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Heterogenization of $[Cu(NCCH_3)_4][BF_4]_2$ on mesoporous AlMCM-41/ AlMCM-48 and its application as cyclopropanation catalyst

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$[Cu(NCCH_3)_4][BF_4]_2$ can be heterogenized by an ion exchange method on mesoporous NaAlMCM-41 and NaAlMCM-48 materials. The heterogenized complex and the homogeneous Cu compound are applicable for the cyclopropanation of olefins at 303 K. Comparable yields are observed for non-bulky olefins, olefins with bulkier substituents lead to lower yields. $[Cu(NCCH_3)_4][BF_4]_2$ grafted on mesoporous surfaces (as heterogeneous catalyst) are relatively stable and recyclable for several catalytic runs with only slight decrease in catalytic activity.

KEY WORDS: catalysis; copper; cycloproponation; heterogenization; mesoporous materials.

1. Introduction

Cyclopropylation reactions are very versatile for synthetic organic chemistry with applications such as cross-couplings, and ring-opening reactions [1–3]. The preferred method for the preparation of cyclopropanes is the direct cyclopropanation of olefinic bonds utilizing diazo compounds (ethyl diazoacetate; EDA) as a carbene source [4,5]. Copper-based complexes have played a prominent role in the *in situ* generation of metal carbenes (or carbenoids) from diazo compounds and of nitrenes from the corresponding sources [4–6]. In this regard, various copper complexes (such as copper bis(oxazoline)) have been immobilized on the surface of zeolites (e.g. zeolite-Y), mesoporous molecular sieves and clays and also Cu^{2+} exchanged zeolite-Y. Such materials are applied as heterogeneous catalysts for azirdination and cycloproponation reactions [7–9]. In most cases, immobilization is carried out by covalent binding. The method used to form this covalent bond may have decisive influence on the catalytic activity and selectivity.

The use of weakly or non-coordinating anions (WCA) is of significant current interest as counter ions both in synthesis and catalysis, due to their potential in enhancing the reactivity of metal complexes [10]. The successful synthesis of a series of acetonitrile complexes of the type $[M(NCCH_3)_6][X]_2$ and $[M_2(NCCH_3)_{8\text{-}10}][X]_4$ where X = BF_4^-, $B(C_6F_5)_4^-$, $B\{C_6H_3(m\text{-}CF_3)_2\}_4^-$, $((C_6F_5)_3B\text{-}C_3H_3N_2\text{-}B(C_6F_5)_3)^-$, exhibiting excellent activities for the polymerization of cyclopentadiene and methylcyclopentadiene in homogeneous phase has been reported [11]. Some of these compounds have been heterogenized by Gonçalves *et al.* and McCann *et al.* The observed catalytic activities, however, were reported to be much lower than in homogeneous phase [12]. Recently, we reported on homogeneous azidirinations catalyzed by $[Cu(NCCH_3)_{2\text{-}4}][B(C_6F_5)_4]$ [13]. The above-mentioned Cu(II) complexes may also be interesting for heterogenization due to the general easier catalyst/product separation procedure in heterogeneous catalysis. Heterogenization of the highly selective homogeneous catalysts is also expected to lead to a combination of the advantages of both catalyst classes. Among the various supporting materials available, the mesoporous silicates, designated as MCM-41 and MCM-48 by Mobil scientist [14] with regular pore size, large surface areas, a large number of surface silanol groups and high chemical and thermal stability, are potential and promising candidates as both catalysts and catalyst supports [15,16]. As already indicated above, the activity of the $[M(NCCH_3)_6][X]_2$ systems drops strongly after heterogenization, when the heterogenization involves a reaction of the cation with the surface or surface fixed ligands, due to the reduction of its Lewis acidity [17]. For example, Mn complexes of the type $[Mn(NCCH_3)_6][B(C_6F_5)_4]_2$ have been grafted on MCM-41 derivatized with pyrazolylpyridine ligands. It was found that the catalytic activity of this system for isobutene polymerization after grafting was greatly reduced (to almost zero) due to the reduction of its Lewis acidity [17].

