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Catalytic oxidation of styrene by manganese(II) bipyridine complex cations immobilized in mesoporous Al-MCM-41

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Manganese 2,2′-bipyridine (bpy) complex cations, $[Mn(bpy)_2]^{2+}$, have been immobilized in mesoporous Al-MCM-41 (Si/Al = 9) and used as a catalyst for the oxidation of styrene by iodosylbenzene, H_2O_2 and tert-butyl hydroperoxide (TBHP). The oxidation products included epoxide, diol and aldehyde. Al-MCM-41-immobilized $[Mn(bpy)_2]^{2+}$ exhibited a higher catalytic activity for styrene oxidation than the corresponding homogeneous catalyst and showed no significant loss of catalytic activity when recycled.

Keywords: Al-MCM-41, Mn(II), immobilization, oxidation of styrene

1. Introduction

Manganese(II) bipyridine complexes have been recognized as potential catalysts for the oxidation of alkanes and alkenes [1–4]. However, their catalytic activity in solution is limited by their tendency to decompose H_2O_2 [5]. Moreover, these homogeneous catalytic processes require liquid–liquid phase-transfer reaction conditions, which limits the reaction rate.

Immobilization of these Mn(II) complexes in the channels of zeolites has been of special interest since it offers the possibility of achieving molecular isolation of the complexes which are very promising catalytic sites [6]. However, complex immobilization in the zeolites requires multi-step "ship-in-bottle" synthesis, wherein the complex is assembled from the ligand-metal ions at the exchange site of the zeolite [6–8]. The major drawback for the use of conventional zeolites is the small pore sizes (4–13 Å), which makes it difficult for substrates to diffuse and access the active sites and for products to diffuse out of the pores [7].

The recently discovered mesoporous aluminosilicate MCM-41 (Al-MCM-41) affords new opportunities for the catalytic conversion of substrates with larger molecular size [9,10]. These materials also are promising for the immobilization of large metal complexes and clusters of potential catalytic significance [11]. In the present study we report the immobilization of Mn(II) bipyridine complex cations in Al-MCM-41 channels by direct ion exchange. The catalytic activity of the Al-MCM-41-immobilized complex for oxidation of styrene with iodosylbenzene (PhIO), H_2O_2 and tert-butyl hydroperoxide (TBHP) as oxidants has been investigated. Oxidation of styrene over the Al-MCM-41-immobilized catalyst shows higher turnover number than that of the homogeneous complex itself, which reveals that molecularly isolated sites are very efficient catalysts.

2. Experimental

Al-MCM-41 with a Si/Al ratio of 9 was prepared following a procedure similar to previously described methods [9,10]. NaOH was added under constant stirring to a solution of cetyltrimethylammonium bromide (Aldrich, [CTMA]Br). Then Al_2O_3 sol (10%, Nacol Chemicals) and tetraethylorthosilicate (Aldrich) were added. The composition of the resultant gel was $1SiO_2{:}0.04Al_2O_3{:}0.24CTAB{:}0.3Na_2O{:}150H_2O$. The mixture was stirred at room temperature for 1 h, and then heated at 383 K in an autoclave for 4 days to complete the crystallization. The product was filtered, thoroughly washed with deionized water, dried in air and calcined at 813 K for 4 h in N_2 and 6 h in air in order to remove the template. Elemental analysis for the Si/Al ratio was performed with inductively coupled plasma emission spectroscopy. The Si/Al ratio of the final product was 9.

Two Al-MCM-41–$[MnL_2]^{2+}$ (where L = 2,2′-bipyridine) samples were prepared by ion exchange of the calcined Al-MCM-41 (200 mg) with known amounts of $MnL_2(NO_3)_2$ (0.073 or 0.2 g) [1] dissolved in 20 ml of a 1 : 9 (vol : vol) DMF and acetonitrile mixture at room temperature for 24 h. The samples were filtered, washed with acetonitrile until no $MnL_2(NO_3)_2$ was detected in the filtrate, and then dried in vacuum at 80°C. Chemical analyses show that the two products have Mn/Al ratio of only 0.05 (5%) and 0.07 (or 7%). Even though a higher concentration manganese complex solution was used,

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the Mn/Al ratio could not be increased further. Therefore, 7% represents the saturation loading of the zeolite.

