Hydroxylation of phenol by iron(II)–phenanthroline(Phen)/MCM-41 zeolite

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Received 24 July 1995; accepted 22 September 1995

MCM-41 mesoporous molecular sieve and iron(II)–Phen/MCM-41 have been prepared and characterized by XRD, IR, NH_3-TPD, BET and UV-Vis. The iron(II)–Phen/MCM-41 molecular sieve + 30% H_2O_2 system is capable of performing hydroxylation of phenol.

Keywords: MCM-41 mesoporous molecular sieve; hydroxylation of phenol; iron(II)–1,10-phenanthroline complex

1. Introduction

Microporous and mesoporous inorganic solids have been used as catalysts or as catalyst supports. Microporous solids include zeolites and their related compounds. Recently, metal complexes, such as FePc–zeolite X or Y [1], iron(III) and manganese(III) tetra-methylporphyrin–zeolite Y [2], zeolite Y-encapsulated Mn–salen (salen = N,N′-ethylenebis(salicylidene-aminato)) [3], have been incorporated into zeolite void structures, providing immobilized enzyme mimics [4] or models of biochemical electron transfer chains [5,6]. The major drawback for their use has been their limited pore size, which makes it difficult for substrates to diffuse into the active sites and for products to diffuse out through their very narrow pore systems [7]. Meanwhile, some examples of reported mesoporous solids, including silicas [8], kanemite [9] and modified layered materials [10], are invariably amorphous or para-crystalline, and their pores are irregularly spaced and broadly distributed in size. More recently, some new mesoporous materials, named MCM-41, have been produced and characterized by pore diameters that can be adjusted between 18 and 200 Å. MCM-41 molecular sieve possesses regular arrays of uniform channels, high surface area and exceptionally high sorption capacities of cyclohexane and benzene [11].

2. Experimental

Infrared spectra were recorded on a Carl Zeiss 75 IR spectrophotometer (Germany); UV-Vis spectra were recorded with a Shimadzu UV-360 spectrophotometer (Japan). X-ray diffraction powder patterns were recorded with a Rigaku D/max-qB X-ray diffractometer (Japan).

Phenol hydroxylation: Catalyst and solvent were added successively into a glass reactor of 25 ml capacity equipped with a stirring machine and a thermostat. The reaction was initiated by adding H_2O_2 (30 wt%) at the set temperature. The gas chromatograph was equipped with a flexible glass capillary column coated with XE-60. Programmed temperature was adopted for product analyses. The initial temperature was 100°C, the final temperature was 190°C.

3. Result and discussion

So far, there are no reports of MCM-41 mesoporous molecular sieve used as a support of metal complexes. A MCM-41 molecular sieve sample (Si/Al = 20) was synthesized following several patents [11]. For the as-synthesized product, interplanar spacings $d_{100} = 44.6$ Å, $d_{110} = 27.4$ Å were observed; they are shown in the corresponding powder X-ray diffration pattern of the bulk sample (fig. 1a). The BET surface area of the prepared samples is 972.4 $m^2\ g^{-1}$. After cation-exchange with NH_4Cl solution and calcination at 400°C for 8 h, the NH_3-TPD curve of the prepared H-MCM-41 was obtained (fig. 2). From the NH_3-TPD of H-MCM-41, it is known to have only one weak acid center, different from HY-zeolite and HZSM-zeolite which have in general two acid centers, one weak and one strong.

The iron(II)–Phen/MCM-41 was prepared in the following way. 5.0 g MCM-41 was mixed with 200 ml of 0.05 M $[Fe(Phen)_3]Cl_2$ solution in alcohol, stirred for 24 h at ambient temperature, then filtered and washed with alcohol untill no $[Fe(Phen)_3]Cl_2$ was detected in the filtrate. The BET area of the obtained iron(II)–Phen/MCM-41 was 880.5 $m^2\ g^{-1}$. The X-ray diffractogram of

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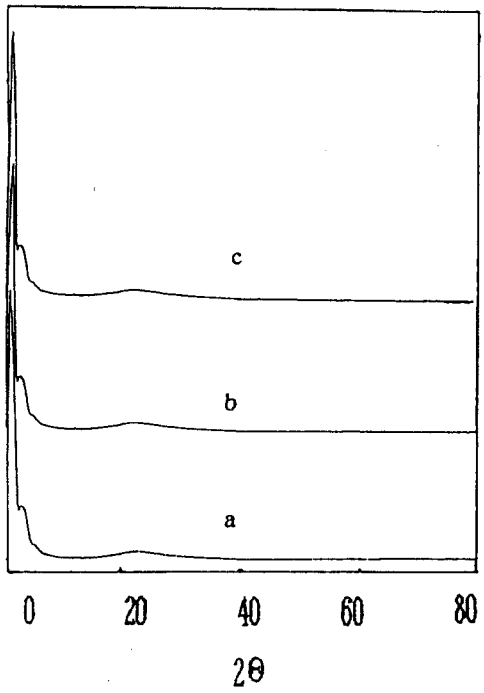

Fig. 1. XRD patterns for MCM-41 (a), iron(II)–Phen/MCM-41 (b) and the ten times used iron(II)-Phen/MCM-41 (c).