In the present work, the copper complex $[Cu(NCCH_3)_4][BF_4]_2$ (**1**) is grafted on NaAlMCM-41 and NaAlMCM-48 by ionic interactions, i.e., the partial ion exchange of Na^+ cations present in the mesoporous materials surface by $[Cu(NCCH_3)_4]^{2+}$, as represented in

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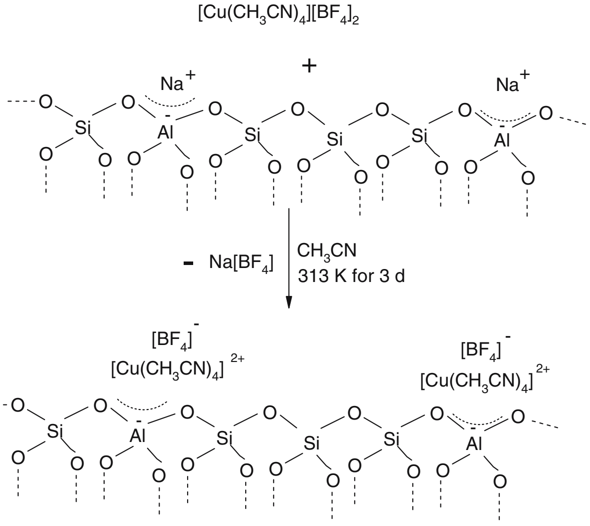


Scheme 1.

Scheme 1. The ionically grafted materials obtained from the heterogenization of the Cu(II) compound **1** were systematically characterized by powder X-ray diffraction (XRD), N_2 adsorption/desorption (BET) analysis, thermogravimetry coupled with mass spectroscopy (TG-MS), and FT-IR spectroscopic methods. The resulting materials prepared from Na-AlMCM-41 and Na-Al-MCM-48 samples are designated as Na-AM41CuBF and Na-AM48CuBF, respectively. The homogeneous complex **1** and heterogeneous Na-AM41CuBF and Na-AM48CuBF are applied for various olefin cyclopropanation reactions using diazoethylacetate, in order to compare the activity of the homogeneous and the heterogeneous copper complexes with respect to their catalytic performance.

2. Experimental

2.1. Synthesis procedure

The following materials, colloidal silica (SiO_2), fumed silica (SiO_2), hexadecyl-trimethyl ammonium bromide (CTABr), 1,3-diacetoxy-1,1,3,3-tetrabutyltin oxide polyethylene glycol dodecyl ether (Brij-30), tetramethyl ammonium hydroxide (TMAOH, 25 wt.%), aluminum nitrate nano-hydrate ($Al(NO_3)_3{\cdot}9H_2O$) and sodium hydroxide (NaOH) are used without purification for the synthesis of the mesoporous materials.

Na-AlMCM-41 with a Si/Al (molar) ratio of 100 is synthesized as described in the literature, [13b,14c] having a typical molar gel composition of: 1 SiO_2:0.2 NaOH:0.27 TMAOH:0.27 CTABr:60 H_2O:0.005 Al_2O_3. A typical synthesis procedure is as follows: first TMAOH is dissolved in water and stirred for 5 min. To this solution fumed silica is slowly added (the resulting solution is designated as A). Another solution, B, is prepared by mixing CTABr and NaOH in distilled water and stirred for about 30 min. Both these solutions, A and B, are mixed together and a gel is formed. Aluminum nitrate is then added to the resulting clear solution and the mixture is stirred for 1 h. The pH of the resulting gel is adjusted to 11.0 with diluted sulphuric acid, and is aged for 16 h. The gel is transferred into a polyethylene bottle and kept in an oven under air for crystallization at 373 K for 3 days. The obtained solid product is washed repeatedly, filtered, and dried at 353 K for 12 h. The as-synthesized sodium form of the material (Na-AlMCM-41) is calcined at 823 K for 2 h in N_2 followed by drying under air for 6 h.

Na-AlMCM-48 is prepared [13b,14c] by the following procedure with a molar gel composition of 5.0 SiO_2:2.5 NaOH:0.87 CTABr:0.13 Brij30:0.025 Al_2O_3:400 H_2O. First, a surfactant mixture solution is prepared by dissolving both CTABr (7.74 g) and Brij30 (1.35 g) simultaneously in distilled water (60 mL). Then, a NaOH solution (2.5 g in 5 mL water) is added to the surfactant solution and stirred for 0.5 h. The silica solution is then added to the above-described solution and the resulting mixture is shaken vigorously for 0.5 h. The resulting gel is kept at 373 K for crystallization. After two days, the mixture is cooled to room temperature (298 K) and the pH of the solution is adjusted to 10 with acetic acid. This procedure is repeated twice. Then, aluminum nitrate is added to the gel and the resulting mixture is kept for 373 K for another 7 days. The resulting final product is filtered and washed with an ethanol/water mixture and dried in an oven at 373 K, followed by calcination in air at 823 K for 6 h.

