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Catalytic epoxidation of unsaturated alcohols on Ti-MCM-41

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Abstract

The catalytic epoxidation of a series of unsaturated terpenic alcohols was carried out on titanium-containing MCM-41 mesoporous materials with *tert*-butylhydroperoxide. A direct comparison between in-framework Ti-MCM-41 and Ti-grafted MCM-41 showed a better performance of the latter, even if the difference between them becomes lower as the alcoholic group approaches the C=C double bond. At 358 K and in both acetonitrile and ethyl acetate, the epoxidation rate of the double bond is ruled, on these catalysts, mainly by electronic factors, which cause the preferential oxidation of internal unsaturations instead of the terminal ones. It is also governed by the OH-function position, so that, particularly in ethyl acetate, the closer the hydroxyl group to the unsaturation, the higher is the conversion rate of the terpene. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Titanium silicate based catalysts as TS-1 have been studied in many selective oxidations, although pore-size limitations reduce applicability to relatively small molecules only [1,25]. The synthesis of larger pore titanium-containing molecular sieves as Ti-beta zeolite circumvented this problem leading to the preparation of supports with large pores (up to ca. 0.7 nm) accessible to bulkier and more functionalized molecules [2]. Later, when the discovery of the M41S class of mesoporous solids, to which both MCM-41 and MCM-48 belong, was reported [3], a wider series of silicates with tunable pore diameters between 1.5 and 10 nm was available. Hundreds of papers in the last five years show how transition metals can be accommodated on such versatile materials either by isomorphous substitution or by grafting a metal precursor onto the support surface [4]. With regard to the alkene epoxidation, titanium-containing MCM-41 solids as well have been prepared incorporating the Ti precursor during sol–gel synthesis [5,6] or anchoring titanocene dichloride onto the already structured silicate [7,26]. The latter catalyst, showing highly dispersed surface active sites, performs mainly better than the former [8]. On the other hand, as a matter of fact, in most cases the performances of these materials were tested only on poorly functionalized molecules, as cycloalkenes or olefinic terpenes, and on catalysts with rather different titanium content, even if varying the metal loading may induce changes in the surface species and may modify, sometimes noticeably, the catalytic features [9].

Now, since these new materials allow the entrance of bulkier substrates, it might be worth studying the

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effect of substituents and checking whether there is any remarkable difference between the behavior on these mesoporous solids and that observed with the well studied homogeneous catalysts.

Taking into account the epoxidation of unsaturated alcohols, although electron-withdrawing groups generally retard the rate of this reaction, it was noted in early 1970s that allylic alcohols react faster and more selectively than the corresponding simple alkenes [10]. Because of this reason, the dependence of reactivity with respect to the distance of OH-group from the double bond, well studied in homogeneous catalysis [11,27], was studied here in the epoxidation of a series of unsaturated terpenic alcohols on titanium-based MCM-41 materials. In fact, though the introduction of an alcoholic function has a negative impact on the amorphous aerogel-catalyzed epoxidations [12], the presence of a polar group close to double bond might also help the hydrophobic unsaturation to approach the hydrophilic surface of the catalyst [13]. A direct comparison is also reported here between the catalytic performances of a Ti-incorporated MCM-41 and a Ti-grafted solid, with comparable metal loadings, in the epoxidation of these polyfunctional compounds.

2. Experimental

2.1. Synthesis

MCM-41 and [Ti]-MCM-41 (Ti ions in the framework) were synthesized according to procedures developed by Mobil researchers [3,14] and Corma et al. [5,15], respectively. Some simplifications to the procedures were employed following suggestions reported by Di Renzo et al. [16]. The samples were prepared using hexadecyltrimethylammonium chloride (Fluka), tetraethyl orthosilicate (Fluka), tetraethyl orthotitanate (Aldrich) and ammonia solution (33 wt.%) (Allied Signal). Following Corma et al. [15] we avoided any alkali metal cations in the reaction mixture. Hexadecyltrimethylammonium chloride was dissolved in ammonia solution at room temperature. After addition of tetraethyl orthosilicate (and tetraethyl orthotitanate for the preparation of [Ti]-MCM-41), the mixture was stirred for 90 min before heating at 343 K for 5 h. The solid product was washed with water, dried at room temperature overnight and finally calcined in air at 823 K for 5 h.

