

高钒掺杂量 MCM-41 合成及表征

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摘要: 采用溶胶-凝胶法, 在氨性条件下合成出高钒掺杂量介孔 MCM-41。以 XRD, 氮气吸附/脱附, 透射电镜, ICP 和拉曼光谱等技术对材料的结构进行了表征。结果表明当钒硅物质的量的比达到 0.14 时材料仍保持规整介孔结构(尽管当钒/硅物质的量的比超过 0.11 时开始有 V_2O_5 晶体出现)。所合成材料室温下在苯的过氧化氢直接羟基化反应中表现出良好的催化性能。

关键词: V-MCM-41; 高含量; 合成; 多相催化; 羟基化; 氨性条件

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Synthesis and Characterization of V-MCM41 with High Vanadium Content

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Abstract: V-MCM-41s with high content of vanadium have been synthesized using sol-gel method under ammonium condition and characterized by using XRD, N_2 adsorption isotherms, HRTEM, ICP and Laser Raman Spectroscopy (LRS) techniques. Regular mesopore structure could be maintained up to the V/Si molar ratio of 0.14, although certain amount of V_2O_5 crystals becomes to disperse on the wall of MCM-41 when n_V/n_{Si} exceeds 0.11. These materials were effective catalysts in the hydroxylation of benzene with H_2O_2 under room temperature.

Key words: V-MCM-41; high content; synthesis; heterogeneous catalysis; hydroxylation; ammonia condition

Much effort has been paid to the introduction of guests into mesoporous silicates^[1,2] since the first report by Mobil Research and Development Corporation in 1992^[3,4]. The incorporation of heteroatoms into pure mesoporous silicates can increase the amounts of defects, the surface acidity and basicity, the redox property, and thus improve their catalytic activity^[5,6].

Vanadium is the essential ingredient of many catalysts. Mesoporous molecular sieves containing vanadium such as V-MCM41 and V-SBA-15 are effective for the selective oxidations, especially for the direct hydroxylation of benzene by H_2O_2 ^[7-9], a green and econom-

ic route for the manufacturing of phenol. The contents of vanadium in the catalysts have an important effect on their activity. A higher loading of vanadium is helpful for the catalytic reactions^[10-12].

However, to the best of our knowledge, most of the V-MCM-41s reported in the literatures are all synthesized under strong alkali aqueous solution, such as KOH and NaOH solution, conditions^[7,8]. The V/Si molar ratios are smaller than 0.04, which limits the catalytic activity of the catalyst. Because it is hard to control simultaneously hydrolyzation of guests and silicon species, it is difficult to incorporate high content of het-

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eroatoms into mesoporous silicate^[1,2,5].

Here we report the synthesis of V-MCM41s with high content of vanadium under ammonia condition. The prepared materials exhibit higher catalytic activities in the hydroxylation of benzene than those with lower vanadium content, especially at room temperature.

1 Experimental

1.1 Synthesis

A typical synthesis of V-MCM-41 was as follows. 0.01 mol cetyltrimethyl ammonium bromide (CTAB), 0.04 mol $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was first dissolved in 80 mL hot water, then 40 mL ammonium solution composed of suitable amount of NH_4VO_3 (0~0.01 mol) was added. After the pH value was adjusted to 9.5~10 with $1 \text{ mol} \cdot \text{L}^{-1} \text{H}_2\text{SO}_4$, the mixture was transferred into Teflon lined stainless steel autoclave and kept at 120°C for 72 h. The products, with molar ratio of $x\text{V}:100\text{Si}$ ($x=2\sim20$), were washed with distilled water for three times, and dried at room temperature. The as-synthesized samples were calcined at 550°C for 5 h in dry air stream with a heating rate of $1 \text{ K} \cdot \text{min}^{-1}$, and cooled down slowly to obtain V-MCM-41s, designated as $x\text{V}$. The same procedure, except KOH aqueous solution instead of ammonium solution, was used to synthesize $x\text{V-K}$.

1.2 Characterization

X-ray diffraction (XRD) patterns were recorded by a Shimadzu XD-3A diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda=0.154168 \text{ nm}$) and Ni filter and operated at 40 kV and 40 mA. The diffractograms were recorded in the 2θ range of $1.5^\circ\sim8^\circ$ at a step of 0.02° , and a scanning speed of $2^\circ \cdot \text{min}^{-1}$ was used.

Nitrogen adsorption-desorption isotherms were measured at the temperature of liquid nitrogen using a Micromeritics ASAP2020 analyzer. Surface areas, pore size distributions and pore volumes of the materials were determined by conventional Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) model from adsorption data.

The vanadium contents were analyzed using a Jarrell-Ash 1100 Inductively Coupling Plasma spectrometer.

