

Molybdenum-based epoxidation catalysts heterogenized in silica matrixes via the sol–gel method

Sergio Teixeira, Kai Dallmann, Ulf Schuchardt, Regina Buffon*

Instituto de Química—Unicamp, Universidade Estadual de Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil

Received 5 July 2001; accepted 22 October 2001

Abstract

$\text{MoO}_2(\text{acac})_2$ has been encapsulated in silica matrixes prepared by hydrolysis/condensation of tetraethylorthosilicate. Alternatively, hybrid organic–inorganic matrixes were prepared by adding 3-(triethoxysilyl)propylethylenediamine or 1,4-bis(triethoxysilyl)benzene to the reaction mixture. All systems were tested in the epoxidation of cyclohexene or *cis*-cyclooctene at 70 °C using *tert*-butyl hydroperoxide as the oxidant. In most experiments, 1,2-dichloroethane as a solvent and a molar ratio of $[\text{Mo}]:[\text{TBHP}]:[\text{olefin}] = 1:130:130$ were employed. The catalysts immobilized in inorganic matrixes prepared in acidic conditions showed high activity in the first run, which could be attributed to the occurrence of homogeneous catalysis; basic conditions led to a significant decrease in activity with a concomitant decrease in the specific surface area of the matrix. Hybrid systems were less active in the first run, but their activities remained almost constant in at least four consecutive runs. Selectivities for epoxides were higher than 97% in all the cases. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Epoxidation; Molybdenum; Sol–gel process

1. Introduction

Soluble Mo(VI) compounds are among the most versatile catalysts for the epoxidation of olefins [1]. Homogeneous catalysis, however, presents several drawbacks, in particular the recovering of the catalyst at the end of the process, warranting a search for supported-molybdenum catalysts. Research done so far has focused on the use of organic polymers as supports. Preparation of such polymer-supported catalysts has usually been based on anion exchange [2], cation exchange [3,4] and chelating ion exchange resins [5–7]. Among these systems, the one based on polybenzimidazole showed the best performance and

stability [8,9]. Nevertheless, several drawbacks have limited the utilization of these systems: (i) the instability of the catalyst due to molybdenum leaching; (ii) the thermo-oxidative instability of the polymer under reaction conditions; (iii) the poor mechanical properties of the organic support. Recently, we described the utilization of a diamino-functionalized silica as a support and $\text{MoO}_2(\text{acac})_2$ or $\text{Mo}(\text{CO})_6$ as molybdenum sources [10]. Although the catalytic activity of these catalysts was lower than those reported for analogous polymer-based systems, molybdenum did not leach from the surface. In the last years, the sol–gel methodology has been applied to immobilize soluble catalysts, using either inorganic [11] or hybrid matrixes [12]. Recently, we reported the use of this approach to prepare rhenium-based epoxidation catalysts [13]. We wish to report here some results concerning the encapsulation of molybdenum

* Corresponding author. Tel.: +55-19-3788-3090;
fax: +55-19-3788-3023.
E-mail address: rbuffon@iqm.unicamp.br (R. Buffon).

catalysts in inorganic and hybrid organic–inorganic matrixes using the sol–gel method.

2. Experimental

2.1. Materials

1,4-Bis(triethoxysilyl)benzene was prepared according to the literature [14]. Tetraethylorthosilicate (TEOS, Aldrich), $\text{MoO}_2(\text{acac})_2$ (Aldrich), ethyl alcohol (Merck), *tert*-butyl hydroperoxide (TBHP, 88 vol.% in cyclohexane, Nitrocarbonyl, SA), cyclohexene (Merck), *cis*-cyclooctene (Aldrich), dichloromethane (Merck), 1,2-dichloroethane (Merck), ethyl acetate (Aldrich) and *tert*-butyl alcohol (Aldrich) were used as received. Toluene (Merck) and tetrahydrofuran (Merck) were distilled under argon over sodium/benzophenone.

