JOURNAL OF CATALYSIS **178,** 207–213 (1998)
ARTICLE NO. CA982145

Metal Ion-Planted MCM-41

2. Catalytic Epoxidation of Stilbene and Its Derivatives with *tert*-Butyl Hydroperoxide on Mn-MCM-41

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Received January 7, 1998; revised April 21, 1998; accepted April 28, 1998

Manganese ion-planted MCM-41 (Mn-MCM-41) prepared by the template ion-exchange (TIE) method has been found to be active for catalytic epoxidation of aromatic olefins. The activity of Mn-MCM-41 was the greatest among those of Mn/MCM-41, Mn/SiO$_2$, Mn/Al$_2$O$_3$, which were prepared by a conventional impregnation method, and Mn-ZSM-5 prepared by an ion-exchange method. The proper reaction conditions have first been determined for *trans*-stilbene as the substrate. The most effective oxidant was *tert*-butyl hydroperoxide (TBHP) at 328–348 K among H$_2$O$_2$, PhIO, TBHP, and O$_2$. The highest yield of 93% of *trans*-stilbene oxide was obtained by using a mixed solvent of acetonitrile and dimethylformamide of 9 : 1 (v/v) at 328 K. Mn-MCM-41 could be used repeatedly for the reaction without decrease in the catalytic activity. The epoxidation of *trans* and *cis* isomers of various aromatic olefins has then been studied. The oxidation of olefins having bulky substituents such as 4-*tert*-butylphenyl and 2-naphthyl could proceed in the mesopores of Mn-MCM-41. The epoxidation of *trans* isomers was easier than that of *cis* isomers. The olefins with *cis* configuration all gave the corresponding *trans* oxides with small amounts of *trans* olefins as by-products. A radical mechanism has been suggested for the oxidation on the basis of the product distributions.

INTRODUCTION

MCM-41 is one of the most attractive porous materials because of its characteristic structure of well-ordered hexagonal mesopores (1, 2). The uniform pore diameter and large surface area are excellent properties as a support for catalysts (3, 4). The framework is made of amorphous silica, and thus, several kinds of techniques have been suggested to introduce catalytically active sites. The method in which the metal ion source is introduced as a reactant into the reaction gel for hydrothermal synthesis has widely been reported (5–18). The ion-exchange method has also been applied to the surface of Al-MCM-41 (19–23). These two methods, however, have several problems; for example, a loosely ordered mesoporous structure or little amounts of metal ions loaded on the surface. In addition, the loading of various metal complexes and the subsequent calcination have been clarified to be useful to yield metal ion-loaded MCM-41 (24–27). Recently, we have reported (28) the "template-ion exchange (TIE)" method as a new preparation technique of metal ion-planted MCM-41. The TIE method has made it easy to prepare a Mn-MCM-41 with various loadings of manganese ion (Si/Mn = 20–320), without any collapse of the mesoporous structure. The catalytic activity of Mn-MCM-41 obtained has been examined here.

Epoxidation of olefinic compounds plays one of the important roles in the syntheses of organic fine chemicals. Stoichiometric oxidation with mCPBA or catalytic oxidation on metalloporphyrin and metallosalen complex, for example Mn-salen complex (29), is well known in homogeneous phase. Liquid phase peroxide oxidations have also been reported on various heterogeneous catalysts (3, 26, 30–37). In this case, Ti-containing porous materials, i.e., TS-1 (3, 30, 31), TS-2 (32), Ti-Beta (3, 30, 31), and Ti-MCM-41 (3, 26, 31), have been preferentially employed as the catalyst and shown good activities. On the other hand, Mn-containing porous materials have been clarified to be active for several oxidation reactions. For example, an oxidation of styrene has been reported on manganese 2,2′-bipyridine (bpy) complex cation immobilized in Al-MCM-41 (23). A manganese-oxo species grafted on MCM-41 is active for the oxidation of propene (24, 25). Cyclohexane (35) and alkanes (37) are also oxidized on Mn-MCM-41. The results indicate the possibility that the Mn-MCM-41 might be active for the epoxidation of olefins.