UHRTEM images were taken on a JEM-2010

UHRTEM (ultrahighresolution transmission electron microscope) instrument at an acceleration voltage of 200 kV.

Laser Raman spectra(LRS) were recorded using a Renishaw In-vira microscopy Raman spectrometer, and an Ar^+ laser with an excitation wavelength of 514.5 nm in a macromode.

1.3 Catalytic test

Benzene hydroxylation was carried out in a two-necked flask(250 mL) equipped with a magnetic stirrer and a reflux condenser. Reaction conditions were as follows: 1.8 mL benzene, 6 mL H_2O_2 (30%), 100 mg catalyst, 30°C reaction temperature, 8 h reaction time and 20 mL acetonitrile as solvent. The products distributions were analyzed by FID detector in a SP-6800A chromatography with a quartz SE-54 capillary column ($0.32 \text{ mm} \times 1 \mu\text{m} \times 30 \text{ m}$). The analysis conditions were as follows: injection with a micro-syringe of $0.5 \mu\text{L}$, a split ratio of 1/200, column oven temperature 140°C , detection temperature 260°C , and vaporization temperature 260°C . Nitrogen was used as carrier gas and the flow rate was $1.5 \text{ mL} \cdot \text{min}^{-1}$. The efficiency of H_2O_2 was examined by iodimetry.

2 Results and discussion

2.1 XRD

The XRD patterns of some samples are shown in Fig.1. For $x\text{V}$ samples, an intense (100) peak at about $2\theta=2^\circ$ together with three weak (110), (200) and (210) peaks in the low angle range, characteristic of MCM41-

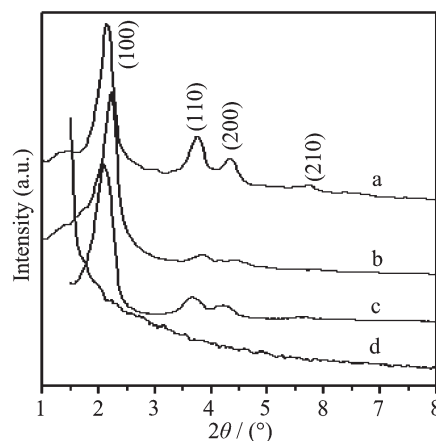


Fig.1 XRD patterns of (a) 10V, (b) 20V, (c) 5V-K, (d) 10V-K

type hexagonal array^[3,4], are clearly observed. Although they become wider and weaker with the increase of vanadium content, these peaks are still visible even for the sample with V/Si molar ratio of 0.20 in the gel, which demonstrates the regular mesoporous structure of V-MCM41 with high vanadium content.

However, for samples prepared under KOH condition, these peaks only exists for the sample with V/Si molar ratio smaller than 0.05, and they disappear as V/Si molar ratio increases to 0.10, suggesting that the mesoporous structure is not formed. This result indicates that it is helpful for the synthesis of V-MCM-41 with high content of vanadium that ammonia aqueous solution of NH_4VO_3 is used as vanadium source.

There are many different kinds of V(V) species. In alkali aqueous solution condition, V(V) presents in form of H_2VO_4^- , HVO_4^{2-} , $\text{V}_2\text{O}_7^{4-}$ and VO_4^{3-} etc.^[13-15] and they transform with the variation of pH values and the concentration of V(V) species. It is supposed that the suitable hydrolyzation rate of sodium silicate with HVO_4^{2-} species aroused from the high vanadium content in MCM-41 in weak ammonium condition whereas VO_4^{3-} mainly existed in KOH aqueous solution cannot hydrolyze with Na_2SiO_3 simultaneously.

2.2 N_2 adsorption/desorption isotherms

The isotherms and the corresponding pore size distributions of some samples are shown in Fig.2. The isotherms are of type IV in the IUPAC classification, typical of mesoporous solid^[16]. All the samples exhibit strong adsorption at a relative pressure range of $0.2 \leq P/P_0 \leq 0.4$. This is a characteristic of capillary condensation of N_2 into uniform mesopores. In general, the isotherms indicate that all the samples possessed good mesoporous structural ordering and a narrow pore size distribution. The narrow pore size distribution seen from

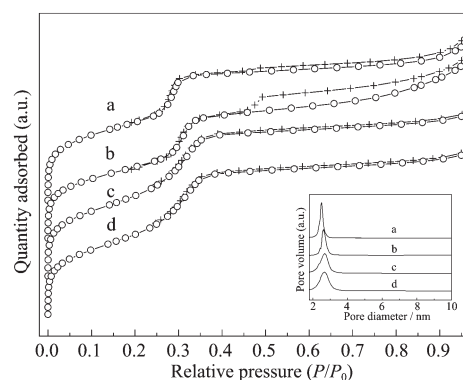


Fig.2 Nitrogen adsorption/desorption isotherms and pore size distributions (inset) of (a)2V, (b)10V, (c)20V, (d)25V

Fig.2 reveals a uniform mesoporosity. The broader pore distributions indicate that the ordering of sample decreases as the content of vanadium increases.