All the grafting procedures are carried out under an oxygen- and water-free argon atmosphere using standard Schlenk techniques if not indicated otherwise. Acetonitrile is dried over calcium hydride and kept over 3 Å molecular sieves.

$[Cu(NCCH_3)_4][BF_4]_2$ (**1**) is synthesized as described earlier [10d,13a]. The mesoporous molecular sieves

Na-AlMCM-41 and Na-AlMCM-48 (1 g) are first pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove physisorbed water. The activated samples (1 g) are treated with 0.2 mmol of complex **1** in 30 mL dry CH_3CN under an argon atmosphere. The mixtures are stirred at 313 K for 3 days. The resulting solutions are filtered off and the white solids are washed repeatedly with CH_3CN until all physisorbed complexes are removed from the surfaces. The washed samples are dried under vacuum at RT.

2.2. Characterization methods

Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). Atomic absorption spectroscopy (AAS; Varian SpectrAA-400 spectrometer) was used to determine the copper content. IR spectra were measured with a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Powder XRD data were collected with a Philips X'pert diffractometer using Cu-Kα radiation filtered by Ni. Nitrogen adsorption–desorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, calcined MCM-41/48 was degassed at 723 K overnight to a residual pressure of about 10–24 mbar. A lower degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume (VP) was estimated from the N_2 uptake at $p/p_0 = 0.95$, using the liquid nitrogen density of 0.8081 g cm^{-3}. The pore size distribution curves (PSD, differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron microscopy (TEM) was executed on a JEOL JEM2010 operated at 120 kV.

2.3. Typical procedure for olefin cyclopropanation

EDA (0.114 g, 1.0 mmol) in 2.0 mL of acetonitrile was slowly added (addition time 1 h) to a 4.0 mL acetonitrile solution of an olefin (5.0 mmol) and catalyst (0.02 mmol; based on Cu content). The reaction was followed by GC-MS. After the reaction was finished the products were identified by GC-MS. Products were isolated by flash chromatography. Yields were determined based on EDA.

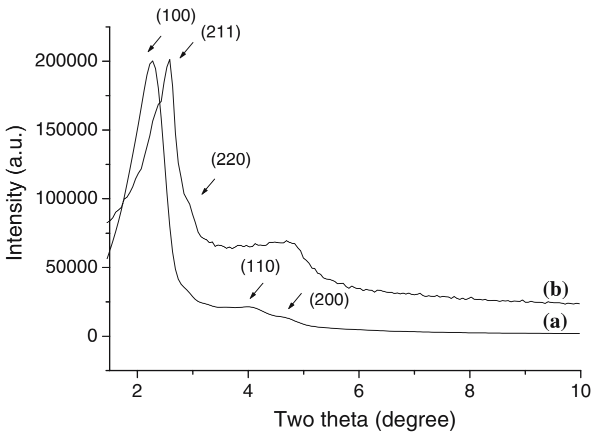


Figure 1. Powder XRD pattern of (a) Na-AM41CuBF, and (b)Na-AM48CuBF.

3. Results and discussion

The powder XRD pattern of copper complex **1** grafted MCM-41 and MCM-48 samples are in full agreement with reported pattern [14,15], indicating the samples to be well ordered (Figure 1) [14,15]. Several distinct Bragg peaks are observed in the $2\theta = 2–8°$ region, which can be indexed to different hkl reflections for a hexagonal unit cell (using the strongest reflection, d_{100}) and a cubic unit cell (using the strongest reflection, d_{211}), respectively. Even after grafting the bulky complex **1** on mesoporous surfaces (Figure 1) the higher 2θ peaks are still observed, indicating the retention of long-range hexagonal and cubic symmetry. Compared to parent MCM-41 and MCM-48 [13b], the grafted samples show a decrease in the relative intensities and broadening of the XRD reflection. There is also a clear shift to higher 2θ values. These changes originate from the immobilization of the copper acetonitrile complexes inside the channels of MCM-41 and MCM-48 [14,15].

