Fe-MCM-41 for Selective Epoxidation of Styrene with Hydrogen Peroxide

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Fe-MCM-41 prepared by direct hydrothermal synthesis catalyzes the epoxidation of styrene with diluted H_2O_2. The selectivity to styrene oxide reached 67% at styrene conversion of 17% over the catalyst with Si/Fe ratio of 86, which is better than that obtained over TS-1 or a titanium-incorporated silica.

Metal ion-incorporated MCM-41, which possesses uniform nano-order mesopore and high concentration of isolated active sites, has attracted much attention as oxidation catalyst in recent years. Ti-MCM-41 was reported to catalyze various oxidation reactions with H_2O_2,[1] but the epoxidation of cyclohexene could not proceed selectively over it with diluted H_2O_2.[2] The epoxidation was also only a minor reaction in the oxidation of alkenes with either H_2O_2 or *tert*-butyl hydroperoxide (TBHP) over V-MCM-41.[3] Mn-MCM-41 prepared by a template-ion exchange method showed high selectivity for the epoxidation of stilbene with TBHP, but when H_2O_2 was used, only its decomposition occurred.[4] Recently, we focus our studies on Fe-MCM-41 for the selective oxidation of hydrocarbons, since iron is the active center in monooxygenase enzymes such as cytochrome P-450, and many iron-containing complexes have been used to catalyze the oxidation of hydrocarbons.[5] In this communication, for the first time, we report the unique catalytic properties of Fe-MCM-41 in the epoxidation of styrene with diluted H_2O_2. So far, the epoxidation of styrene with H_2O_2 has been studied using various metal complexes,[6] titanium incorporated zeolites such as TS-1 and a Ti implanted silica,[7,8] but the selectivity to styrene oxide is not high because of the formation of by-product such as phenylacetaldehyde or benzaldehyde.

Fe-MCM-41 was prepared by both direct hydrothermal synthesis (DHT) and template ion exchange (TIE) methods. For the DHT synthesis, ferric nitrate, sodium silicate and hexadecyltrimethylammonium bromide were used as the sources of iron, silicon and a template, respectively. After hydrothermal synthesis at 150 °C for 48 h, the resultant solid was washed with deionized water, dried at 40 °C in vacuum and finally calcined at 550 °C for 6 h. In the TIE preparation, iron was introduced by exchanging the template cations contained in the uncalcined MCM-41 with the Fe^{3+} ions in an ethanol solution at 60 °C, followed by washing, drying and calcination. For comparison, ferrisilicate with MFI structure and Fe_2O_3/Cab-O-Sil were prepared according to the reference[9] and by the conventional impregnation, respectively. The content of iron in each sample was determined by ICP detection. All the samples were characterized by XRD, N_2 adsorption (77 K), diffuse reflectance UV–vis and ESR spectroscopic measurements. Catalytic reactions were carried out with a batch-type reactor. In a typical run, 0.2 g of catalyst, 10 mmol of styrene, 9.8 mmol of H_2O_2 (30 wt% aqueous solution) and 10 mL of dimethylformamide (DMF, as solvent) were charged in a glass flask and were allowed to react at 73 °C for 2 h with vigorous stirring. The products were identified by GC–MS and quantified by gas chromatography. The consumption of H_2O_2 was determined by iodometric titration.

Figure 1 shows the XRD patterns of Fe-MCM-41. The peaks of (100), (110), (200) and (210) indexed to the hexagonal regularity of MCM-41 were all observed for these samples. The unit cell parameter (a_0), calculated from $2d(100)/\sqrt{3}$, and the results obtained from N_2 adsorption measurements at 77 K are shown in Table 1. The introduction of iron into MCM-41 up to 1.1 wt% (Si/Fe = 86) by DHT method enlarged the unit cell parameter (a_0). Generally, it is expected that a_0 will be increased after the incorporation of metal cations with ionic radius larger than Si^{4+}. Thus, it is likely that a part of Fe^{3+} ions have been incorporated into the framework of MCM-41 to substitute Si^{4+} in the DHT samples. The result that a_0 did not increase significantly with introducing iron by TIE method may suggest that iron cannot be incorporated into the framework of MCM-41 or the incorporated amount is very small by this method.

