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Synthesis, characterization and sulfide oxidation activity of vanadyl Schiff base complexes anchored on MCM-41

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Abstract Vanadyl Schiff base complexes covalently attached on the surface of MCM-41 have been synthesized by anchoring Schiff base and subsequent reaction with $VO(acac)_2$. XRD, nitrogen adsorption and desorption, UV-visible spectroscopy and FT-IR show that vanadyl Schiff base complexes were successfully anchored on the surface of MCM-41 and the mesopore ordering decreased after the anchoring. The so-prepared heterogeneous catalysts have showed high activity for sulfide oxidation.

Keywords Heterogeneous catalysis · Vanadyl Schiff base complexes · Mesoporous · Sulfide oxidation

1 Introduction

As more and more attention has been paid to the environment, the development of environmentally friendly solid catalysts for the process of petrochemical and fine chemical is becoming an area of growing interest [1–4]. In general, solid catalyst is prepared via supporting the soluble active species onto large surface area inorganic carriers [5–8]. Despite the interesting catalytic properties of these catalysts, the problem of leaching of the active species from the solid surface during the catalytic process cannot be excluded. Therefore, it is necessary to design new solid catalysts to avoid or minimize the leaching. In this sense, the recently discovered family of mesoporous MCM-41 materials provide the possibility since they have large surface area and wide range of pore dimensions that ensure easy accessibility of the reactants to active sites, more important, they provide a unique inorganic support that can anchor the active sites on the inorganic oxides [9]. Indeed, much research has been done on the functionalized mesoporous MCM-41 materials [10, 11].

Due to the dramatic environmental impact of sulfur oxides contained in engine exhaust emissions, sulfur content specifications in fuel are becoming more and more stringent worldwide [12, 13]. In America, the sulfur content will be restricted to 15 ppm by 2006. Sulfur-free gasoline will be forced to put into use all over the European Union by 2011. To meet this requirement, beside the deep hydrodesulfurization, other alternative technologies such as oxidation, adsorption, and extraction have been developed in recent years. Among these methods, oxidation desulfurization has particularly received much attention [14–16]. In oxidation desulfurization processes, organic sulfur compounds can be oxidized selectively to their corresponding sulfoxides and sulfones, which can be removed by extraction and adsorption. Recently the oxidation of sulfides over homogeneous vanadium–salen complexes using hydrogen peroxide in mild conditions has been reported [17]. Although this protocol has high sulfide oxidation activity, the homogeneous characteristic makes it very hard to apply to the oxidation of sulfur compounds in light oil. Here we synthesized a heterogeneous catalyst that vanadyl Schiff bases had been covalently attached on the surface of MCM-41 and used as catalysts for sulfide oxidation.

2 Experimental

2.1 Synthesis of MCM-41 [18]

Pure silica MCM-41 was prepared by adding 14.73 g of sodium silicate to an aqueous solution containing 21.85 g

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of CTAB, 3.48 g of acetone and 65.52 g of distilled water at 30 °C, then 1.2 M H_2SO_4 was slowly added into the solution to adjust the pH value to 9.5–10. The final molar composition was 1.0CTAB:1.0acetone:2.0 sodium silicate:0.67H_2SO_4:133H_2O. The resulting mixture was transferred into a polypropylene bottle and reacted at 100 °C under static condition for 5 days, the solid product was recovered after filtration, exhaustive washing with distilled water and ng at 60 °C for 12 h. The surfactant was removed by calcined at 560 °C for 6 h.

2.2 Synthesis of aminopropyl-functionalized MCM-41(1a) [19]

To a suspension of pure MCM-41 (1 g) in degassed toluene, 3-aminopropyltrimethoxysilane (2 mmol) was added, the solution was heated under reflux for 12 h. Then the material was filtered, washed several times with toluene and dried at 80 °C overnight.

2.3 Synthesis of Schiff base functionalized MCM-41(2a) and reduced Schiff base functionalized MCM-41(3a)

To a suspension of aminopropyl-functionalized MCM-41(**1a**) (1 g) in ethanol, salicyladehyde (2 mmol) was added, the mixture was heated to reflux for 20 h, then the solution was filtered, washed with ethanol and dried at 80 °C for 12 h. The reduced Schiff base functionalized MCM-41(**3a**) was prepared by reduction of **2a** with sodium borohydride to give an amine. To a suspension of 2a (1 g) in methanol (50 mL), sodium borohydride (2 mmol) was added slowly, the mixture was stirred at room temperature for 2 h, then the resulting suspension was filtered, washed with methanol and dried at 80 °C for 12 h.

