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Is MCM-41 really advantageous over amorphous silica? The case of grafted titanium epoxidation catalysts†

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MCM-41 can be used in the same way as amorphous silica for the preparation of supported titanium catalysts; MCM-41 does not show clear advantages over silica in epoxidation reactions with either TBHP or H_2O_2; only in one case is a positive effect observed and this involves the recycled catalyst with H_2O_2.

Catalysts based on mesoporous crystalline silicas, especially MCM-41, have been widely applied in recent years.[1] Among the advantages proposed for this type of solid are the presence of a regular porous system, and the large pore size. In many cases comparisons have only been made regarding the behaviour of zeolites and MCM-41, and comparisons with amorphous silica are generally ignored.

Titanium catalysts are among the most important oxidation catalysts[2] and titanium centres can be incorporated in MCM-41[3,4] or amorphous silica[6–9] either within the framework, by substitution of silicon atoms,[3] or by grafting titanium species onto the surface. Several of these catalysts have been used in the epoxidation of alkenes with dilute hydrogen peroxide.[10–12] In the case of MCM-41, grafting has been described as being more efficient than framework substitution.[10,13,14] However, no direct comparison has been made between amorphous and crystalline mesoporous silicas. In this communication we report the behaviour of MCM-41 as a support for $Ti(OPr^i)_4$ using the same methodology employed for amorphous silica.

The synthesis of pure siliceous MCM-41[15] and titanium grafting[7] were carried out as previously described. The titanium loading onto MCM-41 (Table 1) is in good agreement with the surface area of the support (802 $m^2\ g^{-1}$) and the reported density of hydroxy groups[16] (*ca.* 2 OH nm^{-2}). In the case of amorphous silica, this agreement (1.07 mmol g^{-1}, 475 $m^2\ g^{-1}$, 3.7 hydrogen-bridged OH nm^{-2}) is also observed. Treatment of the catalyst with tartaric acid was carried out as described for silica.[12] The Ti content of MCM-Ti(TA) was found to be very similar to that found in the silica counterpart (Table 1).

Si-Ti(OPr^i) has previously been characterised by MAS-NMR,[7] EXAFS[18] and IR.[12] The similarity of the IR spectra of the solids (ESI†), together with the agreement observed in the titanium loading, seem to indicate that the surface species' are similar irrespective of the structure of the silica. The exclusion of water in the preparation method prevents the formation of titania (anatase) on the silica surface, as demonstrated by the absence of a UV absorption above 300 nm.

All the catalysts were tested in the epoxidation of cyclohexene with 30% hydrogen peroxide in *tert*-butyl alcohol at 353 K (Scheme 1). The active hydroperoxotitanium species is able to epoxidise directly cyclohexene with hydrogen peroxide and also to produce free radicals, which give rise to an allylic hydroperoxide. This compound can also be involved in titanium-catalysed epoxidation of cyclohexene, leading to cyclohex-2-en-1-ol as a by-product. Finally, the acidity of the catalyst promotes the hydrolysis of cyclohexene oxide to the corresponding diol. The results of this study are gathered in Table 1.

As far as catalysts prepared with $Ti(OPr^i)_4$ are concerned, MCM-41 leads to a solid that is less active than the silica-based one in terms of both hydrogen peroxide conversion and turnover number to epoxidation products. Moreover, the epoxidation/allylic oxidation selectivity is also slightly lower, indicating a lower contribution of the direct epoxidation. The main advantage of MCM-41 comes from the reusability of the catalyst, in fact the turnover number for epoxidation products is nearly constant up to the third run. However, the epoxidation/allylic oxidation selectivity is almost 50/50, which indicates that only

Table 1 Results obtained in the epoxidation of cyclohexene with dilute H_2O_2 in the presence of titanium catalysts[a]

Catalyst	Run	Ti content[b]	H_2O_2/Ti	Conv. H_2O_2[c]	Yield[d] (24 h)				TON (ep + diol)	(ep + diol)/enol	ep/diol
					ep	diol	enol	chhp			
Si-Ti(OPr^i)	1	1.07	58.4	72	9	21	12	15	17.2	71/29	29/71
	3[e]	0.74	86.7	75	2	2	7	32	3.6	36/64	50/50
MCM-Ti(OPr^i)	1	1.25	50.0	56	9	14	13	10	11.4	64/36	37/63
	3[e]	1.01	61.9	67	3	12	18	17	9.3	44/56	20/80
Si-Ti(TA)	1	0.99	63.0	92	9	32	15	18	25.3	73/27	22/78
	3[e]	0.56	111.6	108	19	28	35	13	52.8	57/43	40/60
MCM-Ti(TA)	1	1.01	61.9	37	5	18	12	1	14.3	66/34	22/78
	3[e]	0.94	66.5	38	10	7	13	4	10.6	56/44	59/41

[a] *Reaction conditions*: 200 mg catalyst, 250 mmol cyclohexene, 12.5 mmol H_2O_2 (30%), 25 mL *tert*-butyl alcohol 353 K, 24 h. [b] mmol g^{-1} [c] % conversion to cyclohexene oxidation products. [d] Determined by gas chromatography. ep = cyclohexene oxide; diol = *trans*-cyclohexane-1,2-diol; enol = cyclohex-2-en-1-ol; chhp = cyclohexenyl hydroperoxide. [e] Ti content after the third run. Ratios are referred to this value.