2.2. Catalyst preparation

2.2.1. Inorganic matrixes

Catalysts I–III. These catalysts were prepared by a procedure described by Blum et al. [15] with small modifications. In a typical preparation, 200 mg of $\text{MoO}_2(\text{acac})_2$ was added to a 50 ml round bottom flask, followed by the addition of 20 ml of THF, 4 ml of degassed H_2O (pH 4 or 10, adjusted with HCl or NH_4OH) and 20 ml of TEOS. After 30 min of magnetic stirring, a homogeneous solution was obtained. On standing for a few hours, the yellow solution became green. Gelation took place from 3 to 5 days. After washing with CH_2Cl_2 in a Soxhlet (14 h), the solid was dried in an oven (95–100 °C), pounded in a mortar and passed through a 120-mesh sieve.

2.2.2. Hybrid matrixes

Catalyst IV. Seven milliliters of 1.2 mol/l HCl, 14 ml of ethyl alcohol, 250.0 mg (1.12 mmol) of *N*-[3-(trimethoxysilyl)-propyl]ethylenediamine and 6.84 g (32.82 mmol) of TEOS were mixed in a 100 ml round bottom flask, leading to a solution of pH = 1.6 which was stirred for 45 min. After the addition of a THF solution of $\text{MoO}_2(\text{acac})_2$ (70.0 mg; 0.21 mmol in 21 ml) the mixture was stirred for 50 min, followed by a dropwise addition of an aqueous solution of Na_2CO_3 (25 ml, 4.13 mmol) which led to a color change from

yellow to green to blue and to a pH increase up to 10.0. Gelation took place in 1 h. The blue gel was allowed to stand overnight, dried under vacuum, washed with CH_2Cl_2 in a Soxhlet (24 h) and dried again under vacuum for 24 h at room temperature.

Catalyst V. 3.46 g (8.56 mmol) of 1,4-bis(triethoxysilyl)benzene, 7.65 ml (36.4 mmol) of TEOS, 10 ml of ethyl alcohol and 1 ml of 1.2 mol/l HCl were added to a 200 ml round bottom flask, leading to a solution of pH = 1.1. After 45 min under stirring, an ethyl alcohol solution of $\text{MoO}_2(\text{acac})_2$ (6 ml: 100.0 mg or 0.31 mmol) was added. When an orange homogeneous solution was obtained (after 20 min under stirring), the addition of 8 ml of an aqueous solution of Na_2CO_3 (1.35 mmol) led to the formation of a green gel. The green gel was treated as described for catalyst IV.

2.3. Catalytic experiments

In experiments without solvent, the desired amount of catalyst (usually, 0.04 mmol of Mo), 5.28 g (45 mmol) of *cis*-cyclooctene and 370 mg (3.60 mmol) of TBHP were added to a two-neck 50 ml round bottom flask equipped with a condenser. Reactions were carried out at 80 ± 2 °C for 5 h (or, sometimes up to 24 h). The reaction was monitored via GC analyses of the liquid phase using *n*-decane as an internal standard (added to the sample after the catalytic experiment). For cyclohexene, most experiments were carried out with a solvent and at 70 °C using a molar ratio of $[\text{Mo}]:[\text{TBHP}]:[\text{olefin}] = 1:130:130$. GC analyses were performed in an HP5890 series II gas chromatograph, equipped with an HP5 capillary column (50 m \times 0.2 mm) and a flame ionization detector. Products were quantified using calibration curves obtained with standard solutions. TBHP consumption was determined by iodometric titration.

2.4. Catalyst characterization

Nitrogen adsorption isotherms were determined at -196 °C with a Micromeritics ASAP 2010 automated porosimeter. All calculations were performed using the associated Micromeritics software. Samples were degassed at 100 °C for a minimum period of 8 h prior to measurements. Samples size varied from 0.40 to 0.65 mg. Molybdenum concentrations were

determined through ICP-AES (Perkin-Elmer Optima 3000 DV).