Ti-MCM-41 (Ti grafted onto the MCM-41 surface) was prepared starting from MCM-41 according to the grafting technique proposed by Thomas and co-workers [7,26], using a solution of titanocene dichloride (Aldrich) in chloroform (Carlo Erba, RPE) and triethylamine (Aldrich).

Ti content was determined by ICP-atomic emission spectroscopy. The samples (50.0 mg) were dissolved with 0.50 ml of aqueous hydrofluoric acid (Fluka; 40 wt.%) in a PTFE beaker. After dissolution, they were transferred into a 1.000 l calibrated flask and diluted to volume with water. For ICP-AES measurements titanium atomic absorption standard solution (1000 μg ml^{-1} in H_2O) was purchased from Aldrich. The Si/Ti atomic ratio of [Ti]-MCM-41 and Ti-MCM-41 samples resulted in 36 and 41, respectively.

2.2. Characterization

The calcined samples were characterized by powder X-ray diffraction (XRD), UV–Vis diffuse reflectance spectroscopy (DRS) and N_2 adsorption–desorption isotherm at 77 K. The XRD patterns were obtained with a Philips automated PW 1729 diffractometer. Scans were taken at a 2θ step of 0.02° (2.5 s per step) in the range 1.5–10° using Cu Kα radiation (Ni filtered). Diffuse reflectance spectra were recorded using a Cary 5 spectrometer in the wavelength range 200–2500 nm. BET specific surface area, pore size distribution and total pore volume were determined from N_2 adsorption–desorption isotherm obtained using a manual volumetric technique. The samples were preheated at 10^{-2} Pa overnight at 393 K and for 2 h at 523 K. The pore structure analysis was based on the method of Brunauer et al. [17].

2.3. Catalytic experiments

Ti-MCM-41, [Ti]-MCM-41 and MCM-41 mesoporous solids were pretreated by heating at 773 K for 4 h in air. The epoxidation reactions of all terpenes were carried out in a glass batch reactor at 358 K. The solvents, acetonitrile (Aldrich, HPLC grade) or ethyl acetate (AcOEt; Carlo Erba, RPE), were previously dried on zeolites (Siliporite A). The terpenes were used as-received (Aldrich), except carvotanacetol **3**, prepared from carveol **5** by hydrogenation with Rh[$(PPh_3)_3$]Cl [18]. Anhydrous *tert*-butylhydroperoxide (TBHP; Aldrich, 5 M solution in decane) was used as oxidant (oxidant to substrate molar ratio=1.1) and the catalyst to substrate ratio was 30 wt.%. Samples were taken after a reaction time of 1, 3, 6 and 24 h and the products analyzed by gas chromatography (HP5890; DB-225 column, 30 m×0.25 mm; FID and MS detectors) and NMR spectroscopy. Turnover frequencies (TOF in mol epoxide $\mathrm{mol_{Ti}}^{-1}\,\mathrm{h}^{-1}$) were computed on the 1 h-conversion value; terpene conversions and 1,2-epoxide selectivities after a reaction time of 24 h. Mesitylene (Carlo Erba, RPE) was used as internal standard.

3. Results and discussion

XRD characterization. XRD patterns of calcined MCM-41, Ti-MCM-41 and [Ti]-MCM-41 samples are shown in Fig. 1. The peaks of the crystalline materials can be indexed in a hexagonal unit cell [14]. The most intense peak is relative to the (1 0 0) plane. The interplanar distance (d_{100}) and the hexagonal unit cell parameter (a) of the samples are presented in Table 1. No clear influence on the unit cell parameter due to the presence of Ti in the framework of MCM-41 has been demonstrated [15]. The d_{100} values were reported to be very sensitive to the degree of organization of the product [15]. Our data in Table 1 shows that MCM-41 and [Ti]-MCM-41 (Si/Ti=36) have about the same unit cell parameter.