As has already been pointed out by several researchers (3, 31, 33–35), the use of mesoporous materials has been recommended highly if one oxidizes organic compounds of large molecular sizes with a bulky oxidant such as *tert*-butyl hydroperoxide (TBHP). In the present work, the first example of catalytic ability of Mn-MCM-41 prepared by the above TIE method for epoxidation of aromatic olefins with TBHP has been studied and the distributions of the

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0021-9517/98 $25.00

products was found to be completely different from those on Ti-MCM-41 reported previously (34).

EXPERIMENTAL

Preparation of Catalysts

The parent MCM-41 was synthesized according to the previous report (38) using $C_{12}H_{25}N(CH_3)_3Br$ as the template. Mn-MCM-41 was prepared by the TIE method as follows: 15 g of as-synthesized MCM-41, which consisted of 60 wt% of SiO_2 and 40 wt% of organic template, was stirred at ambient temperature for 1 h in a manganese(II) acetate aqueous solution (6.7 mmol dm^{-3}, 300 cm^3, Si/Mn = 75) and then the mixture was kept at 353 K for 20 h without stirring. A faintly reddish-white solid was obtained by filtration, washing with water, and subsequent drying at 353 K in air. The resultant sample was calcined in air at 873 K for 6 h and gave pale brownish-gray Mn-MCM-41.

Calcined MCM-41, SiO_2 (Catalysis Society of Japan, JRC-SIO-4), and Al_2O_3 (JRC-ALO-4) were employed as supports. Each support (3.0 g) was suspended in a manganese(II) acetate aqueous solution (11 mmol dm^{-3}, 60 cm^3), stirred at ambient temperature, dried by evaporation under reduced pressure, and finally calcined in air at 873 K for 6 h. The catalysts prepared by the impregnation method have here been abbreviated Mn/Support. Mn-ZSM-5 was prepared from a parent ZSM-5, which had the Si/Al molar ratio of 11.7, by a conventional ion-exchange method (39) with an aqueous manganese(II) acetate and followed by calcination in air at 873 K for 6 h.

The amounts of manganese in the catalysts were determined by inductively coupled plasma emission spectrometry (ICP; Perkin Elmer, Optima 3000) after the samples were dissolved in a HF solution. X-ray powder diffraction patterns (XRD; MAC Science, MXP3, CuKα) and N_2 adsorption–desorption isotherms at 77 K (Quanta Chrome, Autosorb-1) were taken to confirm the mesoporous structure.

Preparation of Aromatic Olefins

trans-Stilbene (Wako pure chemical) and *cis*-stilbene (Aldrich) were used without further purification. Various aromatic olefins with substituents of 4-chlorophenyl, 4-methylphenyl, 4-*t*butylphenyl, and 2-naphthyl were prepared by conventional Wittig reaction of respective aromatic aldehydes with benzylidenetriphenylphosphorane. The typical procedure was as follows: butyl lithium (10.0 mmol, 1.50 *M* in hexane) was added dropwise to a suspension of benzyltriphenylphosphonium chloride (10.0 mmol) in dry THF (25 cm^3) at 195 K (a dry ice-MeOH bath) under an argon atmosphere. After 30 min stirring, the reaction mixture was allowed to warm to ambient temperature by removing the cold bath and was stirred for 30 min. Subsequently, a dry THF solution (10 cm^3) of aldehyde (11.0 mmol) was added at 195 K. The reaction mixture was stirred overnight at ambient temperature. The reaction was quenched by H_2O (20 cm^3) and separated. The aqueous layer was extracted with AcOEt (30 cm^3) three times and the organic layer obtained was dried over $MgSO_4$. The solvent was removed by evaporation and the residue was purified and separated into the *trans* and *cis* isomers by careful silicagel column chromatography (Merck Silicagel 60, hexane and AcOEt as eluent). The isolated yield calculated from starting phosphonium salt of each compound was as follows: *trans*-1-(4-Chlorophenyl)-2-phenylethene, 30%; *cis* isomer, 38%; *trans*-1-(4-methylphenyl)-2-phenylethene, 19%; *cis* isomer, 46%; *trans*-1-(4-*t*butylphenyl)-2-phenylethene, 29%; *cis* isomer, 42%; and *trans*-1-(2-naphthyl)-2-phenylethene, 33%; *cis* isomer, 46%. All *trans*- and *cis*-olefins and their oxides were identified by GC-MS (Hewlett Packard, HP6890 GC + HP5973 MSD system with a 30 m × 0.25 mm × 0.25 μm column of HP-5MS) and NMR (Bruker, ARX400).

