Synthesis of titanium-containing mesoporous molecular sieves with a cubic structure

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A titanium-containing mesoporous material with a cubic structure, Ti-MCM-48, is synthesized by a two-stage hydrolysis method using tetraethylorthosilicate and tetrabutylorthotitanate and found to be more active than Ti-MCM-41 in the epoxidation of bulky alkenes using H_2O_2.

The recent discovery of a new family of mesoporous molecular sieves denoted M41S has received much attention.[1] The M41S family is classified into several members: MCM-41 (hexagonal), MCM-48 (cubic) and other species. Ti- and V-substituted MCM-41 and Ti-substituted hexagonal mesoporous silica (Ti-HMS) have also been synthesized.[2–5] These Ti- and V-substituted mesoporous molecular sieves pioneered the potential for oxidization of bulky molecules which cannot enter into the micropores of zeolites such as TS-1, TS-2 and Ti-beta. MCM-48, characterized by a three-dimensional channel system, may have several advantages over MCM-41 with a one-dimensional channel system when applied to catalytic reactions: for instance, the three-dimensional pore system should be more resistant to blockage by extraneous materials than the one-dimensional pore system. Here we report the synthesis of Ti-MCM-48 and its use as a catalyst for epoxidation of bulky alkenes. The effects of gel composition and the gel preparation method on the structure of mesoporous materials are also reported.

Mesoporous materials were synthesized under hydrothermal conditions at 373 K in a static Teflon bottle for 10 days. The procedures of gel preparation were as follows. For the preparation of pure silica mesoporous materials, an aqueous solution of cetyltrimethylammonium chloride/hydroxide (CTMACl/OH, Cl/OH = 70/30) was added dropwise to tetraethylorthosilicate (TEOS) under vigorous stirring at 278 K. After stirring for 1 h, the mixture was heated at 358 K for 4 h to remove the ethanol produced in the hydrolysis of the TEOS. For the synthesis of titanium-containing mesoporous materials, two types of hydrolysis method were employed. Ti-MCM-48(1) was prepared by a one-stage hydrolysis method: TEOS and tetrabutylorthotitanate (TBOT) were hydrolysed simultaneously after being mixed for 30 min at 298 K. Ti-MCM-48(2) was prepared by a two-stage method. To a 44% solution of TEOS in propan-2-ol, CTMAOH in methanol and water–TEOS (2 : 1 mole ratio) were added to partly hydrolyse the TEOS at 278 K. After 1 h, a solution of TBOT in propan-2-ol was added to this resultant mixture very slowly under vigorous stirring. The mixture was then stirred for 1 h, when the aqueous solution of CTMACl was added. When water glass [SiO_2 (28–30%)–Na_2O (9–10%)] was used as the Si source, sulfuric acid was added to the mixture in order to adjust the pH to 11.6 and CTMACl was used as the template. The molar compositions of the gels subjected to hydrothermal synthesis were as follows: $SiO_2 : xTiO_2 : yNa_2O : CTMA : zH_2O$, where $0 < x < 0.02$, $y = 0$ (TEOS) or 0.32 (water glass), and $46.5 < z < 69.8$. A typical oxidation run used 50 mg of a catalyst in 20 mmol of substrate in a round-bottomed flask, to which was added 24 mmol of an oxidant [H_2O_2 as 30% aqueous solution or *tert*-butyl hydroperoxide (TBHP) as an 80% aqueous solution]. The resulting mixture was stirred at 323 K for 2 h. The products were analysed on a gas chromatograph equipped with a 2 m OV-17 glass column.