Figure 2 depicts the FT-IR spectra of parent calcined mesoporous MCM-41, MCM-48 and the grafted samples. The bands at 1206, 1060, and 794 cm^{-1} are attributed to stretching vibrations of the mesoporous

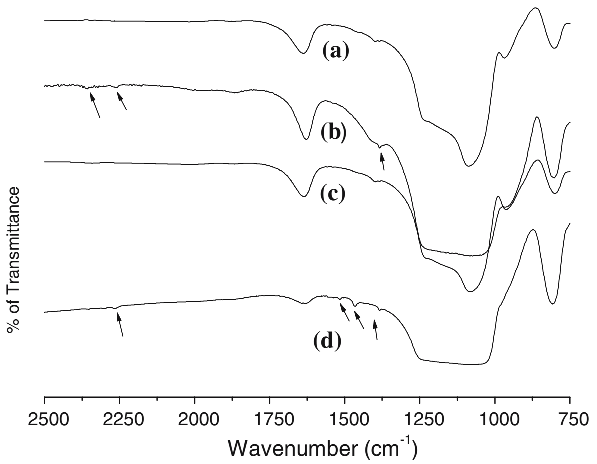


Figure 2. FT-IR spectra of (a) AlMCM-41, (b) Na-AM41CuBF, (c) AlMCM-48 and (d) Na-AM48CuBF.

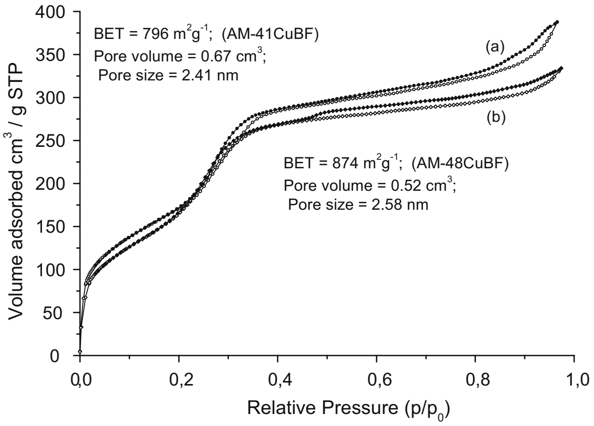


Figure 3. N_2 adsorption/desorption analysis of (a) Na-AM41CuBF, and (b)Na-AM48CuBF.

framework (Si–O–Si). The band around 960 cm^{-1} is assigned to a vibration mode of the silanol (Si–OH) groups in the mesoporous channels [20]. A new weak band around 2300 cm^{-1} can be assigned to nitrile (CN) group vibration of the grafted compounds. Free acetonitrile, however, is not present in the spectra. The ν(CN) vibrations of free $NCCH_3$ would be expected at (ν(CN) = 2253 and 2293 cm^{-1}) [22]. The presence of only one ν(CN) absorption is consistent with the high symmetry of the coordinated $NCCH_3$ around the metal center, as observed for free complex **1**. The heterogenization procedure presented here does, therefore, not disturb the tetrahedral cation coordination sphere. Additional bands appear in the range of 2949 and 2853 cm^{-1} (not shown in the figure) due to C–H stretching vibrations, originating from the nitrile-CH_3 groups. The appearance of bands at 1385 cm^{-1} is due to the remaining $[BF_4]^-$ anion [18].

The low temperature N_2 adsorption/desorption isotherms of parent MCM-41 and MCM-48 [13c] are of type IV according to the IUPAC [18] nomenclature and characteristic for mesoporous solids (surface area 840, 1040 $m^2\ g^{-1}$ pore size 2.74, 2.41 nm and pore volume 0.9, 1.1 $cm^3\ g^{-1}$, respectively, for AlMCM-41 and Al-MCM-48 samples). Well-defined, sharp inflections are observed between the relative pressure (p/p_o) of 0.3 and 0.4, due to capillary condensation of nitrogen inside the primary mesopores [18]. Reversible type IV isotherms similar to the parent MCM-41/MCM-48 [14,15] are obtained for the grafted copper acetonitrile complex samples (Figure 3). However, broader pore size distributions (2.41–2.58 nm) are observed. A (considerable) decrease in surface area (796, 874 $m^2\ g^{-1}$) and pore volume (0.67, 0.52 $cm^3\ g^{-1}$) for the obtained materials indicates that the copper acetonitrile complexes are successfully grafted in the channel of the mesoporous materials [13–15].