Epoxidation of Olefins

Typical reaction procedures were as follows: desired amounts of olefin (0.50 mmol), Mn-MCM-41 (0.050 mmol as Mn), and oxidant were charged into the glass flask with solvent (10 cm^3) and vigorously stirred at 328 or 348 K for 24 or 48 h in an argon atmosphere. Reactions were followed by TLC (Merck, Silica gel 60 F254) and HPLC (Daicel, Chiralcel OB-H; hexane : 2-propanol = 9 : 1 as eluent). The latter was used to evaluate the yields by using 1,4-dibromobenzene as an internal standard. All products were identified GC-MS and NMR after isolation through column chromatography.

RESULTS AND DISCUSSION

Properties of Catalysts Used

The physical properties of Mn-MCM-41 used are listed in Table 1. The preparation of Mn-MCM-41 was repeated three times. The amounts of manganese loaded onto the MCM-41 structure were 1.2 ± 0.2 wt%, indicating the good reproducibility of present TIE method. Each Mn-MCM-41 showed the same diffraction patterns as that of the parent MCM-41. The comparisons of surface area, pore diameter, and pore volume of Mn-MCM-41 with those of MCM-41 clearly show no significant structural difference among them, as has already been reported previously (28). In this paper, further characterization of manganese ions was not carried out.

The contents of manganese in the catalysts prepared by the impregnation method were the similar values to those of Mn-MCM-41 as indicated in Table 1.

TABLE 1

Characterizations of Mn-MCM-41, MCM-41, Mn/Support, and Mn-ZSM-5

Catalyst	Si/Mn ratio[a]	Mn wt%[a]	BET surface area ($m^2\,g^{-1}$)	Pore diameter[b] (nm)
Mn-MCM-41[c]	64	1.4	1060	2.24
Mn-MCM-41[c]	56	1.0	—	—
Mn-MCM-41[c]	73	1.2	960	2.24
MCM-41	—	0	1070	2.24
Mn/MCM-41	76	1.2	1100	2.11
Mn/SiO_2	72	1.3	307	
Mn/Al_2O_3	83[d]	1.3	175	
Mn-ZSM-5[e]	12	3.7	317	

[a] Determined by an ICP analysis.

[b] Calculated from N_2 adsorption–desorption curve by BJH method.

[c] Each sample was prepared by the method described in the text but its Si/Mn ratio was 64 ± 9. The samples with Si/Mn = 64, 56, and 73 were used for the experiments concerning oxidants and solvents, mixed solvents and recycle use, and derivatives, respectively.

[d] Al/Mn ratio.

[e] Si/Al = 11.7.