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† Electronic supplementary information (ESI) available: experimental details of preparation and characterisation of the catalysts, IR spectra and results of the cyclohexene epoxidation with TBHP. See http://www.rsc.org/suppdata/cc/b1/b103057b/

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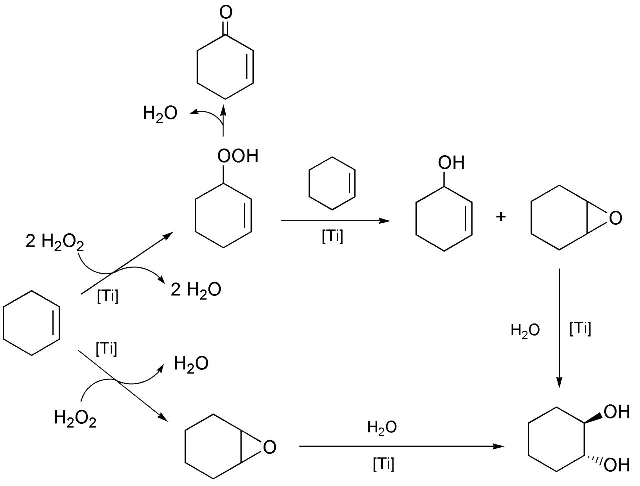

Scheme 1

the radical mechanism takes place with the recovered catalyst. The presence of different titanium species, with either two or three bonds to the surface, or the higher titanium dispersion due to the larger surface area of MCM-41 could be responsible for these differences in behaviour.

Treatment with tartaric acid improves the activity of the silica-based catalyst without causing a modification in the epoxidation/allylic oxidation selectivity. This higher activity is reflected in the higher hydrogen peroxide conversion and the higher turnover number for epoxidation products. It has been shown that some of the titanium species generated in the treatment with tartaric acid are able to pass into solution.[12] However, some other more active species remain on the solid, as shown by the higher turnover number attained with the recovered catalyst. Even with this recovered catalyst the epoxidation/allylic oxidation selectivity is > 50/50, signifying a contribution of the direct epoxidation with hydrogen peroxide. Similar treatment with tartaric acid does not cause the same beneficial effect in the case of the MCM-41 catalyst. This solid is much less active in terms of the productive conversion of hydrogen peroxide and turnover numbers and, in addition, the selectivities are very similar to those obtained with the parent MCM-Ti(OPr^i) catalyst. In this case the species are more strongly bonded to the surface, as demonstrated by the lower degree of titanium leaching.

A particularly interesting point concerns the stability of these catalysts in comparison to other similar systems described in the literature. One of the few studies regarding the stability of grafted titanium species on MCM-41 describes a titanium loss of 50–61% after two reactions, with a total H_2O_2/Ti ratio in the range 228–686.[10] However, this leaching does not seem to be proportional to either the H_2O_2/Ti ratio or the catalytic activity. In our case, titanium loss is 7–19% for MCM catalysts after three runs, with a total H_2O_2/Ti ratio in the range 150–200. These values indicate that the solids described here have a higher stability. The solids described here also show a higher stability in comparison with related silica-based catalysts.[8] This stability is demonstrated by the the fact that catalysts prepared with TiF_4 or tetraneopentyltitanium cannot be used with dilute hydrogen peroxide.

The IR spectra of the recovered catalysts (ESI†) show that some by-products remain adsorbed on the surface.

Another interesting feature of these systmes is the lower content of cyclohexenyl hydroperoxide (chhp) in the final reaction mixture when MCM-41-based catalysts are used. This may be due to a higher activity of these catalysts in the epoxidation with alkyl hydroperoxides or to a more rapid deactivation of the silica-based catalysts. In order to clarify this point, the four catalysts were compared in the epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP). The results (ESI†) show that the catalysts with isopropoxy groups have nearly the same catalytic activity and selectivity. Treatment with tartaric acid noticeably reduces the activity, irrespective of the type of support, but Si-Ti(TA) is clearly more active than MCM-Ti(TA). Thus, the hypothesis regarding the higher activity of MCM-catalysts is not confirmed.

In conclusion, the three factors studied (support, titanium environment and nature of the oxidant) have a significant influence on both the results of the reaction and the stability of the catalyst. Furthermore, the three factors are not completely independent and a careful selection of each parameter is necessary to optimise the behaviour of this kind of catalyst.

Treatment of MCM-41 with tartaric acid has a detrimental effect with both oxidants used (H_2O_2 and TBHP) in such a way that silica-grafted systems become far more active. On using amorphous silica, treatment with tartaric acid leads to a catalyst that is more active in the epoxidation with dilute hydrogen peroxide but is less active with TBHP. Ti(OPr^i) species immobilised on amorphous silica are only slightly more active than those grafted onto MCM-41. However, the use of the crystalline MCM-41 leads to more stable catalysts.

It is clear that none of the supports are particularly advantageous over the others and that the choice of one or other is influenced by other factors concerning the titanium environment and the reaction conditions.

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