Table 1
XRD d_{100} peak and hexagonal unit cell parameter for the calcined samples

Sample	d_{100} (Å)	a (Å)
MCM-41	35.6	41.1
[Ti]-MCM-41 (Si/Ti=36)	35.3	40.8
Ti-MCM-41 (Si/Ti=41)	39.3	45.4

DRS characterization. In Fig. 2, we show the diffuse reflectance UV spectra of [Ti]-MCM-41, Ti-MCM-41 samples and, for comparison, of the purely siliceous MCM-41. Both Ti containing samples have in com-

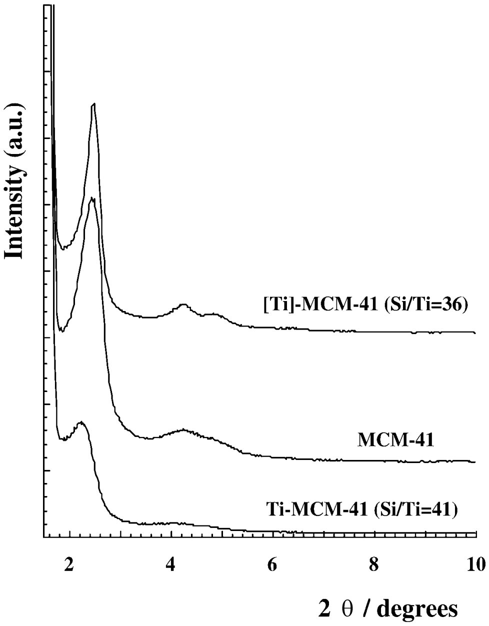


Fig. 1. XRD patterns of calcined MCM-41, [Ti]-MCM-41 and Ti-MCM-41 samples.

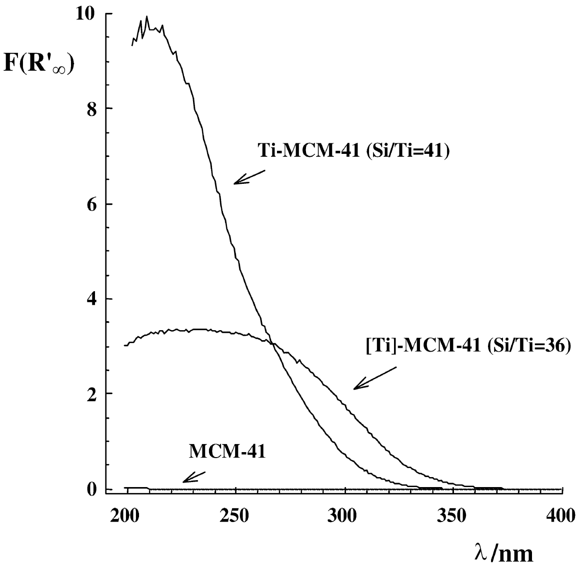
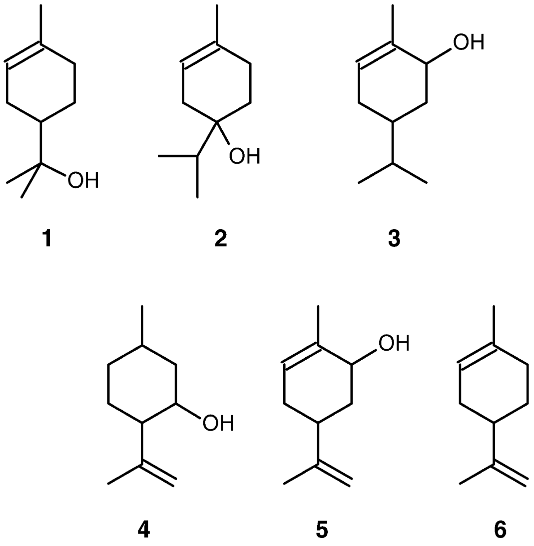