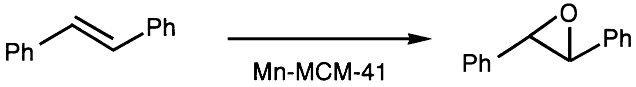
Epoxidation of *trans*-Stilbene

1. Oxidant

First, hydrogen peroxide (H_2O_2), *t*-butyl hydroperoxide (TBHP), iodosobenzene (PhIO), or gaseous oxygen (O_2) was examined as an oxidant for catalytic oxidation in acetonitrile (MeCN) on Mn-MCM-41. The substrate was *trans*-stilbene. The results are summarized in Table 2. Upon the introduction of H_2O_2 at ambient temperature, a bubbling occurred around Mn-MCM-41 and no reaction of *trans*-stilbene was observed. It is clear that H_2O_2 cannot be used as an oxidant at this temperature because of the rapid and waste decomposition to O_2. PhIO could oxidize *trans*-stilbene to the corresponding oxide, although the yield was not so high. In the case of TBHP, a little formation of *trans*-stilbene oxide was detected at ambient temperature in spite of excess amount of oxidant used. The yield was improved to 47% by changing the reaction temperature to 328 K. The oxidation with gaseous O_2 at 328 K showed no reaction. TBHP was employed as an oxidant in the present study since the increase in the yield of oxide with PhIO was very difficult due to its low solubility into the MeCN solution.

TABLE 2

Epoxidation of *trans*-Stilbene with Various Oxidants on Mn-MCM-41 in MeCN[a]



Entry	Oxidant[b] (mmol)	Temperature	Yield of oxide (%)	Recovered olefin (%)	TOF[c] (mmol mol-$Mn^{-1}\,h^{-1}$)
1	H_2O_2 (7.0)	r.t.	0	96	0
2	PhIO (2.0)	r.t.	14	77	58
3	TBHP (7.0)	r.t.	2	87	8.3
4	TBHP (7.0)	328 K	47	2	200
5	O_2 (excess)	328 K	0	89	0

[a] Reaction conditions: 0.50 mmol *trans*-stilbene, 0.050 mmol manganese in Mn-MCM-41 (Si/Mn = 64), 10 cm^3 MeCN, 24 h, under Ar atmosphere, except for entry 5.

[b] The concentration of H_2O_2 was 33% in H_2O and that of TBHP was 70% in H_2O.

[c] TOF (turn over frequency) = (mole of oxide obtained)/(mole of manganese in catalyst used × reaction time).

The by-products in Entry 4 were analyzed by using GC-MS technique. Besides *trans*-stilbene oxide, the formation of benzaldehyde, benzoic acid, *t*-butoxy benzoate, 1,2-diphenylethandione, 2-hydroxy-1,2-diphenylethan-1-one, 1,2-diphenylethanone, diphenylacetoaldehyde, and acetophenone was confirmed. These side reactions including oxidation and carbon–carbon bond cleavage are unwelcome and should be minimized.

The above results should be compared with those on Al-MCM-41-immobilized $[Mn(bpy)_2]^{2+}$ (23). When PhIO, H_2O_2, and TBHP were used as oxidants for styrene, Al-MCM-41-$[Mn(bpy)_2]^{2+}$ gave the oxide yields of 48, 20, and 0%, respectively. The great difference between the reactions on the present Mn-MCM-41 and on Al-MCM-41-$[Mn(bpy)_2]^{2+}$ would result from the reactivity of the substrates or the properties of the actives sites, although the details are unknown.

2. Solvent

The change in the catalytic epoxidation on Mn-MCM-41 with the solvents was investigated and is summarized in Table 3. Since TBHP was added into the solution as a

TABLE 3

Effect of Solvents on Epoxidation of *trans*-Stilbene with TBHP[a]

Entry	Solvent	Time (h)	Yield of oxide (%)	Recovered olefin (%)	TOF (mmol mol-$Mn^{-1}\,h^{-1}$)
4	MeCN	24	47	2	200
6	THF	24	9	25	38
7	MeOH	24	9	57	38
8	DMF	24	26	74	110
9	MeCN + DMF	24	50	48	210
10	MeCN + DMF	96	93	3	97

[a] Reaction conditions: 0.50 mmol *trans*-stilbene, 0.050 mmol manganese in Mn-MCM-41 (Si/Mn = 64 for entries 6–8, Si/Mn = 56 for entries 9 and 10), 10 cm^3 solvent, 7.0 mmol TBHP (70% in H_2O), 328 K, under Ar atmosphere.

