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Activity, selectivity and stability of metallosilicates containing molybdenum for the epoxidation of alkenes

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Abstract

Microporous metallosilicates containing various transition metals have been prepared by the acid-catalyzed sol–gel process. The catalytic activity of the materials has been tested for the epoxidation of cyclooctene with *tert*-butyl hydroperoxide. Silicates containing molybdenum showed high activities and epoxide selectivities. The catalytic activities of catalysts prepared with molybdenyl acetylacetonate as metal precursor are mainly due to metal leached into the homogeneous phase. A catalyst for the heterogeneous phase epoxidation was obtained, using Mo(V)isopropoxide as metal precursor. This catalyst was tested in the epoxidation of various alkenes and conversions increase in the order 1-decene $\approx$ α-pinene $<$ 1-octene $<$ limonene $<$ 1-hexene $<$ cyclooctene $<$ cyclohexene. Quantitative conversions of cyclooctene and cyclohexene with epoxide selectivities around 98% were obtained at 373 K. The catalyst was used in five consecutive reactions and metal leaching is fairly low up to the third reaction. Information about the catalyst structure was obtained by elemental analysis, thermogravimetry, X-ray diffraction and fluorescence, N_2-physisorption, UV–VIS and FTIR spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The development of heterogeneous catalytic systems for the epoxidation of olefins is an highly attractive topic in current chemical research. Epoxidation is one of the fundamental oxidation reactions in industrial chemistry leading to a series of important products. The annual production of more than 11 million tons of ethylene oxide and propylene oxide by epoxidation of ethylene and propylene may illustrate the importance of the reaction. Epoxidation of ethylene is carried out in an economic, heterogeneously catalyzed process using silver catalysts and air as oxidant [1]. Molybdenum catalysts in the homogeneous phase [2] as well as titanium catalysts (titanium(IV)/silica) in the heterogeneous phase [3] are applied for the production of propylene oxide with alkyl hydroperoxides as oxidants. Besides these examples of catalyzed processes, epoxidation with peroxo carboxylic acids is still widely used in industrial chemistry and applied in the epoxidation of long chain olefins, unsaturated esters and acids, terpenes, vegetable oils and polymers (polybutadiene, natural and synthetic rubber and polyesters) [4]. The crucial disadvantage of this method is the formation of large

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amounts of carboxylic acids as by-products and the necessity of their work up and recycling. The use of homogeneous catalytic systems based on metals like Re, Mn and W in combination with hydrogen peroxide as oxidant is the subject of intensive research [5–7]. However, the industrial use of these catalytic systems is limited because of the high catalyst costs and difficulties to separate them from the reaction mixtures.

Since the synthesis and industrial application of titanium silicalite 1 (TS-1) [8], academic and industrial research has focused upon the development of new heterogeneous oxidation catalysts. The use of TS-1 is limited to substrates which can enter the medium pores (5.3 Å × 5.5 Å) of the MF1-structure. To increase the applicability of this type of material, titanium containing molecular sieves with larger pore sizes such as Ti-Beta [9] and Ti-MCM-41 [10] have been prepared, but the catalytic activity of these systems is generally lower compared to TS-1. In this context amorphous titania-silica aero- [11] and xerogels [12] were shown to be remarkably active catalysts in the epoxidation of olefins with *tert*-butyl hydroperoxide. In addition to titanium-substituted molecular sieves, numerous molecular sieves containing other transition metal ions were developed and used as oxidation catalysts [13]. Their catalytic properties with regard to catalyst stability and metal leaching have been critically reviewed [14].

The development of heterogeneous molybdenum catalysts is of particular interest and many attempts have been made to attach molybdenum compounds to functionalized polymeric supports [15] and to synthesize Mo-containing molecular sieves [16]. Preparation of molybdenum-containing silicalite-1 [17] and Mo-incorporation in the framework of MCM-41 [18] were reported but the catalytic properties of the materials were poorly investigated. Amorphous mesoporous silicates containing Ti, W and Mo have been prepared by the sol–gel method and were shown to be active catalysts in the oxidation of alcohols and the epoxidation of alkenes with aqueous H_2O_2 [19]. In the present paper we describe the synthesis of microporous metallosilicates via the sol–gel method and their use as epoxidation catalysts. Our work concentrates on silicates containing Mo and the evaluation of their stability.