Fig. 2. Diffuse reflectance UV spectra of calcined MCM-41, [Ti]-MCM-41 and Ti-MCM-41 samples equilibrated to the ambient atmosphere. The Kubelka–Munk function for MCM-41 is very close to zero in the wavelength range 200–400 nm.

mon the intense UV absorption bands centered at ca. 220 nm due to a charge transfer between framework oxygen to tetrahedral Ti(IV) (see [19] and references therein). Note that the position of the maximum of the band cannot be detected precisely because of the very high values of the Kubelka–Munk function. This band is affected by the presence of adsorbates [19]. We recall that our spectra were recorded after calcination at 823 K in air and equilibration to the ambient atmosphere. It is well known that under these experimental conditions the presence of broad bands at $\lambda \geq 240$ nm are explained as due to tetrahedral Ti(IV) sites that undergo a coordination change to octahedral by insertion of water molecules as extraligands [19]. These bands are especially evident in the spectra of [Ti]-MCM-41. No other spectral features appear and the absence of a band in the range 330–350 nm indicates that no separate TiO_2 (anatase) phase is present in significant amounts in our samples.

Pore structure analysis. The N_2 adsorption–desorption isotherms of our MCM-41, [Ti]-MCM-41 and Ti-MCM-41 samples are classified as reversible type-IV isotherms, a peculiar feature of MCM-41 materials [20]. A sharp step at $P/P_0=0.25$–0.35 indicates a narrow distribution of mesopores. Taking the inflection point at $P/P_0=0.25$–0.35, assuming the application of the Kelvin equation and correcting for multilayer thickness [20,21], we obtain 23–28 Å as the effective mean pore diameters. The specific surface area (BET) data are in the range 750–800 $m^2\,g^{-1}$, even for the less crystalline Ti-MCM-41 sample (see Fig. 1). The total pore volume is about 0.6–0.7 $cm^3\,g^{-1}$ and the average pore diameters obtained from the method of Brunauer et al. [17] are in agreement with those obtained using the Kelvin equation. Considering these results and the unit cell parameter of the hexagonal unit cell obtained by XRD, it is possible to estimate that the wall thickness is about 15 Å for MCM-41 and [Ti]-MCM-41, and about 20 Å for Ti-MCM-41.

Catalytic experiments. Catalytic performance was tested in the epoxidation of four menthenol-like unsaturated alcohols, i.e. α-terpineol **1**, terpinen-4-ol **2**, carvotanacetol **3**, isopulegol **4**, a menthdienol, i.e. carveol **5** and the related diene, i.e. limonene **6** (Scheme 1).



Scheme 1.

First of all, tests on terpene **1** either with Ti-free MCM-41 or without catalyst show that there is no significant auto-oxidation or support-catalyzed contribution to epoxidation: terpene conversion is about 9–10% and the epoxide amount is under the chromatographic detection limit, confirming that titanium is the active site on which oxidation takes place.

Then, the two samples of Ti-containing MCM-41, [Ti]-MCM-41, in which Ti isomorphically substitutes for Si in the framework, and Ti-MCM-41, where the metal is grafted onto the MCM-41 surface, both bearing a very similar titanium loading and fully comparable structural features, were compared under the same conditions in acetonitrile. It is possible to observe that Ti-MCM-41 is more active than [Ti]-MCM-41 by a factor of up to ca. 10 in the case of terpene **1** (Fig. 3). This behavior is in agreement with the supposed higher exposure of active Ti sites obtained by grafting titanocene compounds on the surface of the material [8]. But the gap between the specific activities of the two catalysts becomes smaller as the alcoholic group approaches the C=C bond on the molecule skeleton, as it is evident in Table 2.

In fact, the enhancement in activity noted on Ti-MCM-41 passing from bishomoallylic alcohol **1** to homoallylic and allylic alcohols **2** and **3** is smaller than the one on [Ti]-MCM-41 and this leads to a lower difference between the in-framework and extra-framework material when this sort of enolic substrates have to be epoxidized.