Oxidation of styrene was carried out using 100 mg of Al-MCM-41–$[MnL_2]^{2+}$ (contains 0.83×10^{-2} and 1.16×10^{-2} mmol of Mn for 5% and 7%, respectively) as catalyst, 0.087 mmol of styrene as substrate, 5 ml of acetonitrile in 50 ml round flask, into which 0.47 mmol of PhIO or 3.45 mmol of H_2O_2 or TBHP was added as an oxidant. The products during the reaction were periodically sampled and analyzed by a gas chromatograph (HP 5890) using a SPB-20 capillary column (fused silica, 30 m, 0.5 mm i.d.) and a flame ionization detector. The products were identified by GC-MS.

X-ray diffraction patterns of powdered samples were obtained with a Rigaku X-ray diffractometer equipped with a rotating anode and Cu K_α radiation. Diffuse reflectance UV–vis spectra were recorded with a Shimadzu UV-265 equipped with a Harrick diffuse reflectance integration sphere. Nitrogen adsorption/desorption isotherms at liquid nitrogen temperature were measured on a Coulter Omnisorp 360CX sorptometer using super-pure nitrogen (99.999%). Samples (about 60 mg) were pre-outgassed overnight at 358 K under vacuum (10^{-5} Torr). Surface areas were obtained by the BET method. The size of framework-confined mesopore was determined by Horvath–Kawazoe (HK) analysis [12] of the nitrogen adsorption isotherms.

3. Results and discussion

X-ray powder diffraction patterns of the as-synthesized, calcined and $[MnL_2]^{2+}$ ion-exchanged Al-MCM-41 (Si/Al = 9) samples are presented in fig. 1. The as-synthesized sample exhibits a very strong peak at d spacing of 41.7 Å (100) and three weaker peaks at 23.8 (110), 20.1 (200) and 15.5 Å (210). These four peaks fit a hexagonal unit cell with $a_0 = 48.2$ Å (where $a_0 = 2d_{100}/\sqrt{3}$). The calcined sample exhibits three peaks at 37.4 (100), 21.4 (110) and 18.2 Å (200) with an unit cell size of 43.2 Å. The lattice contraction of about 4.3 Å upon calcination is smaller than the 7–10 Å contraction reported in the literature [13,14]. The mesopore wall thickness is 14.2 Å, as calculated from the difference of the Horvath–Kawazoe (HK) pore (29.0 Å) and the unit cell size (43.2 Å). Thus, the wall thickness is larger than the 8–10 Å values reported for silica MCM-41 [10,15]. We note that the Al-MCM-41 prepared by reaction at 100°C for 2 days becomes amorphous upon stirring in H_2O for 24 h at room temperature. For this latter unstable form of Al-MCM-41, the pore wall thickness is less than 10 Å. The Al-MCM-41 in this work was prepared at 100 °C for 4 days. No decomposition of the structure was noted even after exposure to liquid water for 3 days. The BET surface area of our calcined sample is 920 $m^2 g^{-1}$, which is smaller than the value (>1000 $m^2 g^{-1}$) for the samples with pore wall thickness less than 10 Å. Therefore, the Al-MCM-41 prepared in this work is sufficiently stable to be used as a catalyst support for liquid phase oxidation reactions.

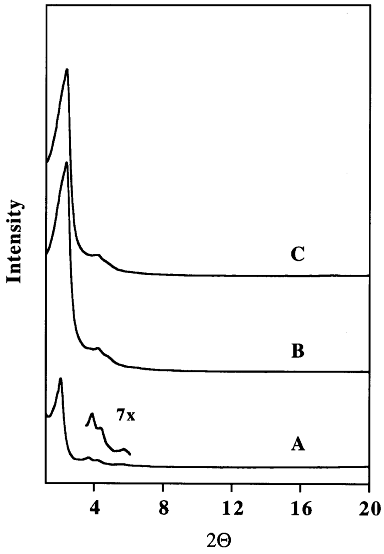

Fig. 1. X-ray powder diffraction patterns of the (A) as-synthesized Al-MCM-41, (B) calcined Al-MCM-41 and (C) Al-MCM-41–$[MnL_2]^{2+}$ (5%).