2. Experimental

2.1. Synthesis of the catalysts

The catalysts were prepared by acid-catalyzed hydrolyzation and condensation of tetraethoxysilane $Si(OEt)_4$ (TEOS) in the presence of transition metal compounds according to the sol–gel process described by Klein et al. [20]. In a typical procedure 147 mmol of TEOS (Aldrich, 98%) and 3 mmol of the transition metal precursor ($ZrOCl_2{\cdot}8H_2O$ (Aldrich, 98%), $Mn(OAc)_2{\cdot}4H_2O$ (Fluka, >99%), $Ti(OEt)_4$ (Aldrich, 20% Ti), $VOSO_4{\cdot}3H_2O$ (Aldrich), $Cr(NO_3)_3{\cdot}9H_2O$ (Aldrich, 99%), $MoO_2(acac)_2$ (Aldrich) or $Mo(O\mathit{i}Pr)_5$ (Alfa Aesar, 5% w/v in isopropanol)) were dissolved in 450 mmol ethanol and 7.46 g of 8 mol/l HCl (53 mmol HCl) were added dropwise to the well stirred solution. The reaction mixture was stirred for 5 min and then allowed to stand at room temperature in an uncovered polypropylene beaker to remove the volatiles by slow evaporation. Usually gel formation and solidification was complete after 4 days and the material was dried, using one of the following procedures. The sample was heated to 338 K at a rate of 0.2 K/min and kept at this temperature for 5 h. After further heating at a rate of 0.5 K/min, the material was kept at 523 K for 5 h. The material was slowly cooled down to room temperature with a cooling rate of 1 K/min (method A). In another procedure the material was dried at 373 K for 24 h and subsequently heated to 473 K, where it was kept for 24 h (method B).

2.2. Characterization of the catalysts

Physisorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 instrument with nitrogen as probe molecule. Prior to measurement the samples were heated to 423 K for 72 h under vacuum. Surface areas were determined using the BET equation in the low pressure region ($p/p_0 = 0.205$). The Horvath–Kawazoe method [21] was used to calculate pore size distribution from nitrogen adsorption isotherms. The metal contents of the silicates were determined by X-ray fluorescence analysis (XRF) on a Spectrace TX-5000 instrument using calibration curves prepared from mixtures of SiO_2 and the transition metal precursors. Infrared spectra were obtained on a Perkin-Elmer 1600 FTIR spectrometer from KBr pellets containing 1% of the catalyst. UV–VIS spectra were recorded with a Cary 5 G spectrometer using the diffuse reflectance technique. Absorptions of the pure silicate without transition metal were determined in blank experiments and subtracted. Thermogravimetric analyses (TGA) were carried out under argon on a DuPont 951 instrument with a heating rate of 10 K/min from 298 to 1273 K. Powder X-ray diffraction (XRD) was performed on a Shimadzu XD-3A diffractometer. Elemental analyses were obtained on a Perkin-Elmer 2400 instrument.

2.3. Catalytic epoxidations

The reactions were carried out without precautions against moisture and oxygen, using a glass tube placed in a temperature equilibrated oil bath and fitted with a reflux condenser. The olefins cyclooctene (Aldrich, 95%), cyclohexene (Merck-Schuchardt, >99%), limonene (Serva, pure), α-pinene (Eucatex), 1-decene (Aldrich, 94%), 1-octene (Aldrich, 98%) and 1-hexene (Alfa Aesar, 98%) were used as received without further purification. In a typical experiment a mixture of 10 mmol of olefin, 15 mmol of *tert*-butyl hydroperoxide (TBHP, 88% in cyclohexane; Nitrocarbono S.A.), 50 mg of catalyst (4.9×10^{-3} mmol Mo) and 2.5 mmol of *n*-decane (Aldrich, 99%) as internal standard for gas chromatography (GC) was magnetically stirred at the indicated temperature for 24 h. In the catalytic tests with various metallosilicates a 47.9% solution of TBHP in ethyl acetate (EtOAc), prepared by removal of water from aqueous TBHP (Aldrich, 70%), was used as oxidant. The course of the reactions was monitored by taking aliquots from the reaction mixtures at different reaction times. The samples were analyzed, using a Hewlett Packard HP 5890 Series II gas chromatograph equipped with a HP Ultra 2 capillary column (50 m × 0.2 mm × 0.33 μm film thickness; crosslinked 5% phenyl methyl silicone) and a flame ionization detector (FID). Products were quantified using calibration curves obtained with standard solutions. Unknown products were separated and identified by GC using the same instrument and a HP 5970 Series mass selective detector (MSD). TBHP consumption was determined after the catalytic reaction by iodometric titration.

