

Strategies to improve the epoxidation activity and selectivity of Ti-MCM-41

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Two strategies to improve the catalytic activity of Ti-MCM-41 materials in the epoxidation of olefins are described; the first approach involves silylation of the surface of Ti-MCM-41 which produces a very hydrophobic catalyst whereas the second approach is based on removal of water from the reaction media; the increase in activity is not due to a change in the intrinsic activity of the Ti sites, but rather to a decrease of the catalyst deactivation by reducing the formation of diols produced by ring opening of the epoxide.

The discovery of TS-1,¹ and its extension to Ti-beta² and Ti-MCM-41³ have broadened the scope of these interesting catalysts to include the oxidation of large hydrocarbon molecules.^{3–6} It has been shown with these catalytic systems that the hydrophobic/hydrophilic properties of the surface are just as important as the number of active sites. Control of the hydrophobicity of the molecular sieve allows the optimization of the adsorption of reactants and products.^{7,8} This is especially true for the epoxidation of olefins where, irrespective of the nature of the oxidant, the epoxide has higher polarity than the olefinic substrate. Consequently, the epoxide competes more favorably for adsorption on the hydroxylated surfaces of the Ti-silicates.⁵ In this respect, the presence of silanol groups as well as the presence of =Ti–OH groups allows adsorption of the epoxide and results in ring opening of the epoxide and the formation of diols. As discussed later, the diols tend to strongly adsorb on the Ti sites and lead to partial deactivation of the catalyst.

We have shown that by decreasing the concentration of the internal silanol groups in Ti-beta, it is possible to significantly increase the selectivity to the epoxide.⁷ In the case of materials such as Ti-silica and Ti-MCM-41, which contain a large number of silanol groups, the silanol content can be reduced by reaction with organosilanes^{9,10} or by introducing organosilanes directly to the synthesis gel of mesoporous materials,^{11–13} and this modification is reflected in the final properties of the catalyst.^{13,14} In this manner it has recently been shown that silylated Ti-MCM-41 gives better selectivity to the epoxide when hydrogen peroxide is used as an oxidant.¹⁴ However, the cyclohexene conversion was 13% of the maximum conversion achievable and the selectivity to the epoxide was only 13%. Thus, as shown previously by us,¹⁵ hydrogen peroxide is not an appropriate oxidant for Ti-MCM-41 and consequently the poor performance is not surprising.

It appears that Ti-MCM-41 has the greatest potential as an epoxidation catalyst when organic hydroperoxides are used as the oxidant.¹⁶ Here we will describe two different strategies that give results superior to those that have been reported up to now. In this way, two different samples of Ti-MCM-41 were prepared. The first sample was obtained from a gel having the following molar composition: SiO₂:0.015 Ti(OEt)₄:0.26 CTABr:0.26 TMAOH:24.3 H₂O where CTABr is cetyltrimethylammonium bromide and TMAOH is tetramethylammonium hydroxide. The silica source, Aerosil-200, was

obtained from Degussa. The crystallization was performed at 100 °C for 48 h in Teflon lined stainless steel autoclaves. The occluded surfactant was completely removed following a two step extraction procedure.

Ti-MCM-41 was silylated with hexamethyldisilazane (HMDS) as the silylating agent. The silylated samples are referred to as Ti-MCM-41S. The silylation was carried out at 120 °C with a solution of HMDS in toluene under inert atmosphere.

The MCM-41 structure was preserved after silylation and the surface area of the silylated sample was close to 1000 m² g⁻¹.

Samples with different levels of silylation were obtained by changing the HDMS/Ti-MCM-41 ratio as shown in Table 1. The carbon content, determined by elemental analysis, was used to calculate the degree of surface coverage (Table 1).

The catalytic activity of these materials was measured in the epoxidation reaction of cyclohexene with *tert*-butylhydroperoxide (TBHP) at 60 °C. The olefin/TBHP ratio was to 4 mol mol⁻¹ and the liquid/catalyst ratio was 20 g g⁻¹.

The results shown in Fig. 1 clearly indicate that the catalyst activity and selectivity increase with the level of silylation and much higher conversions and selectivities than those reported up to now have been achieved in this work. It is of interest that relatively low levels of silylation significantly improve the catalyst selectivity to the epoxide, but that over the range of silylation there is very little influence on the catalytic conversion. On the other hand, a significant improvement in catalytic activity is observed when the silylation gives rise to a surface coverage of >40%. In this case, the selectivity to the epoxide is close to 100%.