3. Results and discussion

Catalysts I, II and III were prepared from tetraethylorthosilicate in order to evaluate the effect of the pH and of the molybdenum content on the activity and surface characteristics of the resulting systems (Table 1). Thus, catalysts I and III were prepared in acidic conditions, but with different molybdenum loadings, and catalyst II was prepared in basic condition. In the case of catalysts IV and V, a hydrolyzable ligand (*N*-[3-(trimethoxysilyl)-propyl]ethylenediamine, catalyst IV) or a co-condensation agent (1,4-bis(triethoxysilyl)benzene, catalyst V) was added to the synthesis solution. The co-condensation agent was expected to reduce the degree of 3D-cross-linking, decreasing the rigidity and improving the swelling properties of the resulting matrix. The presence of both modifiers was also expected to affect the porous system and thus the diffusion of the reagents inside the matrix.

3.1. Matrix characterization

The nitrogen adsorption–desorption isotherms of catalysts I, II and V are of type I (IUPAC classification [16]), characteristic of microporous systems. The lack of hysteresis in their desorption branches suggests that the pores are smooth and cylindrical [17]. The volumes adsorbed at the lowest relative pressure

represent ca. 60, 77 and 85% of the total pore volume for catalysts I, II and V, respectively, indicating in all the cases a large volume of extremely small pores. The Horvath–Kawazoe differential pore volume plots for catalysts I, II and IV are shown in Fig. 1. The plots for catalysts I and V (not shown) are very similar and indicate a straight pore size distribution. BET surface area, pore volume and average pore size determined from the isotherms are presented in Table 1. According to these results, the presence of a rigid co-condensation agent (as in catalyst V), at least in a molar ratio of 1:4 relative to TEOS, has a small influence in the surface area and pore volume of the resulting system.

Catalyst IV is characterized by an isotherm of type IV, with a type H2 hysteresis loop (IUPAC classification [16]), shown in Fig. 2. The shape of this isotherm indicates the presence of ink bottle or narrow-mouth shaped pores [17]. The BJH adsorption pore size distribution is shown in Fig. 1. In a related work, we observed that the presence of a hydrolyzable ligand in the absence of the co-condensation agent led to a nonporous system [13].

3.2. Catalytic activity

In a first series of experiments, the activity of catalysts I–III was compared to that of a homogeneous solution of $\text{MoO}_2(\text{acac})_2$. As shown in Fig. 3, the heterogenized systems are less active, probably due to diffusion problems. The catalysts prepared in acidic conditions (I and III) are more active than that prepared in basic condition (catalyst II). Diffusion is expected to be more difficult with catalyst II, owing to its

Table 1
Some characteristics of the catalysts

Catalyst	Mo loading (wt.%) ^a	pH of water	BET surface area (m ² g ⁻¹)	Porous volume (cm ³ g ⁻¹) ^b	Average pore diameter (nm) ^b
I	1.53	4	538	0.24	0.69
II	1.44	10	369	0.15	0.63
III	3.93	4	ND ^c	ND	ND
IV	0.65	1.6 ^d	262	0.23 ^e	3.05 ^e
V	0.50	1.1 ^d	405	0.19	0.78

^a Determined via ICP-AES analyses.

^b Horvath–Kawazoe method.

^c Not determined.

^d pH of the solution.

^e BJH method (adsorption branch).