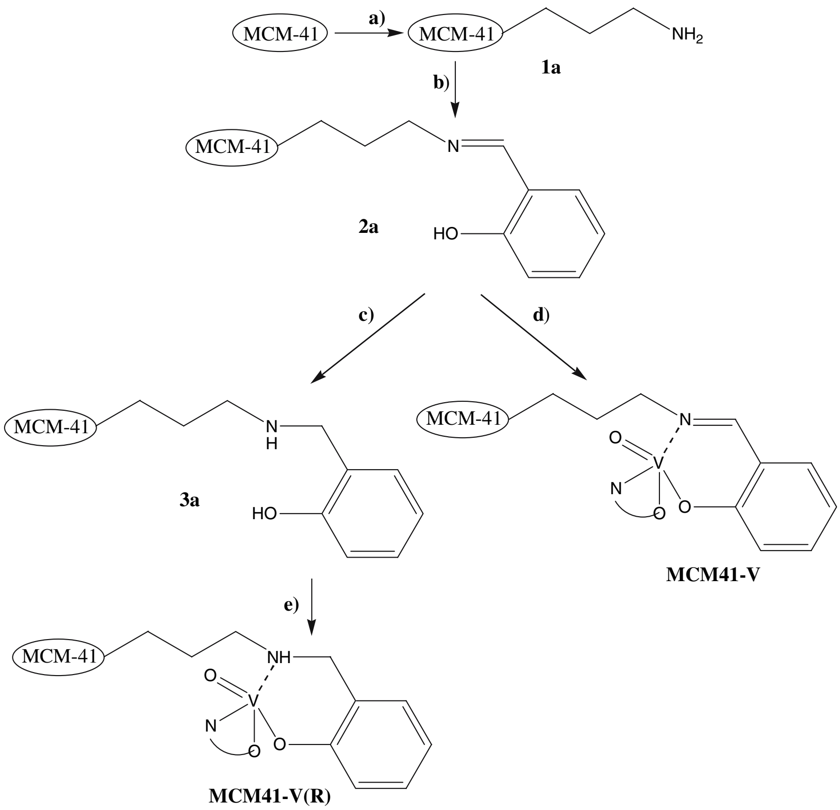
2.4 Synthesis of vanadyl Schiff base functionalized MCM-41(MCM41-V) and vanadyl reduced Schiff base functionalized MCM-41(MCM41-V(R))

To a suspension of **2a** (1 g) in CH_2Cl_2 (30 mL) under N_2, $VO(acac)_2$ (1 mmol) was added. The solution was stirred for 2 days at room temperature, then the solution was filtered, washed with CH_2Cl_2 and dried at 80 °C for 12 h. Vanadyl reduced Schiff base functionalized MCM-41(**MCM41-V(R)**) was prepared under same procedure when **3a** was used as ligand.

The synthetic procedure was listed in Scheme 1.

2.5 Characterization

X-ray diffraction patterns were obtained on a Bruker D8 ADVANCE diffractometer (Cu-Kα). UV-visible spectra were collected on a Shimadzu UV-2550 spectrophotometer



Scheme 1 Synthesis of vanadyl Schiff base functionalized MCM-41. (**a**) 3-aminopropyltrimethoxysilane, toluene, reflux, 12 h; (**b**) salicyladehyde, ethanol, reflux, 20 h; (**c**) sodium borohydride, methanol, rt, 2 h; (**d**) $VO(acac)_2$, CH_2Cl_2, rt, 48 h; (**e**) $VO(acac)_2$, CH_2Cl_2, rt, 48 h

using $BaSO_4$ as reference to characterize the coordination states of V species. IR spectra were recorded on Nicolet Nexus 670. N_2 adsorption and desorption isotherms were measured using a Micromeritics ASAP 2000 system. The sample was pretreated at 250 °C overnight in the vacuum line. The data were analyzed by the BJH (Barrett–Joyner–Halenda) method using the Halsey equation for multilayer thickness. The pore size distribution was calculated from the desorption branch of the isotherm. The vanadium content was analyzed by inductively coupled plasma (ICP) on a Therm IRIS Intrepid II XSP atomic emission spectrometer.

2.6 Oxidation of sulfides

In a typical reaction, MCM41-V(R) (100 mg) was added to a solution of sulfide (1 mmol) and acetonitrile (8 mL), then 30% H_2O_2 (4 mmol) was added. The solution was stirred at 30 °C for 6 h. The reaction mixture was analyzed by gas chromatography (Shimadzu GC-14B) equipped with a DB-1 capillary column using *n*-dodecane as an internal standard.