In a series of leaching experiments the catalyst was separated from the reaction mixture before completion of the reaction. The catalyst was removed by filtration at reaction temperature and the filtrate was immediately allowed to react further in the absence of the catalyst. The reaction mixture before and after filtration was analyzed by GC, taking samples at different reaction times. Recycling tests with repeated use of the catalyst in five consecutive reactions were carried out using, typically, 50 mmol of cyclohexene, 75 mmol of *tert*-butyl hydroperoxide (88% in cyclohexane), 250 mg of catalyst (2.45×10^{-2} mmol Mo) and 12.5 mmol of *n*-decane. The catalyst was removed from the reaction mixture after 8 h by filtration, washed with EtOAc, dried at 473 K for 24 h and subjected to the next catalytic run.

3. Results and discussion

3.1. Catalytic tests

The catalytic activity of various transition metal containing silicates M–SiO_2^T (M = Zr, Mn, Ti, V, Cr and Mo; T = drying method A or B) was evaluated in the epoxidation of cylooctene using *tert*-butyl hydroperoxide (TBHP) as oxidant. The transition metal precursors used in the synthesis of the silicates, cyclooctene conversions and epoxide selectivities are summarized in Table 1. Low catalytic activities and epoxide yields in the range of the control reaction without catalyst were observed, using the materials containing zirconium and manganese. The Ti–SiO_2^A metallosilicate showed moderate activity, in agreement with the results obtained by Maier et al. [12], whereas V–SiO_2^B and Cr–SiO_2^A catalyzed the reaction considerably. However, the molybdenum containing silicate Mo(acac)–SiO_2^B was clearly more active and selective compared to the other materials and, therefore, molybdenum containing silicates were studied in more detail.

3.2. Molybdenum containing silicates as epoxidation catalysts

In order to obtain additional information about the catalytic properties of molybdenum containing silicates, three materials, Mo(O*i*Pr)–SiO_2^A, Mo(acac)–SiO_2^A and Mo(acac)–SiO_2^B were tested as catalysts for cyclooctene epoxidation with TBHP. In the blank experiment 27% of conversion was observed. The

Table 1
Epoxidation of cyclooctene catalyzed by transition metal containing silicates[a]

Catalyst	Transition metal precursor	Conversion[b] (%)	Selectivity (%)
–	–	5	75
Zr–$\mathrm{SiO}_2^{\mathrm{A}}$	$\mathrm{ZrOCl_2 \cdot 8H_2O}$	8	36
Mn–$\mathrm{SiO}_2^{\mathrm{B}}$	$\mathrm{Mn(OAc)_2 \cdot 4H_2O}$	5	81
Ti–$\mathrm{SiO}_2^{\mathrm{A}}$	$\mathrm{Ti(OEt)_4}$	10	88
V–$\mathrm{SiO}_2^{\mathrm{B}}$	$\mathrm{VOSO_4 \cdot 4H_2O}$	35	73
Cr–$\mathrm{SiO}_2^{\mathrm{A}}$	$\mathrm{Cr(NO_3)_3 \cdot 9H_2O}$	43	76
Mo(acac)–$\mathrm{SiO}_2^{\mathrm{B}}$	$\mathrm{MoO_2(acac)_2}$	57	95

[a] Reaction conditions: 10 mmol cyclooctene, 7 mmol TBHP (47.9% in EtOAc), 2.5 mmol *n*-decane and 25 mg of catalyst; 333 K; 24 h.
[b] Maximum conversion relative to TBHP: 70%.

addition of the pure silicate prepared without molybdenum precursor did not show a significant effect on the reaction (Table 2). Although cyclooctene conversion was lower compared to the materials synthesized with the acetylacetonate precursor, the catalyst Mo(O*i*Pr)–$\mathrm{SiO}_2^{\mathrm{A}}$ (Mo content 0.94%) showed the highest turnover number (TN). Furthermore, the drying procedure of the gel influences the catalytic activity. Mo(acac)–$\mathrm{SiO}_2^{\mathrm{A}}$ (Mo content 1.55%), which was dried by slow heating with a well defined temperature profile, was found to be more active than Mo(acac)–$\mathrm{SiO}_2^{\mathrm{B}}$ (Mo content 3.23%), which was dried at elevated temperatures without a controlled temperature increase. Epoxide selectivities for all Mo-containing catalysts were 95% or higher.