Ion exchange of the zeolite with $MnL_2(NO_3)_2$ in a DMF and acetonitrile mixture did not affect the structure of the mesoporous Al-MCM-41. Both Al-MCM-41–$[MnL_2]^{2+}$ (5%) and Al-MCM-41–$[MnL_2]^{2+}$ (7%) exhibit the hexagonal phase with at least two resolved (100) and (110) peaks in the X-ray diffraction pattern (fig. 1C). In addition, the Al-MCM-41-immobilized $[MnL_2]^{2+}$ complexes exhibit a pink color instead of the pale yellow color characteristic of the original $MnL_2(NO_3)_2$. This color change is consistent with the absence of NO_3^- in the coordination sphere of the manganese (see below).

The reflectance spectra of the pink Al-MCM-41–$[MnL_2]^{2+}$ samples showed a broad band at around 530 nm (fig. 2). This band is not observed in the reflectance spectra for Al-MCM-41, $MnL_2(NO_3)_2$, or pure siliceous MCM-41 impregnated with a known quantity of $MnL_2(NO_3)_2$. Therefore, this band can be assigned to the metal-to-ligand charge transfer transition of the nitrate-free $[MnL_2]^{2+}$ cation bonded to the zeolite framework [6,16]. Also, the analytical data of the catalyst are in agreement with the calculated Mn : N : C ratios of about 1 : 4 : 20 for the immobilized complex cations. These results indicate that $[MnL_2]^{2+}$ is anchored to the mesopore walls of Al-MCM-41 probably via coordination to the anionic framework. The binding of $[MnL_2]^{2+}$ to zeolite X or Y through oxygen bridging has also been observed [6].

The nitrogen adsorption–desorption isotherm and the HK pore size distribution for Al-MCM-41 and Al-MCM-41-$[MnL_2]^{2+}$ samples are presented in fig. 3. A

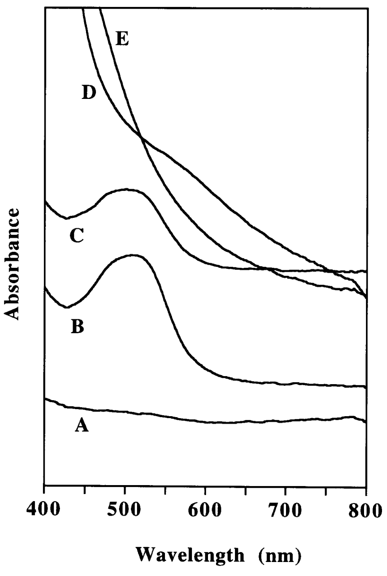

Fig. 2. Reflectance spectra of the (A) Al-MCM-41, (B) Al-MCM-41–$[MnL_2]^{2+}$ (5%), (C) Al-MCM-41–$[MnL_2]^{2+}$ (7%), (D) $MnL_2(NO_3)_2$ and (E) $MnL_2(NO_3)_2$ impregnated pure siliceous MCM-41.

well-defined step appears in the adsorption branch[1] between relative pressures P/P_0 of 0.2 to 0.4. The BET surface areas of Al-MCM-41–$[MnL_2]^{2+}$ (5%) and Al-MCM-41–$[MnL_2]^{2+}$ (7%) are 850 and 811 m^2 g^{-1}, respectively, somewhat lower than that of Al-MCM-41. Also, the pore size of the zeolite is slightly decreased from 2.91 nm for Al-MCM-41 to 2.83 and 2.78 nm for 5 and 7% Al-MCM-41–$[MnL_2]^{2+}$, respectively. These results indicate that the internal pores of Al-MCM-41 are occupied by the $[MnL_2]^{2+}$ complex.