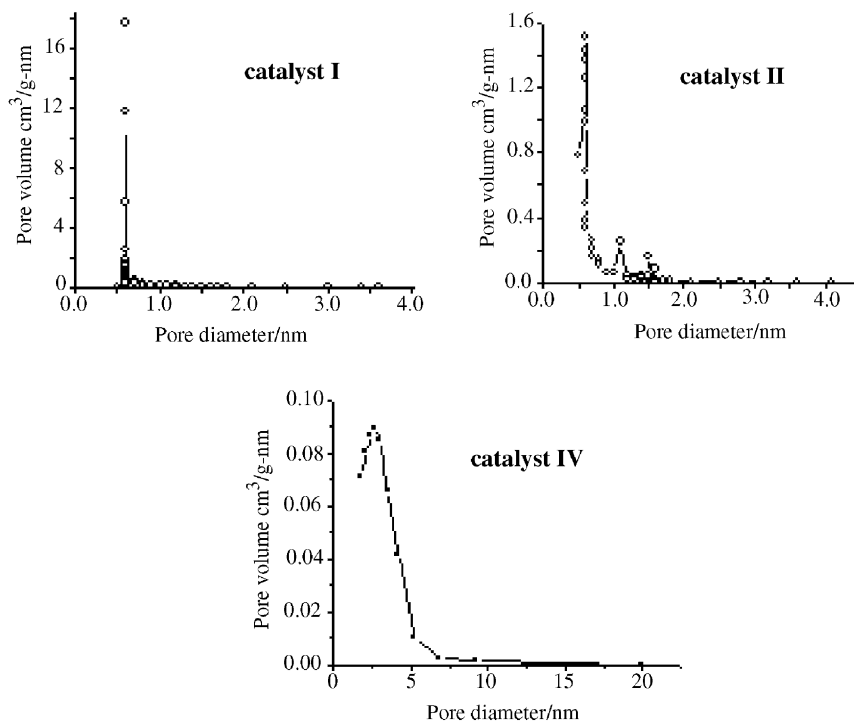


Fig. 1. Differential pore size distributions for catalysts I, II and IV.

smaller surface area and pore volume (Table 1). The influence of the solvent was evaluated with catalyst I. As shown in Fig. 4, the activity is higher in the absence of a solvent. Coordinating solvents (ethyl acetate and *tert*-butyl alcohol) strongly reduce the catalytic activ-

ity. However, toluene and 1,2-dichloroethane lead to good performances and the latter was used in many experiments. Within the experimental error, no differences in activity were observed when using cyclohexene or *cis*-cyclooctene.

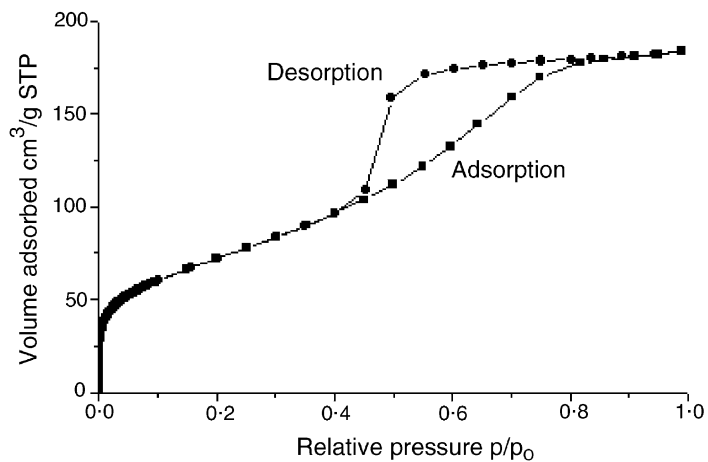


Fig. 2. Nitrogen adsorption/desorption isotherms for catalyst IV.

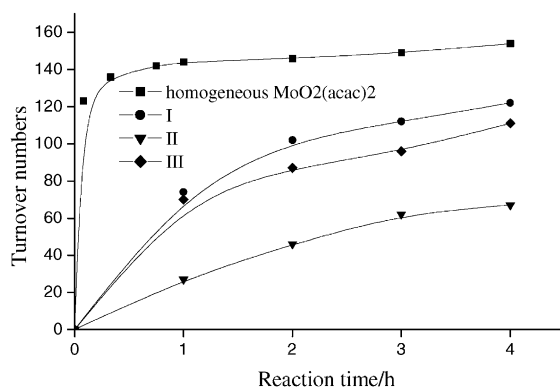


Fig. 3. Epoxidation of cyclohexene with catalysts I–III. [Mo]:[TBHP]:[olefin] = 1:130:130; 3.4 ml 1,2-dichloroethane (solvent); 70 °C.