Catalyst filtration experiments were carried out to investigate whether the reactions are catalyzed in the homogeneous or the heterogeneous phase. The catalysts were separated by filtration at reaction temperature and the reaction mixtures were analyzed before and after removal of the catalysts. Using Mo(acac)–$\mathrm{SiO}_2^{\mathrm{B}}$, it was proven that the catalytic reaction takes place in the homogeneous phase and can be attributed to active species leached from the silicate. The catalyst was removed from the reaction mixture after 5 min (cyclooctene conversion 15%) and the reaction in the absence of the solid catalyst took the same course as the reaction with the solid catalyst present during 24 h. In another filtration experiment, where Mo(acac)–$\mathrm{SiO}_2^{\mathrm{A}}$ was separated from the reaction mixture after 5 min, an increase in cyclooctene conversion from 8 (5 min) to 53% (24 h) was observed, thus indicating that some Mo had leached and was active in the homogeneous phase. On the other hand catalyst filtration experiments with Mo(O*i*Pr)–$\mathrm{SiO}_2^{\mathrm{A}}$ showed that reactions with this catalyst are catalyzed exclusively by the heterogeneous catalyst. The catalyst was separated from the reaction mixture after reaction times of 5, 30 and 150 min, respectively. As shown in Fig. 1 the catalytic reactions stopped immediately after removal of the catalyst and only negligible amounts of epoxide were formed due to non-catalytic reactions. This behavior could be explained on a molecular level by

Table 2
Epoxidation of cyclooctene catalyzed by molybdenum containing silicates[a]

Catalyst	Transition metal precursor	Conversion (%)	Selectivity (%)	TN[b]
–	–	27	52	–
$\mathrm{SiO_2}$	–	28	61	–
Mo(O*i*Pr)–$\mathrm{SiO}_2^{\mathrm{A}}$	Mo(O*i*Pr)$_5$	82	95	1590
Mo(acac)–$\mathrm{SiO}_2^{\mathrm{A}}$	$\mathrm{MoO_2(acac)_2}$	94	97	1123
Mo(acac)–$\mathrm{SiO}_2^{\mathrm{B}}$	$\mathrm{MoO_2(acac)_2}$	89	95	504

[a] Reaction conditions: 10 mmol cyclooctene, 15 mmol TBHP (88% in cyclo-hexane), 2.5 mmol *n*-decane and 50 mg of catalyst; 333 K; 24 h.
[b] Turnover number: mol epoxide/mol metal.

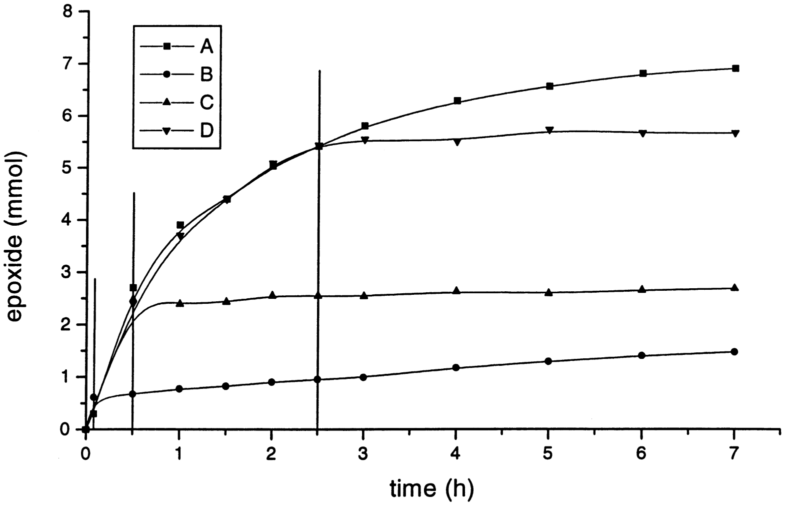

Fig. 1. Epoxidation of cyclooctene catalyzed by Mo(O*i*Pr)–SiO_2^A without (A) and with removal of the catalyst after 5 (B), 30 (C) and 150 min (D). Reaction conditions: 10 mmol cyclooctene, 15 mmol TBHP (88% in cyclohexane), 2.5 mmol *n*-decane and 50 mg of catalyst; 333 K.