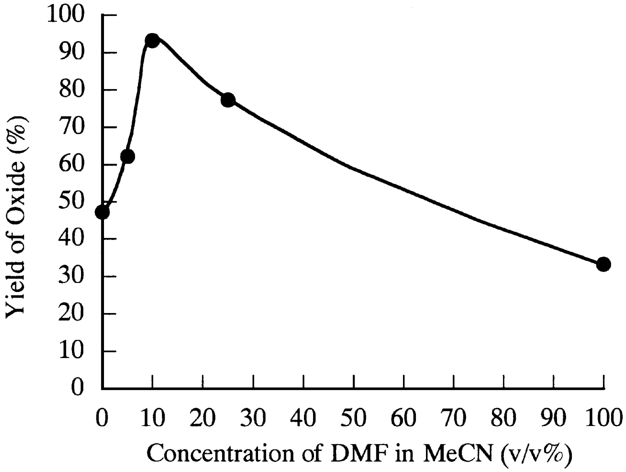


FIG. 1. Change in the yield of *trans*-stilbene oxide as a function of concentration of DMF in MeCN. Reaction conditions: 0.50 mmol *trans*-stilbene, 0.050 mmol manganese in Mn-MCM-41 (Si/Mn = 56), 10 cm^3 solvent, 7.0 mmol TBHP (70% in H_2O), 328 K, 96 h, under Ar atmosphere.

70% aqueous solution, polar solvents such as tetrahydrofuran (THF), methanol (MeOH), and dimethylformamide (DMF) were used to avoid separation of the solvent during the reaction. The yields were in the order MeCN > DMF > MeOH = THF, indicating that MeCN is the best solvent for the epoxidation under the present conditions. On the other hand, it should be noted that DMF is the best solvent from the viewpoint of selectivity; Entry 8 indicates 100% selectivity to the oxide in the DMF solution. The excellent selectivity did not change even at longer reaction times. For example, upon the reaction for 96 h in DMF the yield of *trans*-stilbene oxide increased to 33% while the amount of recovered *trans*-stilbene was 66%. This was in contrast to the selectivity of 47% in MeCN.

The findings suggest the possibility that the combination of two solvents might result in good activity and selectivity. Then, the reaction was examined in various mixtures of MeCN and DMF. Figure 1 shows the yield of oxide as a function of the amount of DMF in MeCN. The highest yield, 93%, was achieved for a ratio of 9 : 1 (v/v) of MeCN and DMF. The great effect of the addition of DMF on the improvement of the selectivity should be explained on the basis of the reaction mechanism, but the detailed mechanism is unknown. The provisional explanation is as follows. The low reaction rate and the excellent selectivity in the DMF solution would be due to the strong interaction of a DMF molecule with the active site. That is, the strong interaction would inhibit the coordination of the substrate and enhance desorption of the product from the active site. The affinity of DMF to the manganese ion might promote separation of *trans*-stilbene oxide from the site, which results in the prevention of deep oxidation of the oxide produced and in the increase in the selectivity.

3. Catalyst

The activities of various catalysts are listed in Table 4, where the catalytic run was performed in MeCN : DMF = 9 : 1 solvent at 328 K for 96 h. Without any catalyst (entry 17), the yield of *trans*-stilbene oxide was 21%. On the other hand, the MCM-41 itself with no manganese ion gave a yield of 23% (entry 18). The closeness of the value for the MCM-41 to that without a catalyst shows that the MCM-41 possesses no catalytic activity for the reaction. The table also shows that the manganese ions are, indeed, the active sites for oxidation.

