting products were collected by washing with water in a centrifuge machine, and then dried at room temperature. Finally, the samples were calcined at 550 °C for 6 h. When the molar ratios of NaOH/TEOS were set up to be 0.2, 0.3, 0.4 and 0.5, the corresponding products were labeled as b1, b2, b3 and b4. V-MCM-41 nanospheres with V/Si molar ratio of 0.01, 0.02, 0.04, 0.06, and 0.08 were synthesized while the radio of NaOH/TEOS was 0.4. The samples were denoted as c1, c2, c3, c4, c5, respectively.

2.2. Analysis of the Catalysts

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance powder diffractometer using Ni filtered Cu K_{α} radiation ($\lambda = 0.154178$ nm).



Figure 2. XRD patterns of the samples c1, c2, c3, c4, c5.

For SEM analysis, the samples were shadowed with gold, and then taken with a Hitachi S4800 Field Emission Scanning Electron Microscopy.

Fourier Transform Infrared (FT-IR) spectra of the samples were obtained in the range of 400–4000 cm⁻¹ with powders dispersed in KBr on Bruker VECTOR22 resolution.

The N₂ (77.4 K) adsorption–desorption measurements were performed with a TriStar 3000 automated gas adsorption analyzer (Micrometrics) in a relative pressure range P/P_0 from 0.01 to 0.99, and before the measurements, calcined samples were outgassed in vacuum at 300 °C for



Figure 1. XRD patterns of samples of V/MCM-41 (A) and V-MCM-41 (B).

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Figure 3. N_2 ads-des isotherms and pore size distribution (inner) of the sample a2.

5 h. The specific surface area and the pore size distribution were calculated from the BET and BJH data, respectively.

The vanadium contents were analyzed using Jarrell-Ash 1100 Inductively Coupling Plasma spectrometer (ICP).

2.3. Catalyst Test

The catalytic activity of V-MCM-41 and V/MCM-41 towards oxidation of styrene was carried out in a twonecked flask. Typically, catalyst (50 mg), acetonitrile

(10 ml), styrene (1.1 ml) and H_2O_2 (2 ml) were mixed. After reaction for 12 h at 50 °C, the catalyst was separated by centrifugation.

The catalytic activity assessment of the V-MCM-41 and V/MCM-41 on direct hydroxylation of benzene was performed as follows: 0.1 g catalyst, 2 ml benzene and 6.89 ml H_2O_2 were added to 15 ml acetonitrile in a 50 ml flask. The reaction mixture was stirred for 10 h with temperature maintained at 40 °C, and then the resulting solution was centrifuged.

The products of the two reactions were analyzed by a SP-6890 gas chromatograph (Lunan Ruihong Chemical Instrument Co. Ltd., China) with 0.32 mm \times 30 m SE-54 capillary column. The conversion and the selectivity of products were calculated by external standard method.

3. RESULTS AND DISCUSSION

3.1. Characteristics of V/MCM-41 and V-MCM-41

The small-angle XRD patterns of V/MCM-41 and V-MCM-41 samples are shown in Figure 1. It is obvious that all the samples exhibit (100) reflection peak at $2\theta \approx 2.4^{\circ}$, and the three other small peaks are indexed to the (110), (200) and (210) reflections, respectively. These XRD results confirm that the samples possess highly ordered two-dimensional hexagonal structure. The intensities of the diffraction peaks become stronger with increase of the amount of NaOH, indicating that the structures cientific Publishers



Figure 4. The FE-SEM images of the V/MCM-41 samples a1-a4.



Figure 5. The SEM images of the V-MCM-41 samples b1-b4.

of the mesoporous materials become more regular along with the increase of the amount of NaOH. Moreover, there is scarcely change of the peak positions, indicating that the amount of NaOH has few effect on the cell parameters.

Figure 2 shows the small-angle XRD patterns of V-MCM-41 samples with different vanadium contents. It can be seen that all the samples possess typical twodimensional hexagonal mesoporous structures. The diffraction peaks shift to small angle with increase of vanadium content, suggesting the incorporation of vanadium species into the silica framework.⁷

Figure 3 shows the N₂ adsorption–desorption isotherms and pore diameter distribution of sample a2, and similar results are observed for the other samples. This sample exhibits a Brunauer type IV isotherm according to the IUPAC classification,³² with hysteresis at the relative pressure range of $0.2 \le p/p_0 \le 0.4$, which is due to the capillary condensation of nitrogen in the pores. The corresponding pore size distribution obtained by the BJH method from the desorption data indicates a uniform and sharp pattern. Figure 4 shows the FE-SEM images of V/MCM-41 with different NaOH/TEOS molar ratios, and Figure 5 shows the SEM images of V-MCM-41 synthesized by sol-gel supermolecular method with different NaOH/TEOS molar ratios. All the samples present regular spherical morphologies and the diameters range from 40 nm to 160 nm with the increase of NaOH amount. The introduction of vanadium has little effect on the morphology of MCM-41. V-MCM-41 nanospheres with fixed diameters can be synthesized by changing the NaOH/TEOS molar ratios.

The mole ratio of V/Si has a great influence on the morphology and particle size of the V-MCM-41 nanospheres. As the molar ratio of V/Si is 0.01, the sample presents regular spherical morphology and a diameter of 120 nm shown in Figure 5(b3). With the increase of vanadium content, the nanospheres become irregular which can be seen from the FE-SEM images shown in Figure 6. Meanwhile, the average diameters increase and change to about 400 nm for the sample with 0.08 molar ratio of V/Si. It is believed that the variation in the ion strength in the synthesis system due to the change of ammonium metavanadate amount causes the change in morphology.