Table 1 shows the results for the catalytic oxidation of styrene in the presence of Al-MCM-41–$[MnL_2]^{2+}$ as catalyst and with PhIO, H_2O_2 and TBHP as oxidants. It is interesting to compare the catalytic activity of the heterogeneous Al-MCM-41–$[MnL_2]^{2+}$ samples and homogeneous $MnL_2(NO_3)_2$ catalyst for styrene oxidation. The reaction conditions are almost identical in both cases, except that the amount of the catalyst was larger for the homogeneous catalyst than the zeolite catalyst. The catalytic activity in terms of turnover number

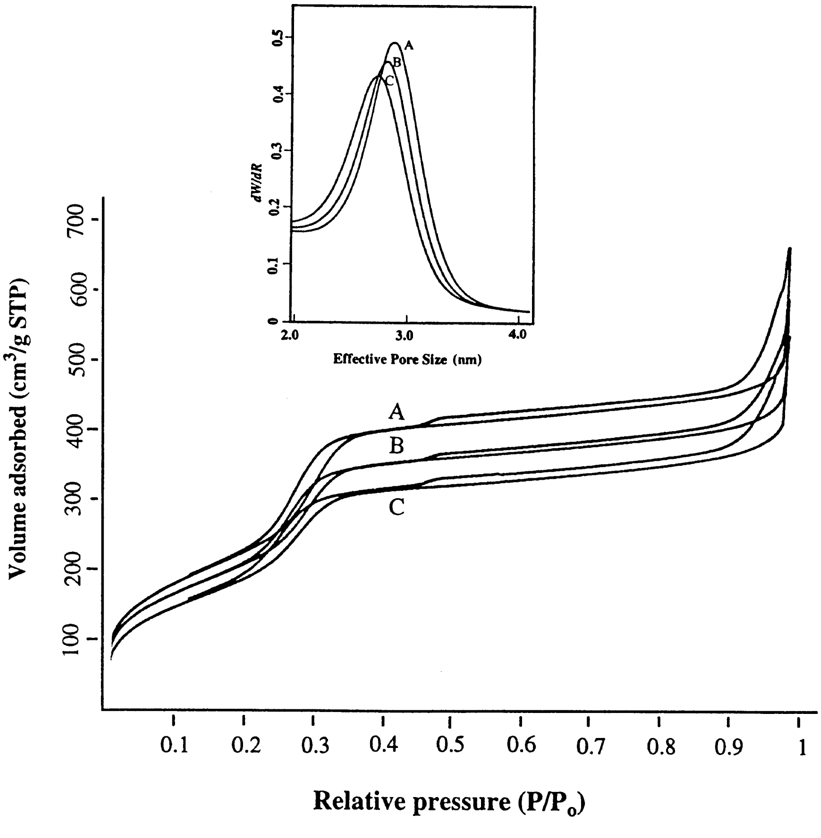

Fig. 3. Nitrogen adsorption and desorption isotherms for (A) Al-MCM-41, (B) Al-MCM-41–$[MnL_2]^{2+}$ (5%) and (C) Al-MCM-41–$[MnL_2]^{2+}$ (7%). (Inset is the Horvath–Kawazoe plots).

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[1] P is the equilibrium pressure of the adsorbate, and P_0 is the saturation pressure of the adsorbate at the temperature of the adsorbent, the adsorbed volume is at standard temperature and pressure.