The TEM images of the grafted samples (Figure 4) are providing strong evidence that the mesoporous structure of the support retains its long range ordering [14,15] throughout the grafting process and that the channels of the materials remain accessible. The uniform TEM image and the corresponding ED pattern (inside) evidences the structural intactness. Elemental analyses (EA) demonstrate that the copper content is 1.6 wt.% (equivalent to 6 wt.% of compound **1** loading on both Na-AM41CuBF and Na-AM48CuBF). The presence of 1.5 wt.% of F confirms that one of the counter ions remains associated with the copper acetonitrile complex after grafting the compound on mesoporous materials surface. The TG-MS spectrum of Na-AM41CuBF shows about 6.5% weight loss up to 1000 °C due to decomposition of the copper acetonitrile complex. The observed mass values m/z^+ = 26, 15 and 19 are corresponding to a cyano methyl and fluorine group of complex **1**, which once again confirms the presence of the Cu-complexes in the mesoporous channels.

The Na-AM41CuBF and Na-AM48CuBF materials were applied in the cyclooctene cyclopropanation with EDA at room temperature and the results are displayed in Table 1. The grafted materials show relatively low activity in the cyclopropanation reaction with prevailing

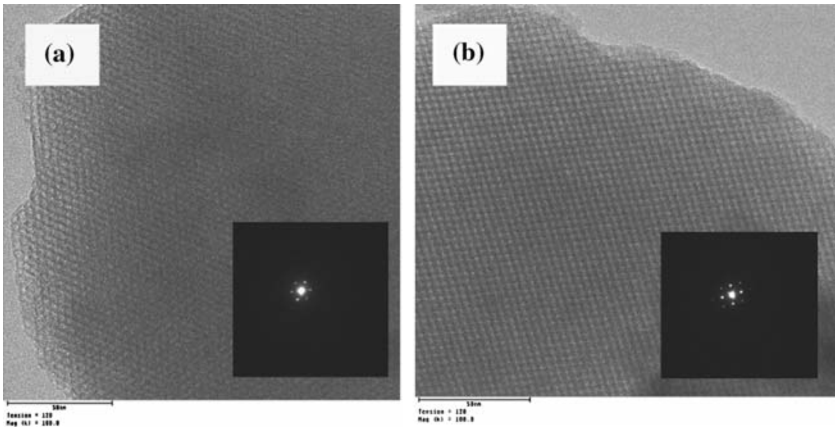


Figure 4. TEM images and ED pattern of (a) Na-AM41CuBF, and (b) Na-AM48CuBF.

Table 1
Cyclopropanation of cyclooctene with various catalysts using EDA[a]

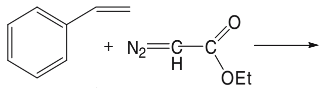
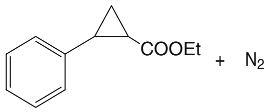
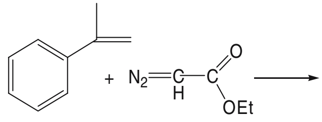
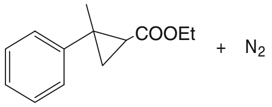
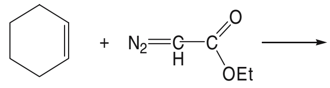
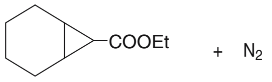
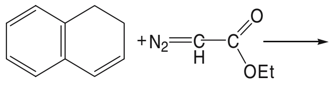
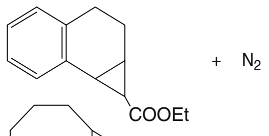
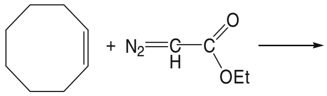
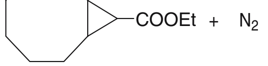
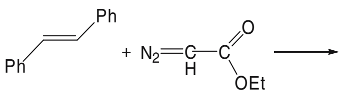
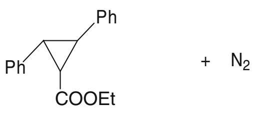
Catalysts	Run	Yield (%)
Complex **1**	–	42
NaAM-48-CuBF	1st run	38
	2nd run	19
	3rd run	19
NaAM-48-CuBF	1st run	18
	2nd run	12
	3rd run	11

[a]Catalyst: Olefins = 1:250;
[b]Based on EDA conversion; Temperature = 298 K; reaction time = 20 h.