The hydrophobicity of Ti-MCM-41S materials was estimated from the weight loss of the fully hydrated sample at 150 °C. We found that there is a linear correlation between the hydrophobicity and the surface coverage with trimethylsilyl groups as shown in Fig. 2. Therefore, one can conclude from Figs. 1 and 2 that in order to obtain a highly active and selective catalyst for epoxidation it is necessary to silylate Ti-MCM-41 above 40% or preferably close to 100%.

Table 1 Silylation conditions and degree of silylation achieved on Ti-MCM-41 catalysts

Sample	Ti content (wt.% TiO ₂)	HMDS/sample	C content (wt.%)	Surface coverage ^a (%)
Ti-MCM-41	1.9	—	—	0
Ti-MCM-41S1	1.9	0.026	4.2	33
Ti-MCM-41S2	1.8	0.034	7.9	63
Ti-MCM-41S3	2.1	0.123	10.3	82
Ti-MCM-41S4	2.0	0.260	11.9	95

^a The calculated surface coverage per trimethylsilyl group is 47.6 Å² molecule⁻¹,¹⁷

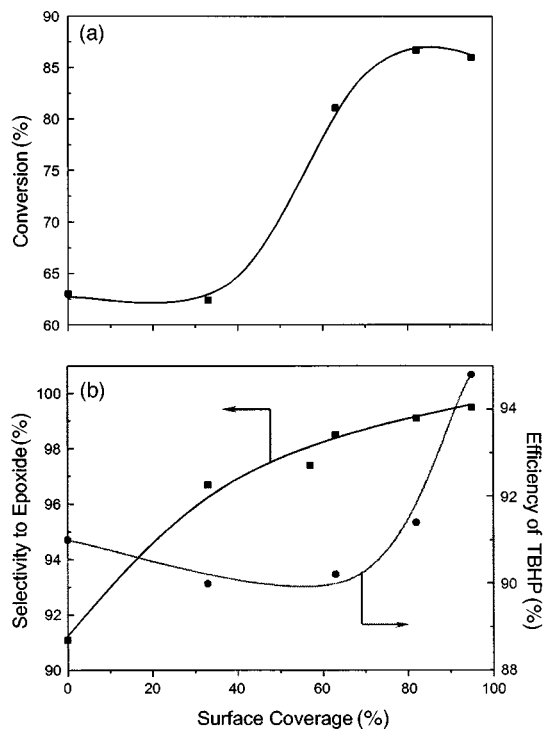


Fig. 1 Catalytic activity in the epoxidation of cyclohexene with TBHP of silylated Ti-MCM-41 at different degrees of surface coverage; (a) catalytic conversion after 30 min of reaction. (b) selectivity to epoxide and efficiency of TBHP at 85% cyclohexene conversion

Nevertheless, it was surprising to find that every hydrophobic Ti-MCM-41 catalysts were required in order to have highly active and selective epoxidation catalysts even when only organic reactants were used. This motivated us to analyze the amount of water contained in the reactants, and it was found by means of ^1H NMR that the TBHP contained 8 wt.% water. Then, we carried out the epoxidation of cyclohexene with TBHP which was dried using 4 Å molecular sieves. With ^1H NMR we determined that no decomposition of TBHP occurred and the remaining amount of water was below the detection limit of ^1H NMR. Under these conditions and using the non-silylated catalyst Ti-MCM-41, which contains 13.5 wt.% water adsorbed on the catalyst, the total conversion and selectivity to the epoxide obtained after 30 min of reaction were 85 and 97%, respectively. These results are very similar to those obtained with the completely silylated sample Ti-MCM-41S4 when using the as-received commercial TBHP.