similar hydrolysis and condensation rates of TEOS and Mo(O*i*Pr)$_5$, which would favor the formation of Si–O–Mo bonds. The molecular design of alkoxide precursors in order to control hydrolysis and condensation rates in the sol–gel process was considered to be a key-factor for tailor-made materials [22]. Elemental analysis showed carbon contents around 2.4% for the silicates obtained with molybdenyl acetylacetonate and a carbon content of 0.1% for Mo(O*i*Pr)–SiO_2^A. These results clearly indicate considerable impurities of organic compounds in the former materials, most probably due to the acetylacetonate ligand. Facile metal leaching from these catalysts could be explained by incomplete hydrolysis of molybdenyl acetyl-acetonate in the sol–gel process and, consequently, hindered formation of Si–O–Mo bonds.

3.3. *Mo(OiPr)*–SiO_2^A *as epoxidation catalyst*

To gain more insight into the catalytic abilities of Mo(O*i*Pr)–SiO_2^A, the effect of the olefin:oxidant ratio, the reaction temperature, the use of different substrates and the possibility of catalyst recycling were investigated. In preliminary experiments it was shown that an olefin:TBHP molar ratio of 1:1.5 favors the epoxide yield significantly, compared to reactions with equal molar amounts of olefin and oxidant. A lower increase in cyclooctene conversion and an epoxide selectivity of 100% were observed increasing the ratio from 1:1.5 to 1:2 (Table 3).

The temperature dependence of cyclooctene epoxidation was investigated and reaction profiles at different temperatures are given in Fig. 2. It can be seen that cyclooctene conversion strongly depends on the reaction temperature. Quantitative olefin conversion within 4 h and 99% selectivity for epoxide are observed at a temperature of 373 K whereas epoxide selectivities of 96% and olefin conversions of 92 and 73% are obtained at temperatures of 353 and 333 K, respectively. Using cyclohexene as substrate (Fig. 3), olefin conversion increases from 87 (333 K) to 94 (353 K) and 100% (373 K), with selectivities for epoxide of 96, 96 and 99%, respectively. Figs. 2 and 3 reveal a larger temperature dependence of cyclooctene epoxidation

Table 3
Effect of olefin:oxidant molar ratio on the Mo(O*i*Pr)–SiO_2^A-catalyzed epoxidation of cyclooctene[a]

Cyclooctene:TBHP ratio	Conversion (%)	Selectivity (%)	TN
1:1	84	96	1652
1:1.5	92	96	1794
1:2	96	100	1957

[a] Reaction conditions: 10 mmol cyclooctene; 10, 15 or 20 mmol TBHP (88% in cyclohexane); 2.5 mmol *n*-decane; 50 mg catalyst (4.9×10^{-3} mmol Mo); 353 K; 8 h.

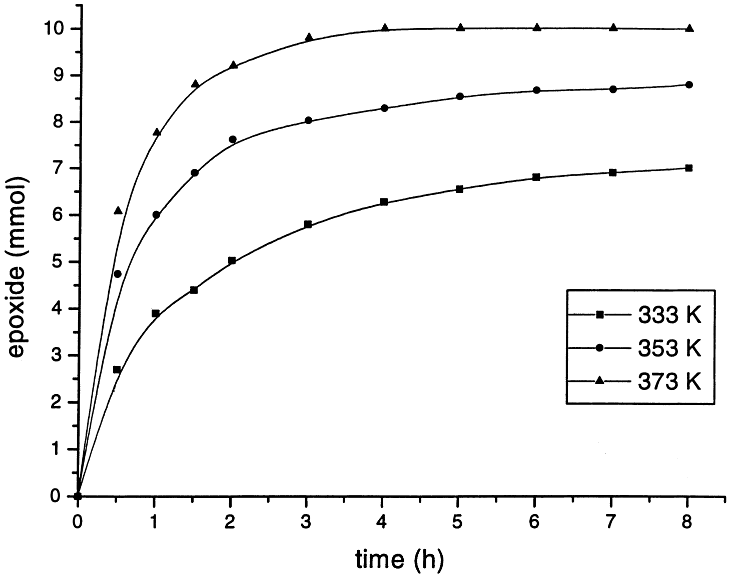

Fig. 2. Reaction profiles for cyclooctene epoxidation catalyzed by Mo(O*i*Pr)–SiO_2^A at different reaction temperatures. Reaction conditions: 10 mmol cyclooctene, 15 mmol TBHP (88% in cyclohexane), 2.5 mmol *n*-decane and 50 mg of catalyst (4.9×10^{-3} mmol Mo).