Catalyst I was also tested in recycling experiments. Although only a slight decrease in activity was observed in the second run, the catalytic activity decreased drastically in the third run (Fig. 5). The decrease in activity was accompanied by a decrease in TBHP consumption (Fig. 6). Quantification of molybdenum in the matrixes after the catalytic reactions showed almost no molybdenum losses; however, leaching experiments, performed via removal of the catalyst after 20 min reaction time and allowing the reaction to proceed in solution (Fig. 7), suggested that catalysis, at least in the first two runs, is ca. 50% homogeneous [18]. These results also suggest that

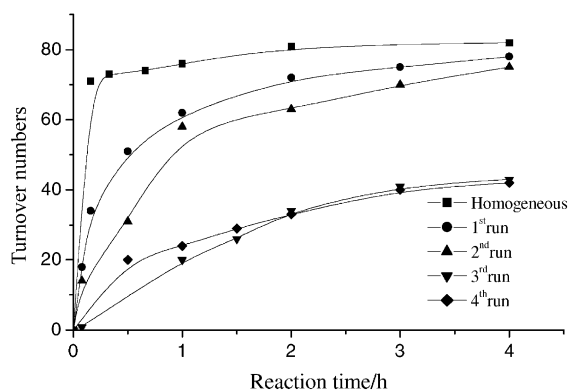


Fig. 5. Catalytic activity of catalyst I in the epoxidation of *cis*-cyclooctene in four runs. Reaction conditions: [Mo]:[TBHP]:[olefin] = 1:80:1000; 80 °C.

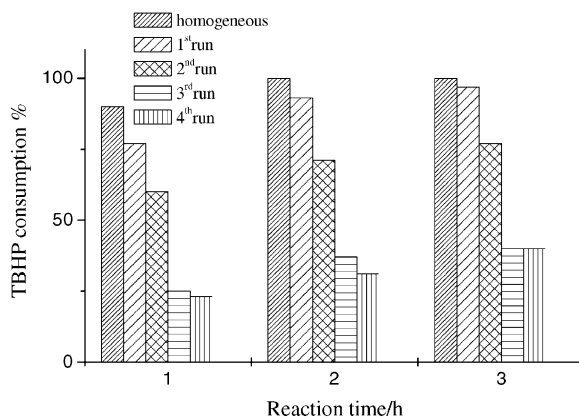


Fig. 6. TBHP consumption in successive runs with catalyst I. Reaction conditions as in Fig. 5.

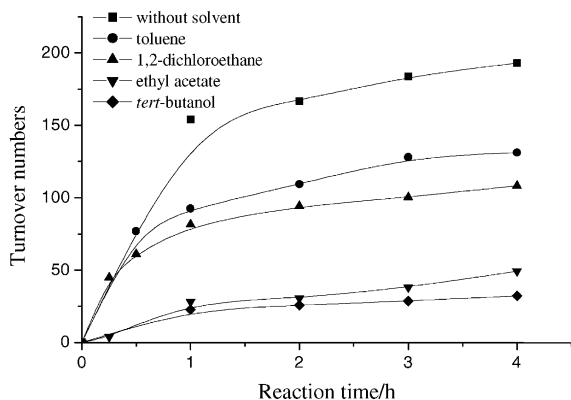


Fig. 4. Effects of the solvent in the epoxidation of cyclohexene with catalyst I. Same conditions as in Fig. 3 (reaction without solvent: [Mo]:[olefin] = 1:1000).

in the third, fourth and subsequent (not shown) runs catalysis would be truly heterogeneous.