The order of activities of Mn-containing catalysts is Mn-MCM-41 > Mn-ZSM-5 > Mn/MCM-41 ≈ Mn/SiO_2 > Mn/Al_2O_3. The better yield and selectivity on Mn-MCM-41 than

TABLE 4

Comparison of Catalytic Activities of Various Catalysts for Epoxidation of *trans*-Stilbene with TBHP in MeCN-DMF[a]

Entry	Catalyst	Temperature (K)	Time (h)	Yield of oxide (%)	Recovered olefin (%)	TOF (mmol mol-Mn^{-1} h^{-1})
10	Mn-MCM-41[b]	328	96	93	3	97
11	Mn/MCM-41[b]	328	96	72	2	75
12	Mn/SiO_2[b]	328	96	68	4	71
13	Mn/Al_2O_3[b]	328	96	59	7	61
14	Mn-ZSM-5[b]	328	96	77	22	80
15	Mn-MCM-41[c]	348	48	71	27	3000
16	Mn-MCM-41[c]	348	72	90	5	2500
17	None	328	96	21	76	—
18	MCM-41[d]	328	96	23	61	—

[a] Reaction conditions: 0.50 mmol *trans*-stilbene, 10 cm^3 MeCN + DMF (9 : 1 v/v), 7.0 mmol TBHP (70% in H_2O), under Ar atmosphere.

[b] Manganese of 0.050 mmol was used in each experiment.

[c] Manganese of 0.0025 mmol was used to demonstrate the high activity of Mn-MCM-41.

[d] 50 mg of the calcined MCM-41.

those on Mn/MCM-41 would result from the difference in the degrees of dispersion of active sites, or of the oxidation states of the manganese ions. It would be worthwhile to note that the manganese-oxo species supported on MCM-41 also showed higher activity for propene oxidation than that on silicagel (24), which agrees well with the present results. The good selectivity on Mn-ZSM-5 suggests that the high dispersion of manganese ions is an important factor for this epoxidation. The moderate reaction rate on Mn-ZSM-5 would be due to its small pore size (0.51 nm × 0.54 nm).

The effect of the amount of catalyst on the reaction was examined. In entry 15, 0.0025 mmol of manganese ions, which was 1/20 of the usual amount of 0.050 mmol, was used as the catalyst. The reaction temperature was raised to 348 K to increase the reaction rate. The yields of *trans*-stilbene were 71 and 90% upon the reaction for 48 and 72 h, respectively. The turnover frequency reached 3.0 mol mol-Mn^{-1} h^{-1}. The findings reveal that the Mn-MCM-41 has a high catalytic activity and the selectivity does not decrease even at high reaction temperature. The latter will be again shown in the next sections.

4. *Recycle Use of Catalyst*

One of the essential advantages in the use of solid catalyst in the liquid phase reaction is easy separation of the catalyst from the solution containing reactants and products. The repeated use of the catalyst was indeed carried out here at 348 K. The first run gave the conversion of 89% to *trans*-stilbene oxide after the 48 h reaction, as shown in Fig. 2. Subsequently, the catalyst used was collected by filtration, dried at ambient temperature, and used again in the second reaction. The same procedures were repeated four times and the results were summarized in Fig. 2. Yields were essentially constant within an experimental error, indicating that the Mn-MCM-41 could be used repeatedly.