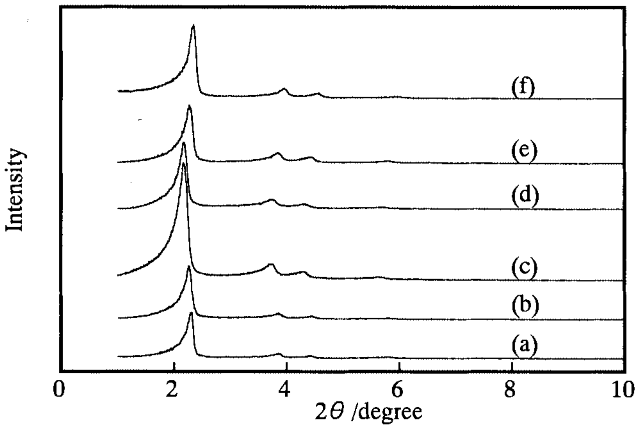

Figure 1. XRD patterns of Fe-MCM-41. (a) MCM-41, (b)–(e) DHT method, (b) Si/Fe = 163, (c) Si/Fe = 105, (d) Si/Fe = 86, (e) Si/Fe = 30, (f) TIE method, Si/Fe = 102.

The coordination environment of iron has been investigated by ESR and UV–vis measurements. Generally, the ESR signal at *g* = 4.3 is assigned to the iron in distorted tetrahedral coordination and is regarded as evidence of framework substitution by iron in zeolites.[10] Figure 2 shows that the relative intensity of the component at *g* = 4.3 for the Fe-MCM-41 by DHT method is similar to that for ferrisilicate with MFI structure and is higher than that for the Fe-MCM-41 by TIE method and Fe_2O_3/Cab-O-Sil. UV–vis spectroscopic studies revealed that the DHT samples with iron content lower than 1.1 wt% exhibited a sharp peak at 265 nm which was almost the same with ferrisilicate zeolite, while the TIE samples resembled Fe_2O_3/Cab-O-Sil. Thus, the iron cations in the DHT samples

Table 1. Properties of the iron-containing catalysts

Catalyst[a]	Fe content /wt%	a_0 /nm	Surf. area /m^2 g^{-1}	Pore dia. /nm
MCM-41	0	4.37	1025	3.0
DHT (163)	0.6	4.61	1043	2.7
DHT (105)	0.9	4.70	1173	3.0
DHT (86)	1.1	4.71	1078	3.0
DHT (50)	1.8	4.65	1016	3.0
TIE (102)	0.9	4.41	1220	2.7
Ferrisilicate (48)	1.9	–	350	0.55
Fe_2O_3/Cab-O-Sil	1.0	–	150	–

[a] DHT and TIE denote the Fe-MCM-41 prepared by DHT and TIE methods, respectively. The number in the parenthesis is the Si/Fe atomic ratio.

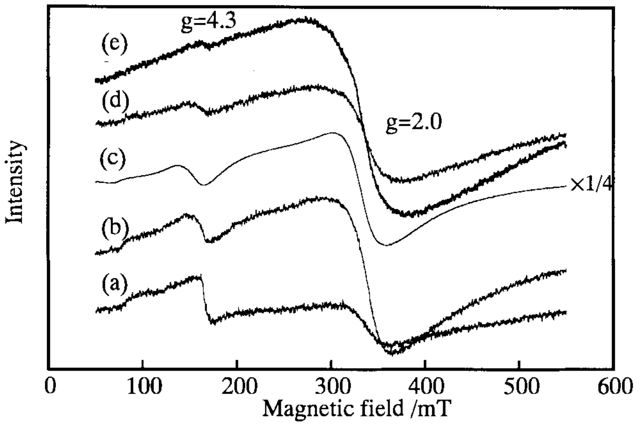

Figure 2. ESR spectra of Fe-containing compounds. (a) and (b), Fe-MCM-41-DHT (Si/Fe=163 and 105), (c) Ferrisilicate (Si/Fe= 48), (d) Fe-MCM-41-TIE (Si/Fe=102), (e) Fe_2O_3/Cab-O-Sil.

with iron content lower than 1.1 wt% were mainly incorporated into the framework of MCM-41, while those in the TIE samples probably existed in the state of Fe_2O_3 cluster.