3 Results and discussion

3.1 Characterization of functionalized MCM-41

The supported vanadyl Schiff base complexes MCM41-V, MCM41-V(R) and their precursors (**1a**, **2a** and **3a**) were fully characterized by XRD, BET, UV, and FT-IR.

3.1.1 XRD

X-ray diffraction patterns of MCM-41, aminopropyl-functionalized MCM-41(**1a**), Schiff base functionalized MCM-41(**2a**), reduced Schiff base functionalized MCM-41(**3a**), vanadyl Schiff base functionalized MCM-41(**MCM41-V**) and vanadyl reduced Schiff base functionalized MCM-41(**MCM41-V(R)**) are shown in Fig. 1. All the samples showed one intense (100) peak, the patterns were similar to that of pure silica MCM-41, indicating that the functionalized MCM-41 materials contain ordered hexagonal arrays of one-dimensional channel structure. However, the peak intensity decreased and the higher order (110) and (200) diffractions became less resolved and disappeared at last, showing that the mesopore ordering decreased as more substance were anchored on the surface of MCM-41. The slight shift of the diffraction peaks of the functionalized materials toward larger 2θ angles indicated a slight shrink of the pore diameter.

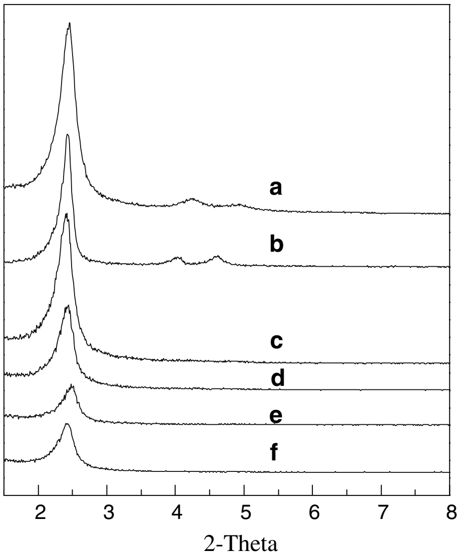


Fig. 1 XRD patterns of (**a**) MCM-41, (**b**) 1a, (**c**) 2a, (**d**) 3a, (**e**) MCM-V, (**f**) MCM-V(R)

3.1.2 N_2 adsorption and desorption

The N_2 adsorption and desorption isotherms of MCM-41, aminopropyl-functionalized MCM-41(**1a**), Schiff base functionalized MCM-41(**2a**), reduced Schiff base functionalized MCM-41(**3a**), vanadyl Schiff base functionalized MCM-41(**MCM41-V**) and vanadyl reduced Schiff base functionalized MCM-41(**MCM41-V(R)**) are shown in Fig. 2. The N_2 adsorption–desorption isotherm of MCM-41 shows a well defined step in the adsorption and desorption curve between partial pressures 0.2–0.4, but the adsorption and desorption curve become more and more placid and the steep increase in adsorption shift to lower pressure as more substance are anchored on the surface of MCM-41, indicating that the functionalized MCM-41 have narrower pore diameter and lower absorption volume which are identical

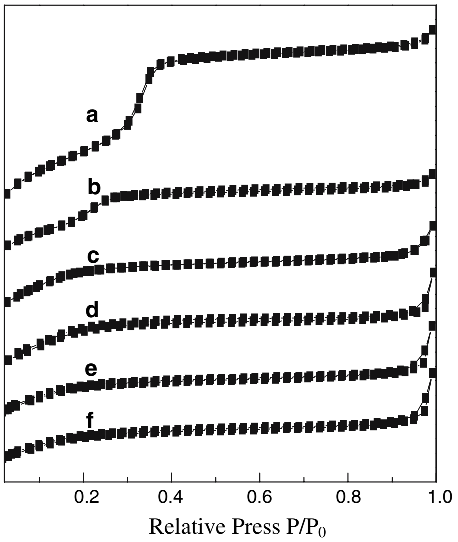


Fig. 2 Nitrogen adsorption–desorption isotherms (**a**) MCM-41, (**b**) 1a, (**c**) 2a, (**d**) 3a, (**e**) MCM-V, (**f**) MCM-V(R)

Table 1 Textural properties of the functionalized MCM-41

Sample	Pore diam (Å)	S_{BET} (m^2/g)	Pore vol (cm^3/g)
MCM-41	23.8	1299	1.07
1a	21.1	964	0.69
2a	16	811	0.6
3a	17.4	811	0.66
MCM41-V	15	708	0.64
MCM41-V(R)	16.2	679	0.62

with the result obtained by XRD. The BJH pore diameter, BET surface, and pore volume of functionalized MCM-41 decreased with the increasing substance anchored on the surface of MCM-41, as shown in Table 1. These results are attributed to the occupation of large organic molecules on the inner surface of the pores. Although the ordering of MCM41-V and MCM41-V(R) decreased, they still remain the high surface area.