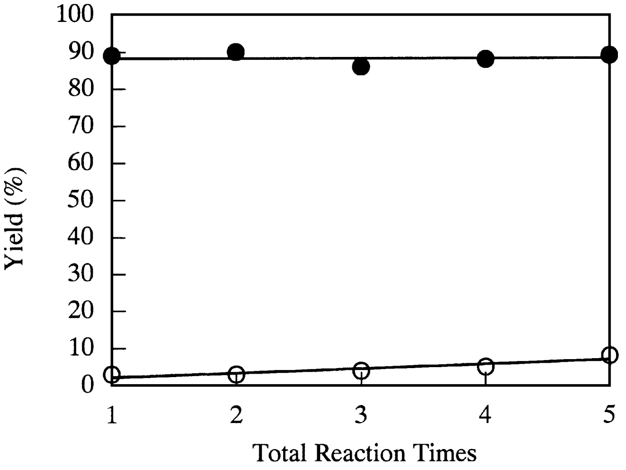


FIG. 2. Change in the activity of Mn-MCM-41 catalyst during the recycle use: (●) *trans*-stilbene oxide obtained; (○) *trans*-stilbene recovered. Reaction conditions: 0.50 mmol *trans*-stilbene, 0.050 mmol manganese in Mn-MCM-41 (Si/Mn = 56), 10 cm^3 MeCN + DMF (9 : 1 v/v), 7.0 mmol TBHP (70% in H_2O), 348 K, 48 h, under Ar atmosphere.

TABLE 5

Epoxidation of *trans*-Stilbene in the Absence of Solid Mn-MCM-41

Entry	Condition	Temperature (K)	Time (h)	Yield of oxide (%)	Recovered olefin (%)
19	Filtrate after reaction[a]	348	48	31	64
20	No catalyst[b]	348	48	26	72

[a] See text.

[b] Reaction conditions: 0.50 mmol *trans*-stilbene, 10 cm^3 MeCN + DMF (9 : 1 v/v), 7.0 mmol TBHP (70% in H_2O), under Ar atmosphere.

There remains an unsolved possibility that the manganese ions supported on MCM-41 would dissolve into the solution during the reaction and the resulting manganese ions in the solution might be active for the epoxidation reaction. Entry 19 in Table 5 was performed to investigate the possibility, in which additional *trans*-stilbene and TBHP were introduced in the filtrate after the usual reaction was carried out at 348 K for 48 h and then the catalyst was removed by filtration. The yield of *trans*-stilbene oxide was 31% at 348 K for 48 h. This value was almost the same as 26% (entry 20), and extremely lower than those which were observed with a catalyst under the same reaction conditions. Figure 2 and Table 5 conclude that the active sites for oxidation are the manganese ions on MCM-41 surface and they can be used repeatedly.

Epoxidation of Stilbene Derivatives and the Reaction Mechanism

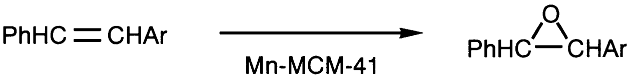
1. *Reactivity of Stilbene Derivatives*

Several kinds of diaryl substituted olefins other than *trans*-stilbene were used in the present epoxidation system as substrates. Not only the *trans* isomer but also the *cis* isomer of each olefin was examined because *cis*-stilbene has been reported to be oxidized more easily than *trans*-stilbene (40, 41). Experimental results of the aromatic olefins were summarized in Table 6. It was found that all of the *trans*- and *cis*-olefins gave the corresponding *trans*-oxides as the sole epoxidized product. In entries 21–24, the recovered amount of *trans*-olefins were as low as that of *trans*-stilbene (entry 10) and corresponding oxides were given in fairly good or excellent yields. It should be noticed that olefins having bulky substituents, such as 4-*tert*-butylphenyl and 2-naphthyl, could be oxidized successfully on the mesoporous catalyst.

Reactions of five kinds of *cis*-olefins gave oxides with *trans* configuration. The formation of corresponding *trans*-olefins was also observed. These results will be discussed in the next section. Comparing the oxidations of the

TABLE 6

Catalytic Epoxidation of Various Stilbene Derivatives on Mn-MCM-41[a]



	Starting olefin		Yield of oxide (%)		Recovered olefin (%)	
Entry	Ar	Configuration	*trans*	*cis*	*trans*	*cis*
10	C_6H_5	*trans*	93	0	3	0
21	4-Cl-C_6H_4	*trans*	81	0	5	0
22	4-Me-C_6H_4	*trans*	97	0	2	0
23	4-*t*Bu-C_6H_4	*trans*	70	0	3	0
24	2-$C_{10}H_7$	*trans*	62	0	1	0
25	C_6H_5	*cis*[b]	50	<1	7	39
26	4-Cl-C_6H_4	*cis*	46	0	9	44
27	4-Me-C_6H_4	*cis*[c]	73	0	9	18
28	4-*t*Bu-C_6H_4	*cis*	60	0	5	20
29	2-$C_{10}H_7$	*cis*[d]	82	0	5	13