Vartuli *et al.* have reported that the surfactant/silica molar ratio (surf/Si) is a critical variable in the formation of M41S materials; cubic mesoporous material MCM-48 was formed when the surf/Si ratio was adjusted to 1–1.5.[6] We attempted the synthesis of mesoporous materials by varying the concentration of the surfactant with the surf/Si ratio kept constant at 1.0. At 20.0 mass% of CTMACl/OH (70/30) (H_2O/CTMA = 69.8), MCM-41 was exclusively obtained. The structure was transformed from hexagonal into cubic with increasing concentration of the surfactant (Table 1), in good agreement with the effect of concentration on the formation of a liquid-crystal phase for the CTMA system;[7] the cubic phase is favoured over the hexagonal phase at higher concentrations for the chloride-containing system. Obviously, the structure of the products was affected not only by surf/Si but also by the surfactant concentration. Using TBOT as the Ti source, Ti-MCM-48-(1) and -(2) molecular sieves were successfully obtained from the gels with the following molar compositions $SiO_2 : 0.01\ TiO_2 : 0.7\ CTMACl : 0.3\ CTMAOH : 46.5\ H_2O$. The increase in the Ti content to Si/Ti = 50 (two-stage hydrolysis method) resulted in the formation of an ill-defined mesoporous material, which showed only one strong (211) diffraction line. Using water glass as the Si source instead of TEOS, MCM-41 was obtained from the gels with the same surf/Si and H_2O/surf ratios from which MCM-48 was obtained; the Si source or the presence of Na affected the structure of the products. It has been shown that the addition of Na^+ dramatically changes the phase diagram of aqueous CTMA.[8]

The X-ray diffraction pattern of Ti-MCM-48 materials closely matched that of the pure silica isomorph reported by Vartuli *et al.*[6] As shown in Fig. 1, Ti-MCM-48(1) exhibited a very strong peak at d = 35.6 Å and medium or weak peaks at d = 31.0, 23.4, 21.8, 19.5, 18.6, 17.9 and 17.2 Å. These eight peaks were indexed on a cubic unit cell with a = 87.2 Å. The nitrogen physisorption isotherms of the Ti-MCM-48 samples and the pure silica isomorph were characteristic of mesoporous materials with uniform pore size. The average pore diameter of all samples determined by the Dolimore–Heal method was 25.2 Å and the BET surface area was *ca.* 1000 $m^2\ g^{-1}$.

The UV–VIS spectra for the Ti-MCM-48 samples are shown in Fig. 2. The band at 220 nm has been assigned to isolated

Table 1 Effect of concentration of surfactant and Si source on the structure of products

Si source[a]	Si/Ti[b]	H_2O/CTMA	Structure
TEOS	0	69.8[c]	hexagonal
TEOS	0	46.5[c]	cubic
TEOS	100	46.5[c]	cubic
TEOS	50	46.5[c]	ill-defined mesoporous
water glass	0	46.5	hexagonal

[a] TEOS: tetraethylorthosilicate, Si/CTMA = 1.0. [b] Ti source: tetrabutylorthotitanate. [c] CTMACl/OH = 70/30. *Hydrothermal synthesis conditions*: 373 K; 10 days; under static conditions.

framework titanium in tetrahedral coordination.[9] Ti-MCM-48(1) showed a broad shoulder at *ca.* 270 nm attributed to extraframework titanium.[10] The anatase band, which occurs at 312 nm, seems to be superimposed on this band. In contrast, Ti-MCM-48(2) proved to be essentially free of extraframework titanium. These results indicate that the two-stage hydrolysis method is favourable for the isomorphous substitution of Ti for Si. This is interpreted in terms of the prerequisite condition for the efficient incorporation of Ti in the zeolite framework observed for TS-1: the rate of hydrolysis of Ti alkoxide should match that of Si alkoxide.[11]

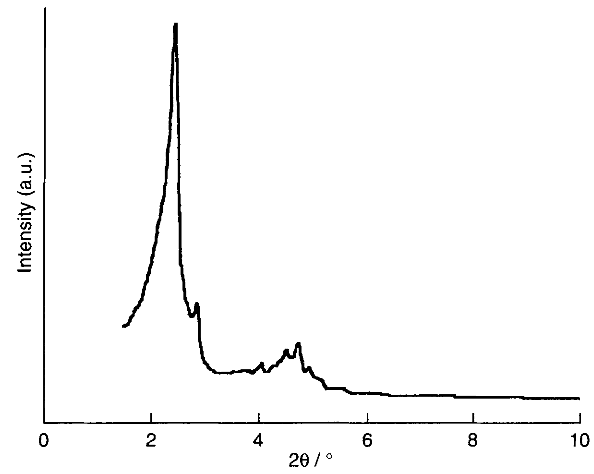

Fig. 1 X-Ray powder diffraction pattern of Ti-MCM-48(1)