3.1.3 Elemental analysis

The vanadium content of the **MCM41-V** and **MCM41-V(R)** was analyzed by treating the catalysts with hydrofluoric/nitric acid mixture and determining the vanadium in the resulting liquor. The vanadium content is shown in Table 2. The vanadium content is 0.52 mmol/g (**MCM41-V(R)**) and 0.62 mmol/g (**MCM41-V**), respectively. Elemental analysis has also been carried out to determine the amount of N incorporated. The results show that the nitrogen content of **MCM-V(R)** and **MCM-V** are 1.04 and 1.16 mmol/g, respectively. From these data it can be concluded that ligand **2a** and **3a** reacted with the $VO(acac)_2$ by the molar ratio of 2.

3.1.4 UV-vis/IR

UV-vis spectroscopy and IR spectrum for Schiff base functionalized MCM-41(**2a**), reduced Schiff base functionalized MCM-41(**3a**) and **MCM41-V** is shown in Figs. 3 and 4. The assignments were refereed to the corresponding complexes which reported in Refs. [20, 21]. In the UV-vis spectroscopy of **2a** (Fig. 3) showed a band centered at ca. 313 nm due to an *n*–л* transition associated with the azomethine group and another band around 251 nm which may arise from a transition involving mainly the л molecular orbital localized on the C=N group and/or the aromatic ring. In the spectra of the reduced Schiff base **3a**, the *n*–л* transition is absent as expected and the 251 nm transition is red-shifted to 278 nm which is overlapped with another absorption band of aromatic ring (Fig. 3). The absorption band of C=N in **2a** (251 nm) gave a remarkable red-shifted (262 nm) when the $VO(acac)_2$ was cooperated (**MCM41-V**).

Table 2 Analytical data of the vanadium-containing MCM-41

Catalyst	V content (mmol/g)	N content (mmol/g)	N/V
MCM41-V(R)	0.52	1.04	2.0
MCM41-V	0.62	1.16	1.9

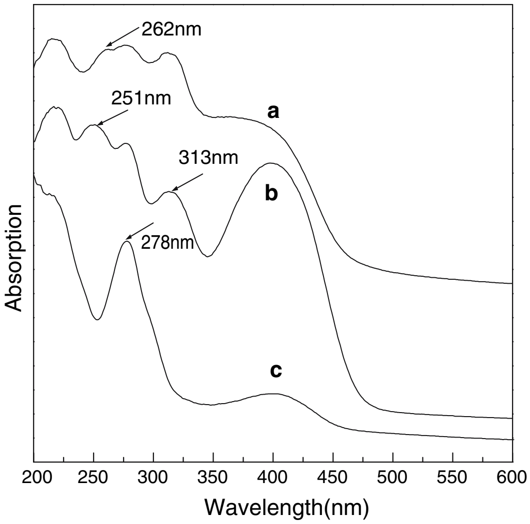


Fig. 3 UV-vis absorption spectra of compound (**a**) MCM41-V; (**b**) 2a; (**c**) 3a

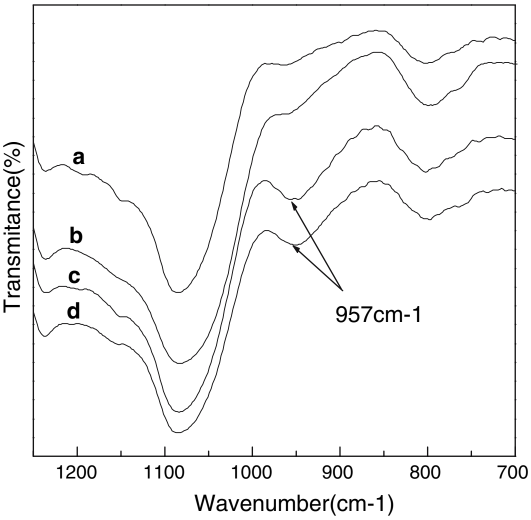


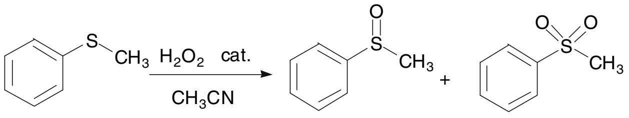
Fig. 4 IR spectra of compound (**a**) 2a; (**b**) 3a; (**c**) MCM41-V; (**d**) MCM41-V(R)