E-selectivity (90% in all the cases), as expected. The three-dimensional pore structure of MCM-48 is beneficial to the reaction, since these grafted materials achieve better performances than the ones grafted on the one-dimensional MCM-41 structure, with regard to activity. There is an considerable decrease of activity in the second run, but then the activity remains the same for further catalytic runs. The initial activity loss may be due to slight leaching of weakly bonded compound **1**. Leaching experiments with Na-AM41CuBF and Na-AM48CuBF were carried out under normal reaction conditions. First the catalyst was treated with CH$_2$Cl$_2$ and styrene for 1 h at room temperature. Then the liquid phase was filtered off from the heterogeneous catalyst. The reaction was carried out using the filtrate after addition of EDA. The filtered solution shows product yields of 4–6% formed after the separation from the catalyst carrier materials. Leaching of active catalyst is therefore not pronounced observed decrease in activity during the recycling experiments may be partially due to adsorption of reactant/product molecules on the active species of the surface.

The homogeneous compound **1** and Na-AM48CuBF were further examined for cyclopropanation reactions of various olefins (see Table 2). The heterogeneous catalysts show in all cases lower yield than the respective homogeneous catalysts. The yield of the final products obviously depends on the electron density of olefinic bond. Olefins with lower electron density lead to better yields compared to higher electron density olefins. In all the cases 90% *E*-selectivity is observed.

Table 2
Cyclopropanation of various olefins using EDA with homogeneous complex **1** and NaAM-48-CuBF as the catalysts[a]

Reactants	Products	Yields (%)	
		Complex (1)	AM48CuBF
		29	26
		27	15
		28	15
		23	13
		42	33
		87	55

[a] Catalyst : Olefins = 1 : 250; [b] Based on EDA conversion; Temperature = 298 K,reaction time = 20 h

4. Conclusion

[Cu(CH$_3$CN)$_6$][BF$_4$]$_2$ is grafted on the surface of mesoporous AlMCM-41 and AlMCM-48 by ion exchange. The grafted materials retains long range ordering and the catalysts are found to be active both in homogeneous and heterogeneous medium for cyclopropanation of olefin reactions. The catalytic activities in homogeneous medium are, however, higher than the activities observed in heterogeneous phase.

Acknowledgments

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References

[1] (a) S.I. Stupp, V. LeBonheur, K. Walker, L. Liu, K.E. Huggins, M. Keser and A. Amstutz, Science 276 (1997) 384; (b) M. Moffit, K. Khougaz and A. Eisenberg, Acc. Chem. Res. 29 (1996) 95; (c) H.A. Klok and S. Lecommandoux, Adv. Mater. 13 (2001) 1217.

[2] (a) W. Meier, Chem. Soc. Rev. 29 (2000) 295; (b) S.A. Jenekhe and X.L. Chen, Science 279 (1998) 1903; (c) J. Ding and G. Liu, J. Phys. Chem. B. 102 (1998) 6107; (d) E. Donath, G.B. Sukhorukov, F. Caruso, S.A. Davis and H. Möhwald, Angew. Chem. Int. Ed. 37 (1998) 2201; (e) H. Duan, D. Chen, M. Jiang, W. Gan, S. Li, M. Wang and J. Gong, J. Am. Chem. Soc. 123 (2001) 12097; (f) S.M. Marinakos, J.P. Novak, L.C. Brousseau, A.B. House, E.M. Edeki, J.C. Feldhaus and D.L. Feldheim, J. Am. Chem. Soc. 121 (1999) 8518; (g) S. Liu and M. Jiang, Chem. J. Chin. Univ. 22 (2001) 1066; (h) F. Ch, S. Lecommandoux, Y. Gnanou and H.A. Klok, Angew. Chem. Int. Ed. 41 (2002) 1339.

[3] (a) Q. Zhang, E.E. Remsen and K.L.Wooley, J. Am. Chem. Soc. 122 (2000) 3642; (b) H. Huang, E.E. Remsen, T. Kowalewski and K.L.Wooley, J. Am. Chem. Soc. 121 (1999) 3805; (c) T. Sanji, Y. Nakatsuka, S. Ohnishi and H. Sakurai, Macromolecules 33 (2000) 8524; (d) R.S. Underhill and G. Liu, Chem. Mater. 12 (2000) 2080; (e) G. Liu, J. Ding and S. Stewart, Angew. Chem. Int. Ed. 38 (1999) 835; (f) S. Stewart and G. Liu, Chem. Mater. 11 (1999) 1048.

[4] (a) P.M. Treichel, D.A. Komar and P.J. Vincenti, Synth. React. Inorg. Met.-Org. Chem. 14 (1984) 383; (b) H. Lebel, J.-F. Marcoux, C. Molinaro and A.B. Charette, Chem. Rev. 103 (2003) 977; (c) R.E. Gawley and S. Narayan, Chem. Commun. (2005) 5109; (d) M. Rubina and V. Gevorgyan, Tetrahedron 60 (2004) 3129.