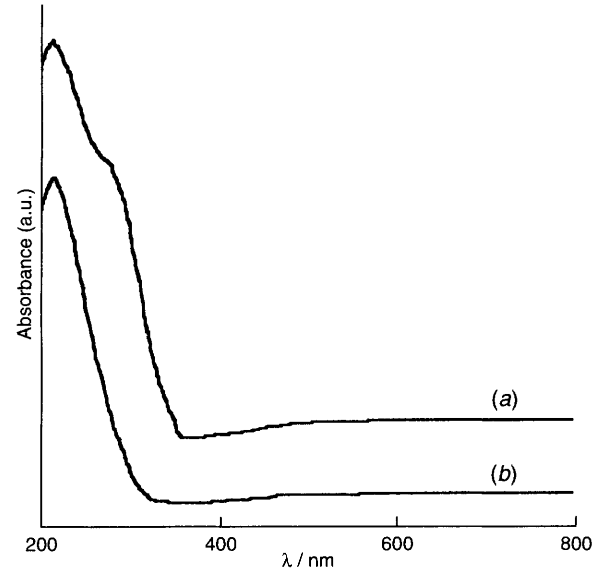

Fig. 2 UV–VIS spectra of (*a*) Ti-MCM-48(1) and (*b*) Ti-MCM-48(2)

Table 2 Epoxidation of cyclododecene on titanium-containing materials

		Turnover number [mol (mol Ti)$^{-1}$] Oxidant	
Catalyst	Si/Ti	H_2O_2	TBHP
Ti-MCM-41(2)	71	0.73 (54/46)[a]	—
Ti-MCM-48(1)	80	1.50 (59/41)[a]	7.1(34/66)[a]
Ti-MCM-48(2)	83	1.61 (58/42)[a]	—
TS-1	79	0	—
TiO_2-SiO_2	85	0.057 (—)[a]	2.6 (30/70)[a]

Reaction conditions: 50 mg catalyst; 20 mmol cyclododecene (*cis*/*trans* = 75/25); 24 mmol oxidant; 323 K; 2 h. The reaction mixtures were separated by use of a funnel into aqueous and organic phases, and both were analysed by gas chromatography. [a] *cis*/*trans* ratio of products.

The oxidation of cyclododecene (*cis*/*trans* = 75/25) was performed using Ti-MCM-48, Ti-MCM-41, TS-1 and amorphous TiO_2–SiO_2 with H_2O_2 or TBHP as the oxidant at 323 K. Ti-MCM-41 was synthesized at surf/Si = 0.6, H_2O/CTMA = 75, and Si/Ti = 80 by the two-stage method. As shown in Table 2, cyclododecene was epoxidized to cyclododecene oxide with either TBHP or H_2O_2 on Ti-MCM-48 and Ti-MCM-41. Preference for the epoxidation of *trans*-isomer was obtained for both oxidants. No other products were detected. The high activity of Ti-MCM-48 materials compared to Ti-MCM-41 may be due to the three-dimensional pore structure of Ti-MCM-48; Ti-MCM-48(2) was slightly more active than Ti-MCM-48(1). Amorphous TiO_2–SiO_2 showed a very low activity in the epoxidation using H_2O_2. Compared with Ti-MCM-48(1), TiO_2–SiO_2 showed a much more substantial difference in activity with H_2O_2 and TBHP, probably owing to severe inhibition of the catalyst by water.[12] No products were obtained with TS-1 probably as a consequence of the inability of cyclododecene to diffuse into the pores of TS-1 (5.6 × 5.3 Å). Ti-MCM-48 was also applicable for the epoxidation of other alkenes. In the oxidation of pent-2-en-1-ol (10 mmol) using Ti-MCM-48(2) (100 mg) with H_2O_2 (60 mmol), oxidation products were obtained in 17% yield (turnover number = 95); selectivities for epoxidation of the double bond and oxidation of –OH group to –CHO were 46 and 54%, respectively. The high reactivity of pent-2-en-1-ol compared to cyclododecene may be ascribed to enhancement by the OH group.[13]

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