Under these conditions in ethyl acetate, on the globally more active Ti-MCM-41, all hydroxy-substituted

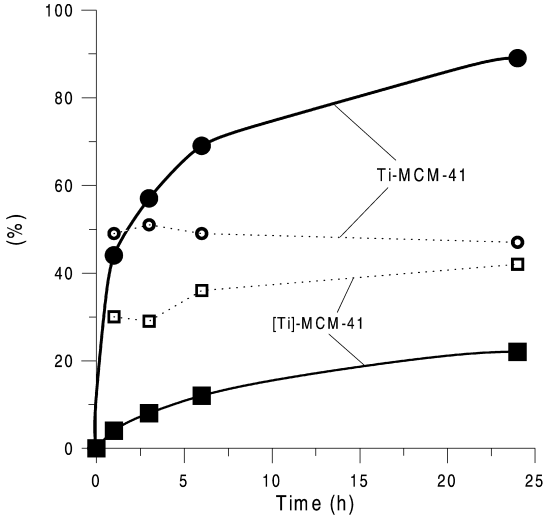


Fig. 3. Terpene conversion (%; solid line) and epoxide selectivity (%; dotted line) pattern for α-terpineol epoxidation in CH_3CN at 363 K on extra-framework Ti-MCM-41 (circles) and on in-framework [Ti]-MCM-41 (squares) samples.

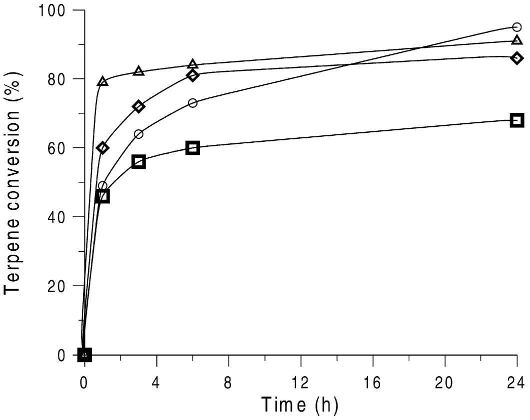


Fig. 4. Activity in carvotanacetol (△), terpinen-4-ol (◇), α-terpineol (○) and limonene (□) epoxidation on Ti-MCM-41 at 353 K in AcOEt.

terpenes **1**–**5** show a higher activity than the unfunctionalized diene, limonene **6** (Fig. 4). In this oxygenated solvent the lesser the distance of the double bond from the alcoholic moiety the higher is the activity in the first 6 h of reaction. After that time, secondary reactions lead to by-products and lower the selectivity to epoxides after a reaction time of 24 h (Table 3). Most of the by-products are due to the acid-catalyzed intermolecular ring closure of the OH-group on the already formed epoxy-ring leading to hydroxy-oxabicyclic species: 2-hydroxy-1,8-cineol and 2-hydroxy-1,4-cineol are obtained in epoxidation of α-terpineol **1** and terpinen-4-ol **2**, respectively. This acidic character has to be attributed on these materials mainly to the Lewis acidic Ti(IV) ions inserted in or grafted onto the siliceous matrix, since no other elements than silicon, oxygen and hydrogen are present [22].

On the other hand, the use of the more basic acetonitrile keeps the selectivity value constant during the whole reaction time (Fig. 3). Nevertheless, in this solvent, a clear dependence of the specific activity of the

Table 2
TOF of terpene epoxidation on [Ti]-MCM-41 and Ti-MCM-41[a]

Substrate	TOF		
	[Ti][b]	Ti[c]	Ti/[Ti] ratio
α-Terpineol (**1**)	2.1	19.6	9.3
Terpinen-4-ol (**2**)	10.3	21.5	2.1
Carvotanacetol (**3**)	21.4	29.4	1.4
Isopulegol (**4**)	8.8	15.2	1.7
Carveol (**5**)	15.1	33.3	2.2
Limonene (**6**)	3.9	20.1	5.2

[a] Reaction conditions: CH_3CN solvent; 30 wt.% catalyst; TBHP:terpene molar ratio=1.1; 358 K.