FT-IR spectrum of Schiff base functionalized MCM-41(**2a**), reduced Schiff base functionalized MCM-41(**3a**), **MCM41-V** and **MCM41-V(R)** are shown in Fig. 4. The characteristics $\nu(V=O)$ of oxovanadium(IV) complexes appears as a band at 957 cm^{-1} after **2a** and **3a** were treated with the $VO(acac)_2$, which are in agreement with the literature [21]. Although the imine stretching vibration in **2a** was overlapped with the absorbance of the bending vibration of adsorbed H_2O around 1,630 cm^{-1}, another two peaks (1,611, 1,535 cm^{-1}) appeared after $VO(acac)_2$ was incorporated. In the IR spectrum of the MCM41-V, the peak at 1,611 cm^{-1} was assigned to the imine stretching vibration that caused by the red-shift of C=N in 2a, another peak at 1,535 cm^{-1} was assigned to the metal-Schiff base vibration, both of which were characteristic vibrations common for metal-Schiff base complexes.

3.2 Oxidation of sulfides

3.2.1 Oxidation of methyl phenyl sulfide in different reaction condition

The oxidation of methyl phenyl sulfide was carried out with different temperature, amount of H_2O_2 and catalysts. The results were listed in Table 3. As vanadyl reduced Schiff base functionalized MCM-41(MCM41-V(R)) was used as catalyst, the conversion of sulfides depended on the reaction temperature and the amount of H_2O_2. In all cases, sulfide was oxidized to sulfoxide and sulfones. As the reaction temperature raised from 20 to 30 °C, the conversion of sulfides changed from 67% to 85%. However, the conversion kept constant when temperature increased further (entry 2–5). Although the conversion increased with the increasing amount of H_2O_2 from 2 to 4 equivalent, it did not have significant change when the amount of H_2O_2 exceeded 4 equivalent (entry 1, 3, 6) at the same reaction condition. The selectivity of sulfoxide decreased with the increase of the amount of H_2O_2 which is due to the further oxidation of sulfoxide



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Vanadyl Schiff base functionalized MCM-41(**MCM41-V**) has lower activity for methyl phenyl sulfide oxidation. The conversion of methyl phenyl sulfide was only 29% at 30 °C and 46% at 50 °C (entry 7, 8). This may be due to the electronic difference of nitrogen atoms in different ligands, which resulted from the coordination of nitrogen atoms to the central metal [17].

3.2.2 Oxidation of other sulfides over MCM41-V(R)

To examine the reactivity of catalyst further, other sulfides also have been investigated (Table 4). Diethyl sulfide gave the corresponding sulfoxide and sulfone in 90% conversion at 30 °C (entry 1). Diphenyl sulfide gave the conversion of 46% at 50 °C (entry 2).The different reactivity was caused by the electronic effect and stereo effect of sulfides.

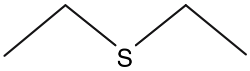
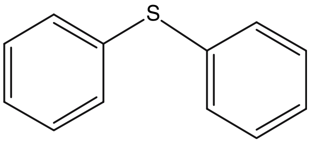
Table 3 Oxidation of methyl phenyl sulfide catalyzed by MCM41-V and MCM41-V(R)

Entry	Cat.	H_2O_2 (equiv)	T (°C)	Conver (%)	Selec. sulfoxide (%)
1	MCM41-V(R)	2	30	52	90
2		4	20	67	81
3		4	30	85	81
4		4	40	84	80
5		4	50	84	80
6		6	30	86 (93[a])	71 (65[a])
7	MCM41-V	4	30	29	81
8		4	50	46	86

Reaction condition: Methyl phenyl sulfide (1 mmol), acetonitrile (8 mL), catalyst: 100 mg, 6 h

[a] Data of 8 h

Table 4 Oxidation of alkyl sulfide using 30% H_2O_2 catalyzed by MCM41-V(R)

Entry	Sulfide	T (°C)	Conver (%)	Sulfoxide (%)
1		30	90	80
2		50	46	86

Reaction condition: Sulfide 1 mmol, 30% H_2O_2 4 mmol, acetonitrile 8 mL, MCM41-V(R): 100 mg

4 Conclusion

In conclusion, we have shown that the novel vanadyl Schiff base functionalized MCM-41(**MCM41-V**) and vanadyl reduced Schiff base functionalized MCM-41(**MCM41-V(R)**) can be prepared by graft vanadyl Schiff bases on the surface of MCM-41. The vanadyl reduced Schiff base functionalized MCM-41(**MCM41-V(R)**) shows very high activity for oxidation of sulfides using hydrogen peroxide. The conversion of sulfides and the selectivity of sulfoxide and sulfone are depending on the temperature, reaction time and the amount of hydrogen peroxide used.

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