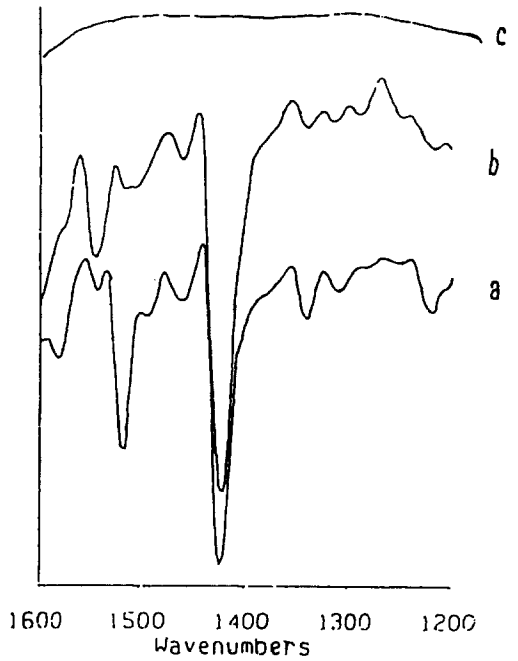

Fig. 3. The infrared spectra of $[Fe(Phen)_3]Cl_2$ (a), iron(II)–Phen/MCM-41 (b) and MCM-41(c).

this supported metal complex is shown in fig. 1b. According to the infrared spectra of MCM-41 (fig. 3c), iron(II)–Phen/MCM-41 (fig. 3b) and $[Fe(Phen)_3]Cl_2$ (fig. 3a), MCM-41 has no obvious IR-peak in the range of 1200–1600 cm^{-1}, but the supported iron(II)–Phen/MCM-41 and non-supported $[Fe(Phen)_3]Cl_2$ have similar infrared spectra in this area, which shows that the metal complex has been successfully immobilized in MCM-41. The ligand 1,10-phenanthroline may exist and be adsorbed by MCM-41 in the $[Fe(Phen)_3]Cl_2$–alcohol solution during the preparation of iron(II)–Phen/MCM-41. A comparison of the diffuse reflectance adsorption spectra of Phen/MCM-41 (fig. 4a) with iron(II)–Phen/MCM-41 (fig. 4b) reveals a bathochromic shift for the iron(II)–Phen/MCM-41. This evidences the formation of the complex, and also shows the successful immobilization of $[Fe(Phen)_3]^{2+}$ in the channel of MCM-41 zeolite.

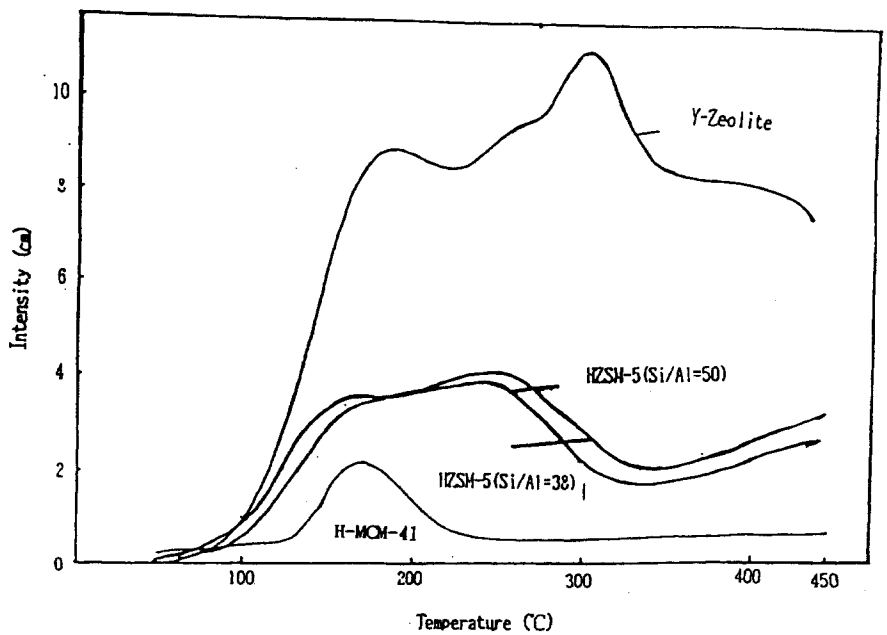

Fig. 2. NH_3-TPD curves of different zeolites.

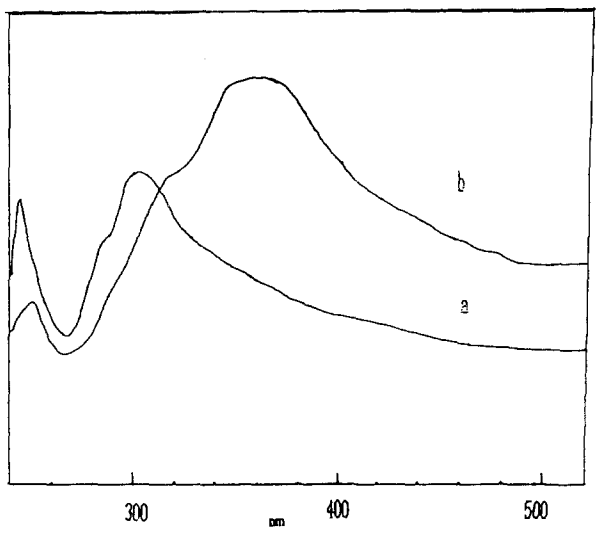

Fig. 4. The diffuse reflectance adsorption spectra of Phen/MCM-41 (a) and iron(II)–Phen/MCM-41 (b).