[5] (a) M.P. Doyle and D.C. Forbes, Chem. Rev. 98 (1998) 911; (b) S.B. Park, H. Nishiyama; Y. Itoh and K. Itoh, J. Chem. Soc. Chem. Commun. (1994) 1315; (c) G. Maas, Chem. Soc. Rev. 33 (2004) 183.

[6] I.J. Munslow, K.M. Gillespie, R.J. Deeth and P. Scott, Chem. Commun. (2001) 1638.

[7] (a) S. Taylor, J. Gullick, P. McMorn, D. Bethell, P.C.B. Page, F.E. Hancock, F. King and G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (2001) 1714; (b) R.J. Clarke and I. Shannon, Chem. Commun. (2001) 1936; (c) J. Gullick, S. Taylor, P. McMorn, D. Bethell, P.C.B. Page, F.E. Hancock, F. King and G.J. Hutchings, J. Mol. Catal. A: Chem. 182–183 (2002) 571; J. Mol. Catal. A: Chem. 180 (2002) 85; (d) S. Taylor, J. Gullick, N. Galea, P. McMorn, D. Bethell, P.C.B. Page, F.E. Hancock, F. King, D.J. Willock and G.J. Hutchings, Topics Catal. 25 (2003) 81; (e) S. Taylor, J. Gullick, P. McMorn, D. Bethell, P.C.B. Page, F.E. Hancock, F. King and G.J. Hutchings, Topics Catal. 25 (2003) 43; (f) Y. Wan, P. McMorn, F.E. Hancock and G.J. Hutchings, Catal. Lett. 91 (2003) 145; (g) N.A. Caplan, F.E. Hancock, P.C.B. Page and G.J. Hutchings, Angew. Chem. Int. Ed. 43 (2004) 1685; (h) J.M. Fraile, J.I. Garcia, C.I. Herrerias, J.A. Mayoral and M.A. Harmer, J. Catal. 221 (2004) 532; (i) D. Ryan, P. McMorn, D. Bethell and G.J. Hutchings, Org. Biomol. Chem. 2 (2004) 3566; (j) J.M. Fraile, J.I. García, C.I. Herrerías, J.A. Mayoral, S. Gmough and M. Vaultier, Green Chem. 6 (2004) 93; (k) M.L. Kantam, V. Neeraja, B. Kavita and Y. Haritha, Synlett (2004) 525.

[8] (a) J.M. Fraile, J.I. Garcia, M.A. Harmer, C.I. Herrerias, J.A. Mayoral, O. Reiser and H. Werner, J. Mater. Chem. 12 (2002) 3290; (b) A. Cornejo, J.M. Fraile, J.I. Garcia, M.J. Gil, C.I. Herrerias, G. Legarreta, V. Martinez-Merino and J.A. Mayoral, J. Mol. Catal. A: Chem. 196 (2003) 101.

[9] (a) C. Langham, P. Piaggio, D. Bethell, D.F. Lee, P. McMorn, P.C.B. Page, D.J. Wilock, C. Sly, F.E. Hancock, F. King and G.J. Hutchings, Chem. Commun. (1998) 1601; (b) C. Langham, S. Taylor, D. Bethell, P. McMorn, P.C.B. Page, D.J. Wilock, C. Sly, F.E. Hancock, F. King and G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2 (1999) 1043; (c) C. Langham, D. Bethell, D.F. Lee, P. McMorn, P.C.B. Page, D.J. Wilock, C. Sly, F.E. Hancock, F. King and G.J. Hutchings, Appl. Catal. A: Gen. 182 (1999) 85; (d) Y. Traa, D.M. Murphy, R.D. Farley and G.J. Hutchings, Phys. Chem. 3 (2001) 1073.

[10] (a) S.H. Strauss, Chem. Rev. 93 (1993) 927; (b) I. Krossing and I. Raabe, Angew. Chem. Int. Ed. 43 (2004) 2066; (c) M. Vierle, Y. Zhang, E. Herdtweck, M. Bohnenpoll, O. Nuyken and F.E. Kühn, Angew. Chem. Int. Ed. Engl. 42 (2003) 1307; (d) M. Vierle, Y. Zhang, K. Köhler, C. Häßner, A.M. Santos, E. Herdtweck, O. Nuyken and F.E. Kühn, Chem. Eur. J. 10 (2004) 6323.