[b] Turnover frequency (h^{-1}) on [Ti]-MCM-41 (in-framework) after 1 h reaction.

[c] Turnover frequency (h^{-1}) on Ti-MCM-41 (extra-framework) after 1 h reaction.

Table 3
Terpene epoxidation in acetonitrile and ethyl acetate on Ti-MCM-41 (from grafted titanocene dichloride)[a]

Substrate	Solvent			
	CH_3CN		AcOEt	
	C (%)[b]	S (%)[c]	C (%)[b]	S (%)[c]
α-Terpineol (**1**)	90	51	95	17
Terpinen-4-ol (**2**)	78	61	86	15
Carvotanacetol (**3**)	87	77	91	56
Isopulegol (**4**)	73	80	78	41
Carveol (**5**)	82	73	82	69
Limonene (**6**)	62	79	68	62

[a] Reaction conditions: 30 wt.% catalyst; TBHP:terpene molar ratio=1.1; 358 K.

[b] Terpene conversion after 24 h reaction.

[c] 1,2-Epoxide selectivity after 24 h reaction.

catalyst on the position of the OH-moiety with respect to the C=C bond is not evident (Table 2). In fact, taking into account Table 2, even if carvotanacetol **3** reacts faster than the other three terpenic monoenols, some of the unsaturated alcohols display a slower reactivity than the olefinic terpene **6**.

The alcoholic function indeed might play a key role in enhancing epoxidation rate, as observed on homogeneous systems [11,27], binding in some way the titanium–mesoporous hydrophilic surface. So, decreasing the distance between the C=C bond and the OH-group, the oxygen transfer from the hydroperoxy species bound to the Ti center to the unsaturated terpene becomes easier, at least in ethyl acetate.

Anyway, even if the presence of the alcoholic group promotes the reaction, the overall nucleophilic character of the unsaturation is mainly ruled by the number of substituents on the double bond. As a matter of fact, on carveol **5**, which bears two double bonds, in both solvents a preferential attack of oxygen to the allylic C=C rather than the terminal one was noted using Ti-MCM-41 (in acetonitrile endocyclic to exocyclic epoxide ratio=83:17). This may be due to the higher electron-rich character of the trisubstituted unsaturation with respect to the exocyclic one, rather than to the presence of the OH-group close to the double bond. In fact, a similar regioselectivity was observed on the non-hydroxylated diene **6** too (in acetonitrile endocyclic to exocyclic epoxide ratio=80:20). Such a regioselectivity in limonene epoxidation is comparable to that observed on Ti-supported silica gels [23]. This is a clue that on these mesoporous catalysts the electronic effects are more determining factors than the steric effects, which cause instead a preferential oxidation of the side-chain double bond on narrower-pore molecular sieves as Ti-beta [24]. The same reason may furthermore account for the difference in activity between the two homoallylic alcohols, **2** and **4** (Table 2): the less substituted terminal double bond is less prone to epoxidation than the internal one.

Among the five terpenic alcohols in Table 3, a good selectivity to epoxide was achieved with Ti-MCM-41 on isopulegol **4** in acetonitrile, the main by-product (ca. 5% selectivity) being the related ketone only, isopulegone. Lower epoxide selectivities due to acid-catalyzed intermolecular ring closure were observed, as discussed above, mostly when the final bicyclic compounds are not particularly strained. However, as these compounds come from the rearrangement of the already formed terpene epoxides, it is possible to say that the global selectivity to oxidized products is still higher than the epoxide selectivity observed, which means a good to excellent TBHP efficiency.

Besides, negligible presence of products oxidized in allylic position to give rise to α,β-unsaturated alcohols or ketones, is consistent with a non-radical mechanism of epoxidation [8].

4. Conclusions

Although the extra-framework Ti-MCM-41 displayed globally a higher epoxidation rate than in-framework [Ti]-MCM-41, the difference in activity between them decreased as the OH-group approaches the C=C double bond on the molecule skeleton. Besides, on Ti-MCM-41 in ethyl acetate a clear dependence of the conversion rate on the distance of the unsaturation from the alcoholic function was observed. Weakly basic solvents as acetonitrile have to be chosen if high selectivities after long time reactions are requested.