Catalysts prepared in hybrid matrixes were tested only in the epoxidation of *cis*-cyclooctene. As it can be seen in Figs. 8 and 9, these systems are less active than those prepared in inorganic matrixes: with a hybrid matrix a reaction time of 8 h was necessary to obtain a TON = 60, while 1 h was enough with inorganic matrixes (Figs. 3 and 5).¹ In recycling experiments, however, the hybrid matrixes behaved better since the

¹ Initial turnover frequencies in the first run derived from Figs. 3, 8 and 9: catalysts I and III: 70 h⁻¹; catalyst II: 24 h⁻¹; catalyst IV: 24 h⁻¹; catalyst V: 22 h⁻¹.

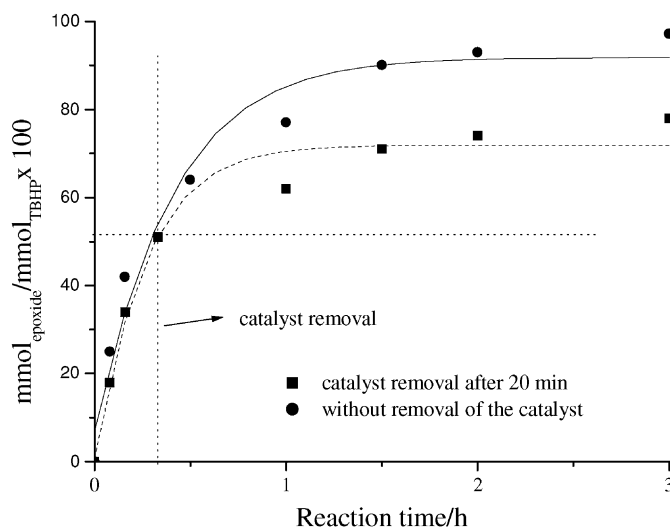


Fig. 7. Leaching experiment with catalyst I. Reaction conditions as in Fig. 3.

catalytic activity remained almost constant for at least four runs (catalyst IV, Fig. 8). In all the cases, hybrid or inorganic matrixes, the selectivity to the epoxides was higher than 97%.

When all results are taken together, it seems that the catalytic activity cannot be directly related to the type of the porous system: diffusion would be easier in a mesoporous matrix. However, at least with the catalyst

prepared in this work (catalyst IV), other factors such as the presence of a chelating ligand and the total surface area must also play a role.

In spite of the lower reaction rates observed in the heterogenized systems, the hybrid catalysts can be recycled with almost no decrease in activity, offering a promising route to the preparation of molybdenum-based heterogeneous catalysts.

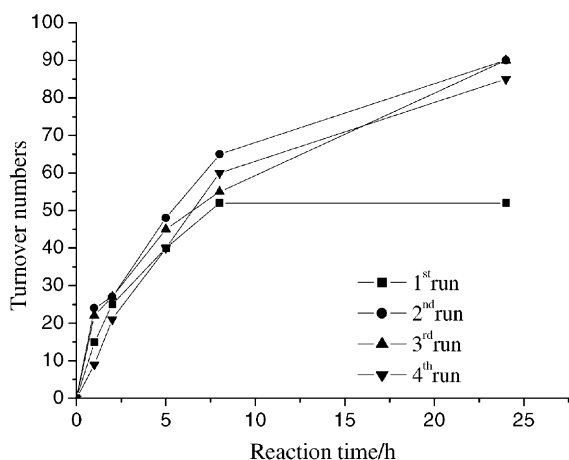


Fig. 8. Catalytic activity of catalyst IV in the epoxidation of *cis*-cyclooctene in four runs. Reaction conditions: [Mo]:[TBHP]:[olefin] = 1:100:500; 80 °C.