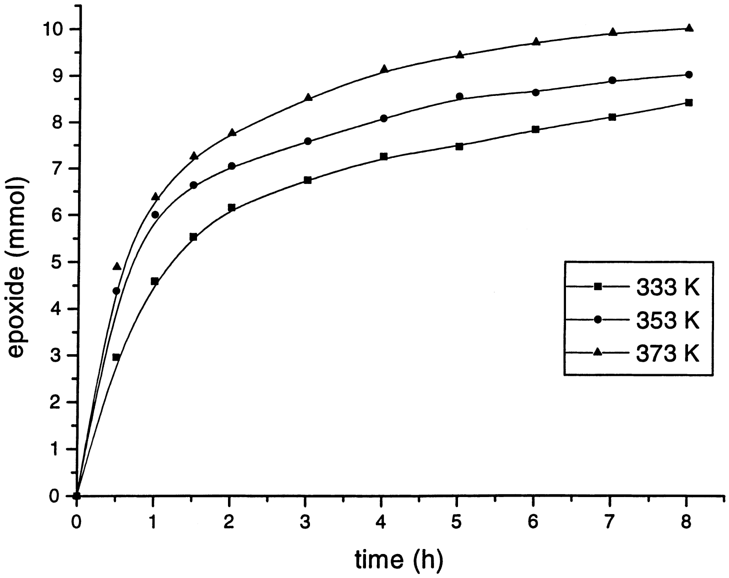

Fig. 3. Reaction profiles for cyclohexene epoxidation catalyzed by Mo(O*i*Pr)–SiO_2^A at different reaction temperatures. Reaction conditions: 10 mmol cyclohexene, 15 mmol TBHP (88% in cyclohexane), 2.5 mmol *n*-decane and 50 mg of catalyst (4.9×10^{-3} mmol Mo).

Table 4
Epoxidation of various alkenes with Mo(O*i*Pr)–SiO_2^A as catalyst[a]

Alkene	Conversion (%)		Selectivity (%)		TN	
	8 h	24 h	8 h	24 h	8 h	24 h
Cyclohexene	94	98	96	96	1835	1973
Cyclooctene	92	96	96	96	1794	1876
Limonene[b]	65	81	89[c]	86[c]	1183[d]	1427[d]
α-Pinene[b]	32	44	41	34	265	306
1-Hexene	79	86	92	92	1488	1621
1-Octene	30	51	71	79	434	822
1-Decene[b]	26	44	77	80	408	718

[a] Reaction conditions: 10 mmol alkene, 15 mmol TBHP (88% in cyclohexane), 2.5 mmol *n*-decane and 50 mg of catalyst (4.9×10^{-3} mmol Mo); 353 K.

[b] *n*-Butylether used instead of *n*-decane.

[c] $\sum$ mmol epoxides (mono- and di-epoxide)/$\sum$ mmol products.

[d] $\sum$ mmol epoxides (mono- and di-epoxide)/mmol metal.

compared to reactions with cyclohexene, probably due to olefin size and hindered access of the larger cyclooctene to the active sites of the catalyst.

The catalytic activity of Mo(O*i*Pr)–SiO_2^A in the epoxidation of various cyclic and linear alkenes was tested and the results are summarized in Table 4. In general, an increase in epoxide yield was observed with decreasing steric demand of the olefin. Thus, high olefin conversions and epoxide selectivities were observed in reactions with less bulky cyclic olefins like cyclohexene and cyclooctene. Lower epoxide yields were obtained with the terpenes limonene and α-pinene. Epoxidation of limonene yielded a mixture of 86% monoepoxides (80% epoxidation at the ring double bond and 6% epoxidation at the side chain) and 14% diepoxides. A large drop in alkene conversion and selectivity for epoxide was observed with the bulkier α-pinene, most probably due to steric restrictions and isomerization reactions of the first formed epoxide. As expected, the reactivity of linear α-olefins is lower compared to cyclic olefins. It can be seen in Table 4 that epoxide yield increases with decreasing chain length of the olefin. While reactivities of 1-decene and 1-octene were found to be in the same range, a considerable increase in epoxide yield was observed with 1-hexene as substrate. These results clearly indicate that, besides the intrinsic reactivity of the double bond, olefin size and accessibility to the active sites of the catalyst are the major limiting factors of the catalytic reaction.