[11] (a) K.R. Dunbar, J. Am. Chem. Soc. 110 (1988) 8247; (b) W.E. Buschmann and J.S. Miller, Chem. Eur. J. 4 (1998) 1731; (c) F.A. Cotton and K.J. Wiesinger, J. Am. Chem. Soc. 30 (1991) 871; (d) R.T. Henriques, E. Herdtweck, F.E. Kühn, A.D. Lopes, J. Mink and C.C. Romão, J. Chem. Soc. Dalton Trans. (1998) 1293; (e) F.A. Cotton and F.E. Kühn, J. Am. Chem. Soc., 118 (1996) 5826; (f) F.E. Kühn, J.R. Ismeier, D. Schön, W.M. Xue, G. Zhang and O. Nuyken, Macromol. Rapid Commun. 20 (1999) 555; (g) F.E. Kühn, D. Schön, G. Zhang and O. Nuyken, J. Macromol. Sci. Pure Appl. Chem. 37 (2000) 971; (h) P. Ferreira and F.E. Kühn, Trends Inorg. Chem. 7 (2001) 89.

[12] (a) M. McCann, in: *Catalysis by Di- and Polynuclear Metal Cluster Complexes*, eds. R.D. Adams and F.A. Cotton (Wiley-VCH, New York, 1998), pp. 145–166; (b) M. McCann and E.M.G. Coda, J. Mol. Catal. A: Chem. 109 (1996) 99; (c) M. Pillinger, I.S. Gonçalves, A.A. Valente, P. Ferreira, D. Schön, O. Nuyken and F.E. Kühn, Des. Monomers Poly. 4 (2001) 269; (d) M. Pillinger, I.S. Gonçalves, P. Ferreira, J. Rocha, M. Schäfer, D. Schön, O. Nuyken and F.E. Kühn, Macromol. Rapid Commun. 22 (2001) 1306; (e) M. Pillinger, I.S. Gonçalves, A.D. Lopes, P. Ferreira, J. Rocha, G. Zhang, M. Schäfer, O. Nuyken and F.E. Kühn, Phys. Chem. Chem. Phys. 4 (2002) 696; (f) M. Pillinger, C.D. Nunes, P.D. Vaz, A.A. Valente, I.S. Gonçalves, P.J.A. Ribeiro-Claro, J. Rocha, L.D. Carlos and F.E. Kühn, Phys. Chem. 4 (2002) 3098.

[13] (a) Y. Zhang, W. Sun, A.M. Santos and F.E. Kühn, Catal. Lett. 101 (2005) 35; (b) A. Sakthivel, A.K. Hijazi, M. Hanzlik, A.S.T. Chiang and F.E. Kühn, Appl. Catal. A: Gen. 294 (2005) 161.

[14] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, Nature 359 (1992) 710.

[15] (a) R. Ryoo, S.H. Joo and J.M. Kim, J. Phys. Chem. B 103 (1999) 7435; (b) A. Sakthivel and P. Selvam, Catal. Lett. 84 (2002) 37; (c) A. Sakthivel, J. Zhao, M. Hanzlik, A.S.T. Chiang, W.A. Herrmann and F.E. Kühn, Adv. Syn. Catal. 347 (2005) 473; (d) M. Jia, A. Seifert and W.R. Thiel, Chem. Mater. 15 (2003) 2174.

[16] (a) K. Moller and T. Bein, Chem. Mater. 10 (1998) 2950; (b) D.E. De Vos, M. Dams, B.F. Sels and P.A. Jacobs, Chem. Rev. 102 (2002) 1085; (c) C. Bianchini and P. Barbaro, Topics Catal. 19 (2002) 17; (d) C. Li, Catal. Rev.-Sci., Eng. 46 (2004) 419.

[17] (a) S. Gago, Y. Zhang, A.M. Santos, K. Köhler, F.E. Kühn, J.A. Fernandes, M. Pillinger, A.A. Valente, T.M. Santos, P.J.A. Ribeiro-Claro and I.S. Gonçalves, Microp. Mesop. Mater. 76 (2004) 131; (b) A. Sakthivel, A.K. Hijazi, H.Y. Yeong, K. Köhler, O. Nuyken and F. E. Kühn, J. Mater. Chem. 15(41) (2005) 4441.

[18] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscow, R.A. Pierotti, T. Rouquerol and T. Siemienewska, Pure Appl. Chem. 57 (1985) 603.