Table 1
Oxidation of styrene by PhIO, H_2O_2 and TBHP mediated by Mn(II) bipyridine complexes immobilized in Al-MCM-41[a]

Oxidant	Catalyst	Conversion[b] (%)	Selectivity[c] (%)				Reaction time (h)	TON[d]
			A	B	C	D		
PhIO	$MnL_2(NO_3)_2$	81	15	42	12	30	4	7
	Al-MCM-41–$[MnL_2]^{2+}$ (5%)	94	9	51	40	0	1	34
	Al-MCM-41–$[MnL_2]^{2+}$ (7%)	94	9	50	41	0	1	24
H_2O_2	$MnL_2(NO_3)_2$	12	0	0	0	100	72	3
	Al-MCM-41–$[MnL_2]^{2+}$ (5%)	55	9	36	7	47	72	58
	Al-MCM-41–$[MnL_2]^{2+}$ (7%)	52	8	29	12	52	72	39
TBHP[e]	$MnL_2(NO_3)_2$	32	[e]	–	–	–	24	8
	Al-MCM-41–$[MnL_2]^{2+}$ (5%)	94	–	–	–	–	12	99
	Al-MCM-41–$[MnL_2]^{2+}$ (7%)	92	–	–	–	–	12	69

[a] In a typical experiment 0.47 mmol of iodosylbenzene or 3.5 mmol of H_2O_2 or TBHP was added to a solution of styrene (0.87 mmol) and catalyst (0.04 mmol of $MnL_2(NO_3)_2$ or 100 mg of supported catalyst) in 5 ml of anhydrous acetonitrile at room temperature.

[b] Conversion (%) in the case of PhIO as oxidant is based on the moles of IPh formed in the reaction. For the H_2O_2 and TBHP systems the conversion is based on the consumption of styrene.

[c] A, benzaldehyde; B, styrene oxide; C, phenylacetaldehyde; D, diol.

[d] Millimoles of converted substrate/millimoles of manganese for the total reaction time shown.

[e] More than ten oxidation products were formed in this system; selectivities were not determined.

(moles of styrene converted per mole of catalyst) is superior in the case of Al-MCM-41–$[MnL_2]^{2+}$ to the homogeneous $MnL_2(NO_3)_2$ regardless of what oxidant is used. The turnover number for the Al-MCM-41 catalyst apparently depends upon the $[MnL_2]^{2+}$ loading. The turnover number was higher for Al-MCM-41–$[MnL_2]^{2+}$ (5%) than for Al-MCM-41–$[MnL_2]^{2+}$ (7%) for all oxidants. The selectivity of products varies only slightly as a function of loading for PhIO and H_2O_2 as oxidants. The higher activity for the 5% catalyst may indicate that only completely isolated complex sites are efficiently active for catalytic reaction.

In general, pore size restrictions preclude the use of bulky TBHP for the oxidation of organic compounds over conventional transition-metal complex encapsulated zeolite catalysts [17]. However, the mesoporous Al-MCM-41–$[MnL_2]^{2+}$ catalyst is very active for styrene oxidation by bulky TBHP. Unfortunately the reaction is highly non-selective, with over ten oxidation products being observed. Unlike TBHP oxidations, the major products obtained in the Al-MCM-41–$[MnL_2]^{2+}$–H_2O_2 system were styrene oxide and diol. Small amounts of benzaldehyde (double bond cleavage product) and phenylacetaldehyde (rearrangement product) also were observed. In the Al-MCM-41–$[MnL_2]^{2+}$–PhIO systems, the major products were styrene oxide and phenylacetaldehyde. Diol was not observed in this reaction.

The catalytic activity of the Al-MCM-41–$[MnL_2]^{2+}$–PhIO and Al-MCM-41–$[MnL_2]^{2+}$–H_2O_2 systems are lower than the Al-MCM-41–$[MnL_2]^{2+}$–TBHP system, but the epoxide selectivities are higher. Among these three reaction systems, the Al-MCM-41–$[MnL_2]^{2+}$–PhIO system exhibits the highest reaction rate in terms of oxidant consumption. In addition, unlike Ti-β and Ti-HMS and Ti-MCM-41 with H_2O_2 as oxidant [18–20], where the major product of styrene oxidation in CH_3CN is benzaldehyde, the immobilized Mn(II) bipyridine catalysts show very low double bond cleavage activity. In accord with the mechanism proposed in early studies [21,22] for the homogeneous oxidation of olefin by Mn(porphyrin), Mn(TPP) and Mn(bpy), the anchored $[MnL_2]^{2+}$ complex may also form a high-valence manganese species first and then a transition-state complex with the olefin which undergoes oxygen insertion.