Table 2 shows the results of epoxidation of styrene with diluted H_2O_2. Styrene oxide and benzaldehyde were two main products over most catalysts. Styrene glycol and benzoic acid were also observed with low selectivities. Although the conversion of H_2O_2 reached 45%, MCM-41 without iron exhibited very low conversion of styrene, suggesting that iron was mainly responsible for the conversion of styrene with H_2O_2. The increase in iron content up to 1.1 wt% (Si/Fe = 86) in the DHT sample remarkably increased the conversion of styrene. Further increase in iron content did not raise the conversion of styrene but increased that of H_2O_2. Thus, the efficiency of H_2O_2 for the formation of styrene oxide was the highest (7.8%) over the catalyst with Si/Fe ratio of 86. Considering the characterization result that iron could be incorporated into the framework of MCM-41 up to a content of ca. 1.1 wt%, we suggest that the iron sites inside the framework are responsible for the conversion of styrene. The selectivity to styrene oxide was increased to 66.5% with a slight increase in styrene conversion by adding H_2O_2 slowly to the reactant mixture during the reaction. The efficiency of H_2O_2 used for epoxidation was also remarkably increased to 15.4% at the same time.

Table 2. Epoxidation of styrene with H_2O_2

Catalyst[a]	Styrene	H_2O_2	Selectivity /%	
	conv. /%	conv. /%	Epoxide	Benzaldehyde
MCM-41	2.1	45	36.8	52.2
DHT (163)	7.4	63	42.9	43.0
DHT (105)	13.8	86	41.8	37.3
DHT (86)	15.5	89	43.9	34.8
DHT (86)[b]	16.8	74	66.5	33.5
DHT (50)	13.6	94	40.9	39.1
TIE (102)	3.5	95	45.7	45.9
Fe_2O_3/Cab-O-Sil	6.6	82	33.8	43.0
Ferrisilicate (48)	1.9	–	58.2	41.8
TS-1[c]	35.4	–	2.0	22.8
Ti-SiO_2[d]	4.8	–	55.5	44.5

[a] DHT and TIE denote the Fe-MCM-41 prepared by DHT and TIE methods, respectively. The number in the parenthesis is the Si/Fe atomic ratio. [b] H_2O_2 was added slowly (0.1 mL at the beginning and then 7.5 μL/min). [c,d] See refs. (7) and (8).

For the Fe-MCM-41 by TIE method, the conversion of styrene was notably lower as compared with the catalyst by DHT method although the consumption of H_2O_2 was higher. Fe_2O_3/Cab-O-Sil showed not only lower conversion of styrene but also worse selectivity to styrene oxide. Thus, the coordination environment of iron is vital for the epoxidation of styrene with H_2O_2. It is probable that the iron highly isolated in the framework of MCM-41 accounts for the effective activation of H_2O_2 for the epoxidation reaction, while iron oxide cluster catalyzes the decomposition of H_2O_2. Ferrisilicate with MFI structure showed higher selectivity to styrene oxide but lower styrene conversion probably due to the diffusion limitation.

The results for TS-1, a well-known catalyst for the epoxidation of alkenes with H_2O_2, and a Ti-implanted SiO_2 were also shown in Table 2. TS-1 produced mainly phenylacetaldehyde.[7] The Ti-SiO_2 with highly isolated titanium ions prepared by ion beam implantation exhibited 55.5% of selectivity to styrene oxide at 4.8% of conversion at 65 °C. However, the products shifted to benzaldehyde as the conversion increased to > 5% at 85 °C.[8] Therefore, the Fe-MCM-41 prepared by DHT method is a very unique catalyst for the epoxidation of styrene with diluted H_2O_2. The repeated runs of the catalyst did not show significant decrease in activity, and the leaching test suggested that the iron inside the framework was stable during the reaction.

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