2.3 HRTEM

Fig.3 depicts the HRTEM images of 10V sample. The ordered hexagonal pore arrangement of the sample is clearly visible, and the pore size is 2.5~2.7 nm, in good agreement with the average pore size calculated by BJH model from N_2 adsorption isotherm (Table 1). Also,

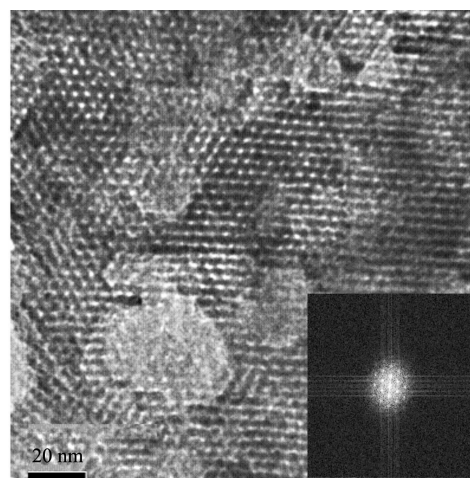


Fig.3 HRTEM image and the SAED pattern (inset) of 10V sample

Table 1 Structure parameters and catalytic performances of some samples

Sample	n_V / n_{Si}	Surface area / ($\text{m}^2 \cdot \text{g}^{-1}$)	Average pore diameter / nm	Pore volume / ($\text{m}^3 \cdot \text{g}^{-1}$)	Conversion of benzene / %	Selectivity of phenol / %	Efficiency of H_2O_2 / %
2 V	0.014	835	2.38	0.756	1.2	100	62.1
5 V	0.037	883	2.56	0.803	6.2	100	47.4
10 V	0.064	1033	2.80	0.958	11.5	100	32.6
15 V	0.110	1070	2.98	0.915	12.6	100	14.4
20 V	0.140	1055	2.80	0.843	15.1	100	13.9

the selective area electron diffraction (SAED) patterns demonstrate the typical hexagonal MCM41 structure.

2.4 Laser Raman

No characteristic peaks of V_2O_5 are found in wide angle XRD patterns. LRS spectra of some samples are shown in Fig.4. For 10V and 15V samples, the bands at about 994, 701, 525, 480, 404 and 282 cm^{-1} , characteristic of crystalline V_2O_5 ^[17-19], are not found. This indicates that there are no separated V_2O_5 phases existing in the samples. In contrast, a peak at 920 cm^{-1} attributed to the V-O-Si bond (asymmetric stretching vibration)^[17,20] is observed. This suggests that the vanadium species are in the framework of MCM-41. As V/Si molar ratio increases to 0.20, crystalline V_2O_5 is emerged.

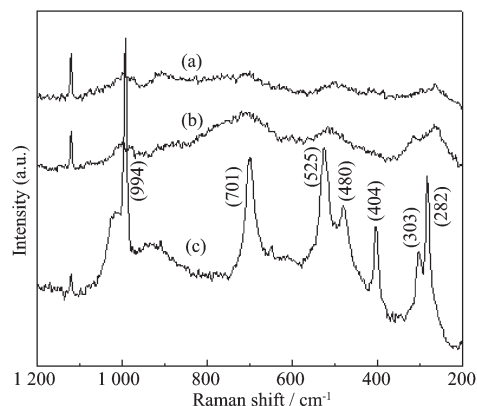


Fig.4 Laser Raman spectra of (a) 10V, (b) 15V, (c) 20V

2.5 Catalytic performance

Catalytic activities of the materials with different vanadium content in benzene hydroxylation under room temperature are given in Table 1. It could be found that V-MCM-41 is an efficient catalyst for the hydroxylation of benzene under room temperature. The selectivity of phenol is all 100%. The conversion of benzene increases with the vanadium content when the V/Si molar ratio is smaller than 0.11 and further increase in vanadium content leads to decrease in catalytic activity, suggesting that V(V) species in the framework of MCM41 are more effective as the active sites than other type of vanadium species. Detail study for the catalytic activity is in progress.

3 Conclusions

V-MCM-41 with high content of vanadium was

synthesized through sol-gel method under ammonium aqueous solution conditions. The vanadium atom is mainly in the framework of MCM-41 when V/Si molar ratio is smaller than 0.11 V_2O_5 will appear when the ratio is higher than 0.11. Catalytic test indicates that the prepared samples are efficient catalysts for the hydroxylation of benzene under room temperature.

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