Because $[MnL_2]^{2+}$ is anchored on the mesopore wall of Al-MCM-41, it is anticipated that this catalyst would exhibit high stability for catalyst recycling. Therefore, the Al-MCM-41–$[MnL_2]^{2+}$ samples were recovered by filtration and used again for oxidation of styrene with PhIO, H_2O_2 and TBHP. The activities for Al-MCM-41–$[MnL_2]^{2+}$ (7%) for two successive oxidations of styrene are listed in table 2. The catalytic activities obtained for the second run are over 90% of those for the first run. These results indicate that the $[MnL_2]^{2+}$ is stabilized on the surface of Al-MCM-41. In contrast, the recycling of pure siliceous Al-MCM-41 impregnated with $MnL_2(NO_3)_2$ shows complete loss of catalytic activity after the first catalytic cycle.

After two successive oxidations, Al-MCM-41–$[MnL_2]^{2+}$ (7%) was recovered and examined by XRD (fig. 4). Neither H_2O_2 nor TBHP alters the structure of Al-MCM-41. For PhIO, however, AlMCM-41–$[MnL_2]^{2+}$ (7%) exhibits two new peaks at *d* spacings of 12.8 and 6.4 Å (fig. 4C) which were easily removed by heating at 200°C for 3 h without causing any change of XRD patterns of Al-MCM-41. These new peaks may be attributed to iodoso- and/or iodoxy-benzene formed as a by-product of the oxidation reaction [7]. Interestingly, this by-product from oxidant tends to form micro-lamel-

Table 2
Recycling of Al-MCM-41–$[MnL_2]^{2+}$ (7%) for styrene oxidation[a]

Oxidant	Number of recycling	Conversion (%)	Selectivity (%)		Reaction time (h)
			epoxide	diol	
PhIO	1st	94	52	0	1
	2nd	88	51	0	1
H_2O_2	1st	52	36	47	72
	2nd	45	34	49	72
TBHP	1st	92	–	–	12
	2nd	87	–	–	12

[a] After the first run for oxidation, the sample was recovered by centrifugation and dried at 80C for 10 h in nitrogen stream. See table 1 for reaction conditions.

lar crystals on the catalyst in presence of solvent at low concentration.

4. Conclusions

Al-MCM-41 is a promising support for directly immobilizing bulky $[MnL_2]^{2+}$ cations. The completely isolated and anchored $[MnL_2]^{2+}$ species are superior to homogeneous $[MnL_2](NO_3)_2$ in terms of peroxide oxidation activity and selectivity. Immobilization may very likely occur by electrostatic interaction between anion oxygen sites on the channel walls of Al-MCM-41 and $[MnL_2]^{2+}$. The channels of Al-MCM-41 are sufficiently large to allow the relatively large substrate and oxidant to access catalytic centers easily, and for products to move out of the channel freely. These materials show great promises for avoiding the limited pore size restrictions encountered by the conventional zeolite-encapsulated metal complexes.

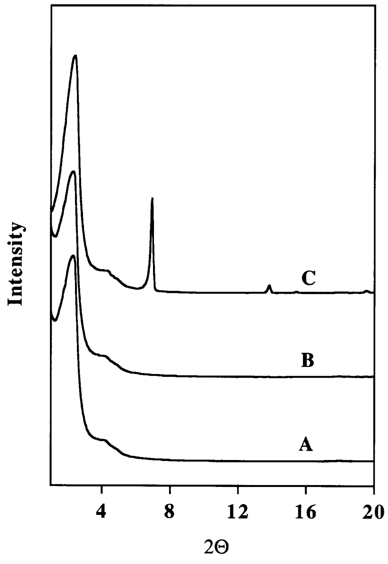

Fig. 4. X-ray powder diffraction patterns of Al-MCM-41–$[MnL_2]^{2+}$ (7%) after two cycles as catalyst for oxidation of styrene by (A) H_2O_2, (B) TBHP and (C) PhIO.

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