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Figure 6. The FE-SEM images of the V-MCM-41 samples c2–c5. Delivered by Ingenta to: West Virginia University/ Health Sci Ctr Llb IP: 79.133.106.70 On: Tue, 21 Jun 2016 08:21:58

The FT-IR spectra of the samples a2 and b2 are shown in Figure 7. The broad bands at ca. 1090 cm⁻¹ and ca. 810 cm⁻¹ are assigned to the asymmetric and symmetric stretching vibrations of Si—O respectively,³³ and the band at 460 cm⁻¹ to the bending vibration of surface Si—O groups.³⁴ A weak peak at 960 cm⁻¹ attributed to Si—O—V band position³⁵ is observable for the two samples, proving the incorporation of vanadium atoms in the framework of V-MCM-41. In addition, the spectra of all the samples don't exhibit the bands at 2921 cm⁻¹ and 2851 cm⁻¹, which are attributed to the vibrations of C—H bands, indicating the completely removal of the template agent from the as-synthesized samples.

3.2. Catalytic Activities of the V-MCM-41 and V/MCM-41 Samples 3.2.1. Catalytic Activities of V/MCM-41 Nanospheres

The catalytic activities of spherical V/MCM-41 with different diameters towards styrene oxidation are presented in Figure 8(A). All the samples exhibit high activity, which increases with the decrease of MCM-41 diameter. For example, the styrene conversion and benzaldehyde selectivity are 72.8% and 91.6% respectively when the spherical MCM-41 with 160 nm diameter is used as the support, and a conversion of 85.5% and selectivity of 93.5% are obtained with the 40 nm diameter of support. The same phenomenon is also observed in the hydroxylation of benzene as shown in Figure 8(B).

Considering the fact that the total vanadium content and number of active sites on unit surface area for each reaction are controlled identical, the differences of catalytic performance must be caused by the diameter of support. Small particle size is more beneficial to the diffusion of the reagent molecules. As a result, the smaller the particle



Figure 7. FT-IR spectra of the samples a2 and b2.

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6.2

c5



Figure 8. The catalytic properties of V/MCM-41 in the styrene oxidation reaction (A) and hydroxylation of benzene (B).

size is, the faster the reagent and product spreads, and the better the catalytic performance becomes.

3.2.2. Catalytic Activities of V-MCM-41 Nanospheres with Different Diameters

The catalytic activities of V-MCM-41 nanospheres with different diameters towards the oxidation of styrene are presented in Table I. These catalysts are efficient in the reaction and the activities increase with the decrease of the diameter. Particularly for the sample with the spherical

Table I. The catalytic properties of samples in styrene oxidation.

Sample	Average diameters (nm)	V/Si (%)	Styrene conversion (%)	Benzaldehyde selectivity (%)
b1	40	1.03	94.1	96.5
b2	80	0.98	90.5	95.8
b3	120	1.07	87.6	94.3
b4	160	1.08	85.3	93.1
V-MCM-41-ir	/	1.06	75	90
V_2O_5	/	/	20	88.5

Notes: Reaction conditions: catalyst amount 0.1 g, styrene 1.1 mL, CH₃CN 10 mL, 30% H₂O₂ 2 mL, temperature 50 °C and duration 6 h.

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Table II. The catalytic properties of samples in the hydroxylation of benzene.					
Sample	V/Si (%)	Benzene conversion (%)	Phenol selectivity (%)		
c1 (b3)	1.07	2.8	100		
c2	1.6	4.4	100		
c3	3.2	7.7	100		
c4	5.0	9.8	100		

Notes: Reaction conditions: catalyst amount 0.1 g, benzene 2 ml, CH₃CN 15 ml, 30% H₂O₂ 6.89 ml, temperature 40 °C and duration 10 h.

100

10.1

diameter of about 40 nm, it gives a styrene conversion of 94.1% and a selectivity of 96.5% for benzaldehyde. Meanwhile, all the samples display higher activity than V_2O_5 and V-MCM-41 with irregular morphology. It is also found that the catalytic activities of V-MCM-41 are better than that of V/MCM-41 with the same vanadium content and similar size. These results demonstrate that the vanadium species in the framework are the main active sites. Similar conclusion can be obtained in the hydroxylation of benzene.

3.2.3. Catalytic Activities of V-MCM-41 Nanospheres with Different Vanadium Contents Towards Hydroxylation of Benzene

In order to improve the conversion of benzene in the reaction at low temperatures, V-MCM-41 nanospheres with higher vanadium content were synthesized. Table II shows the catalytic activities of the V-MCM-41 samples with different vanadium contents. The conversion of benzene increases with vanadium content while the phenol selectivity remains at 100%, although the morphology of the catalysts tend to be irregular and the diameter to be larger. However, as the molar ratio of V/Si increases from 5.0 to 6.2, the conversion of benzene doesn't change any more, possibly due to overloaded vanadium species on the surface, which blocked the channels.

4. CONCLUSION

V/MCM-41 and V-MCM-41 nanospheres have been successfully synthesized by the impregnation and sol–gel supermolecular method respectively. These nanospheres have regular shape and tunable sizes. All the samples display superior catalytic activities in the oxidation of styrene and hydroxylation of benzene to V_2O_5 and MCM-41, and the catalyst particle has great influence on the catalytic activity. Better catalytic performance is observed on the samples with smaller particle sizes. Increase of vanadium content also results in higher conversion of benzene, but an overloading of vanadium species has negative influence on the morphology and catalytic activity of the samples.

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