Catalyst recycling experiments were carried out with repeated use of Mo(O*i*Pr)–SiO_2^A in the epoxidation of cyclohexene. The results of five consecutive catalytic runs are summarized in Table 5. Cyclohexene

Table 5
Catalytic activity of Mo(O*i*Pr)–SiO_2^A after repeated use as catalyst in the epoxidation of cyclohexene[a]

Catalytic run no.	Conversion (%)	Selectivity (%)	TBHP selectivity[b] (%)	TN	Catalyst Mo content[c] (%)
Blank	10	20	90	–	–
1	94	96	97	1835	100
2	87	98	97	1733	n.d.[d]
3	82	99	99	1652	98
4	82	98	94	1631	n.d.
5	82	96	95	1611	61

[a] Reaction conditions: 50 mmol cyclohexene, 75 mmol TBHP (88% in cyclo-hexane), 12.5 mmol *n*-decane and 250 mg of catalyst (2.45×10^{-2} mmol Mo); 353 K; 8 h.

[b] mmol epoxide/mmol TBHP consumed.

[c] Values relative to initial catalyst Mo content.

[d] Not determined.

conversion decreases from 94% in the initial reaction to 82% in the third run and remains constant in the following reactions. The initial decrease in alkene conversion is probably due to the blocking of catalytically active sites in the silicate. Selectivity for epoxide varies only slightly with values around 97% in all reactions. TBHP concentrations after the reactions were determined and it can be seen in Table 5 that nearly all oxidant is consumed for epoxide formation, without significant non-productive TBHP decomposition. Catalyst filtration experiments in the initial reaction at 353 K with removal of the catalyst after a reaction time of 1 h showed immediate interruption of catalytic epoxidation, thus indicating heterogeneous catalysis. Monitoring the metal content in the catalyst, a loss of only 2% Mo up to the third reaction was observed. After the third catalytic run the Mo content decreases remarkably. Considering detailed studies on the stability of vanadium- and chromium-substituted molecular sieves [14], this behavior is somewhat expected. Vanadium and chromium in their highest oxidation states are presumed to be bound to framework defect sites and therefore susceptible to leaching. Although structural flexibility of the amorphous silicates should facilitate Mo-incorporation, occupation of extra-framework positions is supposed because of the larger ionic radius of molybdenum. Furthermore, reactions of molybdenum with epoxides to give soluble Mo(VI)-1,2-diol complexes have been reported [23] and would also explain leaching of the metal from the silicate framework. However, a total turnover number of more than 5000 without considerable catalyst decomposition shows that it is possible to obtain useful heterogeneous epoxidation catalysts via the sol–gel method, which could be further optimized.

3.4. Characterization of Mo(O*i*Pr)–SiO_2^A

In order to obtain information about the catalyst structure, Mo(O*i*Pr)–SiO_2^A was characterized by elemental analysis, thermogravimetry, X-ray diffraction, N_2-physisorption, UV–VIS and FTIR spectroscopy. Combustion analysis showed slight impurities of organic compounds in the silicate (0.1% carbon). The considerable hydrogen content (2.4%) can be attributed to surface hydroxyl groups and water. The presence of water was confirmed by TGA, where a weight loss of about 10% was observed up to 523 K. Powder XRD analysis confirmed the amorphous nature of the silicate.

In the N_2-adsorption experiments a Type 1 isotherm typical of microporous materials [20] was obtained. From the adsorption isotherm a monomodal narrow pore size distribution with a median pore diameter