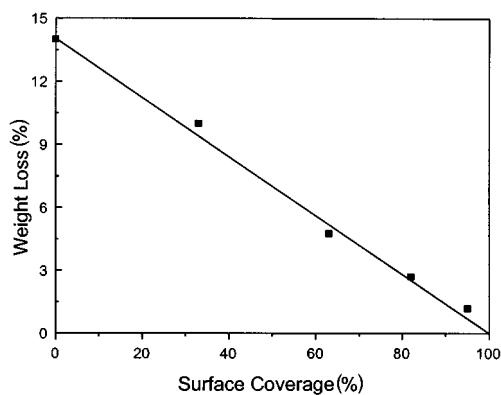


Fig. 2 Variation of the hydrophobicity, calculated as the weight loss at 150 °C by thermogravimetry, with the degree of silylation of Ti-MCM-41 catalysts

An additional experiment was carried out with dry TBHP and dry catalyst Ti-MCM-41. After 30 min the conversion was 91% and the selectivity was 100%. These results are the best conversion and selectivity to epoxide ever reported using Ti-based catalysts for epoxidation processes.

We conclude that the presence of water is responsible for the ring opening of the epoxide. However, its influence goes beyond the selectivity effect, since the diols resulting from the ring opening of the epoxide strongly decrease the catalytic conversion. We have seen this effect by performing the epoxidation reaction using dried TBHP, but adding 3.07 mmol of cyclohexanediol which corresponds to a typical amount of the diol formed during the catalytic experiments when non-dried TBHP is used. Under these conditions, the conversion is significantly reduced to 13% after 30 min of reaction. This result suggests that the increase in activity observed when using either silylated Ti-MCM-41 or non silylated Ti-MCM-41 with dry reactants is due to the significant decrease in the formation of diols which act as catalyst poisons for the Ti sites.

In conclusion we have presented two different strategies that can be used to obtain remarkably active and selective epoxidation catalysts based on Ti-MCM-41. The first strategy relies on the use of highly silylated samples and greater than 40% silylation coverage is required. In this case water can be present in the reaction media up to levels of 3 wt.%. On the other hand, one can use non-silylated catalysts, but in this case water must be removed from the reaction media.

It is also concluded in this work that the increase in activity observed with the silylated hydrophobic catalyst or with the absence of water in the reaction medium, is probably not due to a change of the intrinsic activity of the Ti catalytic sites but rather to a decrease in catalyst deactivation. An increase in catalyst stability is obtained by reducing the formation of diols that are produced by ring opening of the epoxide in the above conditions.

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Notes and References

- 1 M. Taramasso, G. Perego and B. Notari, *US Pat.*, 4 410 501, 1983.
- 2 M. A. Cambor, A. Corma, A. Martínez and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1992, 589.
- 3 A. Corma, M. T. Navarro and J. Pérez-Pariente, *J. Chem. Soc., Chem. Commun.*, 1994, 197.
- 4 T. J. Pinnavaia and W. Zhang, *Stud. Surf. Sci. Catal.*, 1998, **117**, 23.
- 5 S. Gontier and A. Tuel, *J. Catal.*, 1995, **157**, 124.
- 6 A. Corma, M. T. Navarro, J. Pérez-Pariente and F. Sánchez, *Stud. Surf. Sci. Catal.*, 1995, **84**, 69.
- 7 T. Blasco, M. A. Cambor, A. Corma, P. Esteve, J. M. Guil, A. Martínez, J. A. Perdigón and S. Valencia, *J. Phys. Chem. B*, 1998, **102**, 75.
- 8 M. A. Cambor, A. Corma, P. Esteve, A. Martínez and S. Valencia, *Chem. Commun.*, 1997, 795.
- 9 H. P. Wulff, *US Pat.*, 3 923 843, 1975.
- 10 K. A. Koyano, T. Tastumi, Y. Tanaka and S. Nakata, *J. Phys. Chem.*, 1997, **101**, 9436.
- 11 S. L. Burkett, S. D. Simis and S. Mann, *Chem. Commun.*, 1996, 1367.
- 12 C. E. Fowler, S. L. Burkett and S. Mann, *Chem. Commun.*, 1997, 1769.
- 13 A. Corma, J. L. Jordá, M. T. Navarro and F. Rey, *Chem. Commun.*, 1998, 1899.
- 14 T. Tatsumi, K. A. Koyano and N. Igarashi, *Chem. Commun.*, 1998, 325.
- 15 T. Blasco, A. Corma, M. T. Navarro and J. Pérez-Pariente, *J. Catal.*, 1995, **156**, 65.
- 16 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
- 17 Insight II Molecular User Guide, San Diego, Biosym/MSI, 1995.

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