While in microporous titanosilicates the steric constraint due to pore narrowness may often modify epoxidation activity and selectivity, in these mesoporous materials the pore size is not so crucial. Therefore, the catalytic performances of the catalysts ought to be controlled by tuning the chemical environment around the active sites and by modifying the hydrophobic/hydrophilic feature of the surface species according to the polar character of the substrate to be epoxidized.

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References

[1] B. Notari, Adv. Catal. 41 (1996) 253.
[2] M.A. Camblor, A. Corma, J. Pérez-Pariente, J. Chem. Soc., Chem. Commun. (1992) 589.

[3] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[4] A. Corma, Chem. Rev. 97 (1997) 2373.
[5] A. Corma, M.T. Navarro, J. Pérez-Pariente, J. Chem. Soc., Chem. Commun. (1994) 147.
[6] P.T. Tanev, M. Chibwe, T.J. Pinnavaia, Nature 368 (1994) 321.
[7] T. Maschmeyer, F. Rey, G. Sankar, J.M. Thomas, Nature 378 (1995) 159.
[8] R.D. Oldroyd, J.M. Thomas, T. Maschmeyer, P.A. MacFaul, D.W. Snelgrove, K.U. Ingold, D.D.M. Wayner, Angew. Chem. Int. Ed. Engl. 35 (1996) 2787.
[9] L. Marchese, E. Gianotti, V. Dellarocca, T. Maschmeyer, F. Rey, S. Coluccia, J.M. Thomas, Phys. Chem. Chem. Phys. 1 (1999) 585.
[10] M.N. Sheng, J.G. Zajacek, J. Org. Chem. 35 (1970) 1839.
[11] R.A. Sheldon, J. Mol. Catal. 7 (1980) 107.
[12] M. Dusi, T. Mallat, A. Baiker, J. Mol. Catal. A 138 (1999) 15.
[13] T. Tatsumi, M. Yako, K. Yanagisawa, K. Asano, in: M.G. Scaros, M.L. Prunier (Eds.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1994, p. 341.
[14] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10 834.
[15] T. Blasco, A. Corma, M.T. Navarro, J. Pérez-Pariente, J. Catal. 156 (1995) 65.
[16] F. Di Renzo, H. Cambon, R. Dutartre, Micropor. Mater. 10 (1997) 283.
[17] S. Brunauer, R.Sh. Mikhail, E.E. Bodor, J. Colloid Interf. Sci. 24 (1967) 451.
[18] R.E. Ireland, P. Bey, Org. Synth. 53 (1973) 63.
[19] L. Marchese, T. Maschmeyer, E. Gianotti, S. Coluccia, J.M. Thomas, J. Phys. Chem. B 101 (1997) 8836.
[20] P.J. Branton, P.G. Hall, K.S.W. Sing, J. Chem. Soc., Chem. Commun. (1993) 1257.
[21] J.D. Carruthers, P.A. Cutting, R.E. Day, M.R. Harris, S.A. Mitchell, K.S.W. Sing, Chem. Indust. 50 (1968) 1772.
[22] A. Bhaumik, T. Tatsumi, J. Catal. 182 (1999) 349.
[23] C. Cativiela, J.M. Fraile, J.I. Garcia, J.A. Mayoral, J. Mol. Catal. A 112 (1996) 259.
[24] J.C. van der Waal, M.S. Rigutto, H. van Bekkum, Appl. Catal. A 167 (1998) 331.
[25] M. Taramasso, G. Perego, B. Notari, US Patent No. 4 410 501 (1983).
[26] R.D. Oldroyd, G. Sankar, J.M. Thomas, D. Özkaya, J. Phys. Chem. B 102 (1998) 1849.
[27] A.H. Hoveyda, D.A. Evans, G.C. Fu, Chem. Rev. 93 (1993) 1307.