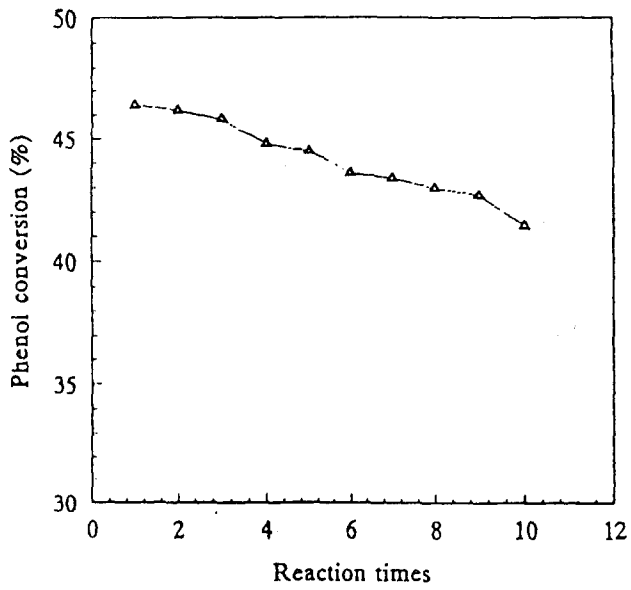

Fig. 5. The relation between reaction times and phenol conversion.

The supported complex iron(II)–Phen/MCM-41 is capable of performing as a catalyst in the hydroxylation of phenol, using 30% H_2O_2 as the oxygen atom transfer reagent. After reaction the mixture was analyzed with a gas chromatograph equipped with a flexible glass capillary column coated with XE-60. In an identical reaction procedure, the immobilized metal complex iron(II)–Phen/MCM-41 has a higher catalytic activity than that of its free equivalent $[Fe(Phen)_3]Cl_2$ and MCM-41 (table 1).

We found iron(II)–Phen/MCM-41 could be used many times to catalyze phenol hydroxylation with little decrease of phenol conversion (fig. 5). The X-ray diffractogram taken after the catalyst had been used ten times is shown in fig. 1c. It is much the same as those of the non-used iron(II)–Phen/MCM-41 (fig. 1b) and MCM-41 (fig. 1a). Chemical analysis showed 9.5% loss of $[Fe(Phen)_3]^{2+}$ from the immobilized iron(II)–Phen/MCM-41.

In conclusion, MCM-41 is a good catalyst support for $[Fe(Phen)_3]Cl_2$; the good immobilization may be due to the adsorption and static coulombic interaction between the walls of the channels of MCM-41 and $[Fe(Phen)_3]^{2+}$. The better catalytic activity of the supported iron(II)–Phen/MCM-41 zeolite is attributed to the high concentration of catalyst and substrate in the channels of the MCM-41. The channels are sufficiently large to allow the substrate and oxidant to approach catalytic activity centers, but also for products to move out of the channel. This can solve the problems happening to the zeolite-encapsulated metal complexes because of the limited pore size, and make it possible for the larger ligand metal complexes to be immobilized in the channels and for large substrates to enter the pores freely.

The titanium(IV) silicalites TS-1 [12,13] and TS-2 [14,15] have been shown to catalyze a variety of synthetically important oxidations with 30% H_2O_2 aqueous hydrogen peroxide under mild conditions. The successful hydroxylation of phenol demonstrated here with the MCM-41 zeolite-supported metal complex seems to open a new route for the hydroxylation of phenol.

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Table 1
The catalytic activities of MCM-41, $[Fe(Phen)_3]Cl_2$, and iron(II)–Phen/MCM-41 [a]

Catalyst	Phenol conversion (%)	Product selectivity (%)			H_2O_2 conversion (%)
		CAT	HQ	PBQ	
MCM-41	0.00	0.00	0.00	0.00	0.00
$[Fe(Phen)_3]Cl_2$	27.50	70.07	28.18	1.75	57.69
iron(II)–Phen/MCM-41	53.10	58.00	41.81	0.18	85.30

[a] CAT = catechol, HQ = hydroquinone, PBQ = *p*-benzoquinone. Reaction time: 6 h; temperature: 40°C; concentration of phenol: 0.35 mol/ℓ. Molar ratio phenol/H_2O_2 = 0.8. MCM-41 molecular sieve: 100 mg; iron(II)–Phen/MCM-41: 100 mg (containing 8 mg $[Fe(Phen)_3]Cl_2$); $[Fe(Phen)_3]Cl_2$: 8 mg. Volume of reacting mixture = 15 ml.

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