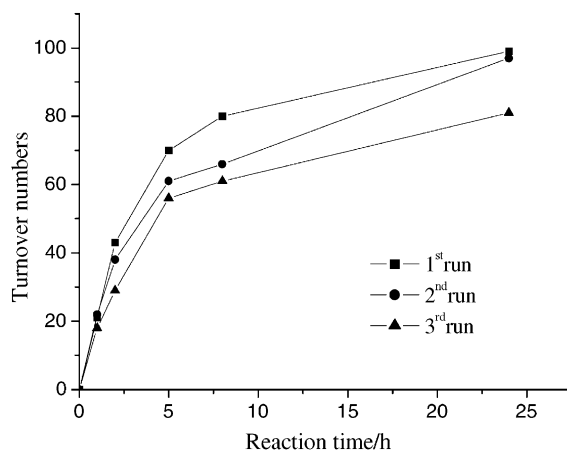


Fig. 9. Catalytic activity of catalyst V in the epoxidation of *cis*-cyclooctene in three runs. Reaction conditions as in Fig. 7.

4. Conclusions

The heterogenization of $\text{MoO}_2(\text{acac})_2$ inside the porous systems of silica matrixes or hybrid organic–inorganic matrixes containing either 3-(triethoxysilyl)propylethylenediamine or 1,4-bis(triethoxysilyl)benzene leads to active catalysts for the epoxidation of cyclic olefins. The hybrid catalysts can be recycled at least four times without significant change in catalytic activity. No correlation between the type of the porous system and the catalytic activity or selectivity could be observed.

Acknowledgements

Financial support from FAPESP as well as fellowships from CNPq (to ST) and FAPESP (to KD) are gratefully acknowledged.

References

- [1] G.W. Parshall, S.D. Ittel, *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes*, Wiley, New York, 1992.
- [2] J. Sobczak, J. Ziólkowski, *J. Mol. Catal.* 3 (1978) 165.
- [3] S. Ivanov, R. Boeva, S. Tanielyau, *J. Catal.* 56 (1979) 150.
- [4] R. Boeva, S. Kotov, N.I. Jordanov, *React. Kinet. Catal. Lett.* 24 (1984) 239.
- [5] S. Bhaduri, H. Khwaja, *J. Chem. Soc., Dalton Trans.* (1983) 415.
- [6] T. Yokoyama, M. Nishizawa, T. Kimura, T.M. Suzuki, *Bull. Chem. Soc. Jpn.* 58 (1985) 3271.
- [7] D.C. Sherrington, S. Simpson, *J. Catal.* 131 (1991) 115.
- [8] M.M. Miller, D.C. Sherrington, *J. Catal.* 152 (1995) 368.
- [9] M.M. Miller, D.C. Sherrington, *J. Catal.* 152 (1995) 377.
- [10] E.F.M. Barradas, A.R. Cestari, C. Airoidi, R. Buffon, *Braz. J. Chem. Eng.* 15 (1998) 146.
- [11] J. Blum, D. Avnir, H. Schumann, *Chemtech* 29 (1999) 32.
- [12] E. Lindner, T. Schneller, F. Auer, H.A. Mayer, *Angew. Chem. Int. Ed.* 38 (1999) 2155.
- [13] K. Dallmann, R. Buffon, *Catal. Commun.* 1 (2000) 9.
- [14] D.A. Loy, G.M. Jamison, B.M. Baugher, S.A. Myers, R.A. Assink, K.J. Shea, *Chem. Mater.* 8 (1996) 656.
- [15] J. Blum, A. Rosenfeld, N. Polak, O. Israelson, H. Schumann, D. Avnir, *J. Mol. Catal. A* 107 (1996) 217.
- [16] K.S.W. Sing, D.H. Everett, R.A. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603.
- [17] C.J. Brinker, G.W. Scherer, *Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing*, Academic Press, San Diego, CA, 1990, pp. 522–525.
- [18] R.A. Sheldon, M. Wallau, I.W.E.C. Arends, U. Schuchardt, *Acc. Chem. Res.* 31 (1998) 485.