[a] Reaction conditions: 0.50 mmol *trans*-stilbene, 0.050 mmol manganese in Mn-MCM-41 (Si/Mn = 73 for entries 21–29), 10 cm^3 MeCN + DMF (9 : 1 v/v), 7.0 mmol TBHP (70% in H_2O), 348 K, 48 h, under Ar atmosphere.

[b] Contains 1.5% of *trans*-olefin.

[c] Contains 5.2% of *trans*-olefin.

[d] Contains 2.7% of *trans*-olefin.

respective *trans* and *cis* isomers, *trans* isomers were more rapidly oxidized than *cis* isomers. In case of 2-naphthyl, the amount of oxide obtained from the *cis* isomer was greater than that from the *trans*, but the amount of olefin recovered in the former reaction was larger than that in the latter. This suggests the easier oxidation of the *trans* isomer and the oxide produced. The higher reactivity of the *trans* isomer is in contrast to the higher reactivity of the *cis* isomers on Mn-salen complex (40) and Ti-MCM-41 (34). In general, *trans* isomers could reach the active sites more easily in pores due to the smaller steric hinderance than *cis* isomers. This cannot explain, however, the difference between the results on Mn- and Ti-MCM-41 catalysts; more detailed study on the reaction mechanism should be carried out in the future.

The shape selectivity was more clearly confirmed on Mn-ZSM-5. With *trans*-stilbene, Mn-ZSM-5 catalyst gave *trans*-oxide in 77% yield, as already mentioned (entry 14), while neither *trans*- nor *cis*-epoxide was produced from *cis*-stilbene under the same reaction conditions, and most of the substrates were recovered as such.

2. Reaction Mechanism

As described in Table 6, the *cis*-olefins were converted to the *trans* products. In entry 25, for example, the epoxidation of *cis*-stilbene gave *trans*-stilbene oxide as the major product and the yield was 50%. The yield of *cis*-stilbene oxide was less than 1%. In addition, 7% *trans*-stilbene was obtained. It was confirmed in separate experiments that the isomerizations between *trans*-stilbene oxide and *cis*-stilbene oxide under the same reaction conditions and between *trans*-stilbene and *cis*-stilbene in the absence of the oxidant did not proceed. Thus, the geometric change from *cis* to *trans* observed should occur during the catalytic oxidation process. In general, two kinds of reaction mechanisms have been suggested for the metal ion-catalyzed epoxidation (42). The first is a concerted addition of oxygen, which is widely reported on various ions. The second is a radical epoxidation mechanism.

On titanium-loaded MCM-41 (34), *cis*-stilbene oxide was the sole oxidation product in the *cis*-stilbene oxidation, which suggests the radical-free oxidation mechanism. In the same literature, it has been mentioned that Ti-MCM-41 could not catalyze an epoxidation of *trans*-stilbene. The product distribution and isomerization observed on the present Mn-MCM-41 are completely different from these. It could be suggested that the oxidation on Mn-MCM-41 proceeds through the radical oxidation mechanism: The active oxygen species on manganese reacts with stilbene to yield an intermediate radical which has a long enough lifetime to rotate around the single carbon–carbon bond and isomerize. Thus, the thermodynamically stable *trans* isomer could become the major product and a part of the intermediates would undergo the reverse reaction to give *trans*-stilbene.

ACKNOWLEDGMENTS

Financial support by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Culture, and Sports of Japan is gratefully acknowledged. When the authors began the present study, professor Tsutomu Katsuki of Kyusyu University gave helpful suggestions and discussion. Our great thanks are given to him. The authors also thank Dr. Hiroshi Takeguchi for analysis of by-products by GC-MS.

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