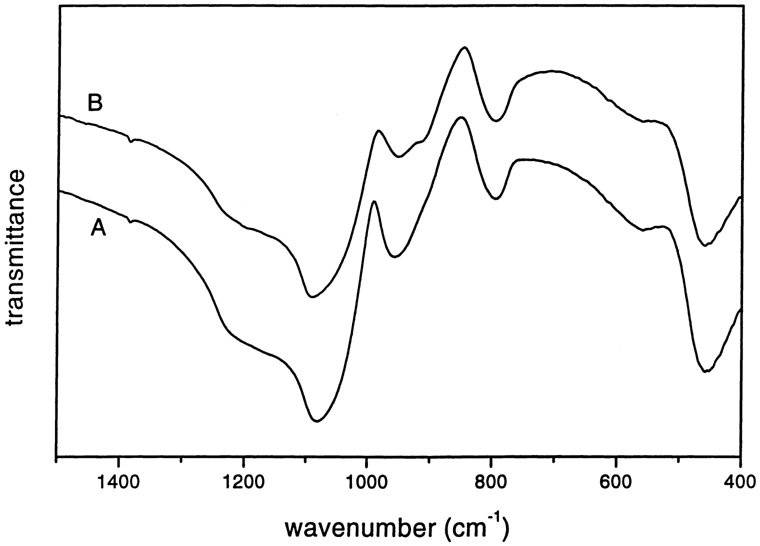

Fig. 4. IR spectra of SiO_2 (A) and Mo(O*i*Pr)–SiO_2^A (B).

of 0.71 nm, a micropore volume of $0.18\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ at $p/p_0 = 0.995$ and a BET surface area of $368\,\mathrm{m}^2\,\mathrm{g}^{-1}$ were calculated.

The UV–VIS spectrum of Mo(O*i*Pr)–$\mathrm{SiO}_2^\mathrm{A}$ shows a broad strong absorption around 320 nm with a shoulder at 250 nm and a broad weak band between 550 and 700 nm. The spectral features suggest the presence of more than one Mo species. However, the broad nature of the bands and the strong dependence of UV absorptions on a wide variety of parameters [24] complicate assignment of the absorptions.

The FTIR spectrum of the catalyst (Fig. 4) is dominated by absorptions at 457, 553, 799 and 1081 (broad shoulder at about $1180\,\mathrm{cm}^{-1}$) which can be attributed to Si–O–Si bending and stretching vibrations. The absorptions are typical of silicate structures and are only slightly shifted compared to the Mo free silicate. Apart from these bands, two characteristic bands, a stronger one at $957\,\mathrm{cm}^{-1}$ and a weak absorption at $915\,\mathrm{cm}^{-1}$, were observed. The former can be assigned to surface Si–OH vibrations [25] and probably superposes absorptions of Si–O–Mo bonds. A band around $960\,\mathrm{cm}^{-1}$ observed for Mo-containing silicalite-1 [17] was attributed to Si–O–Mo vibrations. IR spectra of Mo-containing xerogels [19] showed a band at approximately $950\,\mathrm{cm}^{-1}$ which was assigned to Si–OH vibrations. It was pointed out that there is some partial contribution of $(\mathrm{SiO})_3\mathrm{Si{-}O{-}Mo}$ and/or $(\mathrm{SiO})_2\mathrm{Mo{-}O}$ vibrations. Mo-containing MCM-41 [18] showed an absorption at around $963\,\mathrm{cm}^{-1}$ which was attributed to both Si–OH and Si–O–Mo vibrations. The absorption at $915\,\mathrm{cm}^{-1}$ is not present in the spectrum of the metal free silicate and appears in the range of Mo–O vibrations [26]. Depending on the preparation mode, a shoulder at $905\,\mathrm{cm}^{-1}$ was observed for Mo-containing MCM-41 and assigned to Mo–O vibrations of tetrahedral molybdate species attached to the surface [18]. Although structural information from the IR spectrum of Mo(O*i*Pr)–$\mathrm{SiO}_2^\mathrm{A}$ is limited, the weak band at $915\,\mathrm{cm}^{-1}$ can be considered as a characteristic feature and is attributable to Mo–O vibrations.

4. Conclusions

Transition metal containing amorphous silicates can be prepared via a simple acid-catalyzed sol–gel process and are active catalysts for the epoxidation of alkenes with TBHP. Silicates containing molybdenum exhibit the best activities and selectivities, confirming once more the unique catalytic properties of Mo in epoxidation reactions. Catalyst stability with regard to metal leaching strongly depends on the transition metal precursor used in catalyst synthesis. Using Mo(V)isopropoxide as precursor a stable catalyst can be obtained which catalyzes the reaction in the heterogeneous phase and can be used up to three times. The rates of epoxidation depend on the structure of the olefin. Small olefins are epoxidized more readily owing to the microporous nature of the catalyst. From our results we conclude that metallosilicates prepared by the sol–gel method are promising heterogeneous oxidation catalysts. Besides a wide variety of preparation parameters the choice of the appropriate transition metal precursor seems to be one of the crucial factors on the way to active, selective and stable heterogeneous catalysts.

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