ACTIVITIES AND STABILITIES OF REDOX MOLECULAR SIEVE CATALYSTS IN LIQUID PHASE OXIDATIONS. A REVIEW

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The use of redox molecular sieves as heterogeneous catalysts for liquid phase oxidations with H_2O_2 and alkyl hydroperoxides is reviewed. Emphasis is placed on titanium- and chromium-substituted molecular sieves as examples of catalysts operating *via* peroxometal and oxometal pathways, respectively. Various titanium-substituted molecular sieves were shown to be stable, heterogeneous catalysts for, *e.g.*, olefin epoxidation, but the remarkable activity of the progenitor of this family of catalysts, titanium-silicalite (TS-1), has not been equalled. The catalytic activity of chromium-substituted molecular sieves was shown to be entirely due to small amounts of homogeneous chromium species leached from the catalyst during reaction. The catalytic activities and stabilities of other materials, including zirconium-substituted hexagonal mesoporous silicas and a vanadium bipyridyl complex encapsulated in zeolite Y, were also tested. They were either unstable (vanadium) towards leaching or showed low activity (zirconium). Attempts to incorporate molybdenum in silicalite were unsuccessful and previously reported activity was shown to be due to the blank reaction. A review with 64 references.
**Key words:** Heterogeneous catalysis; Oxidations; Molecular sieves; Zeolites; Metal-complexes; Redox reactions; Titanium; Zirconium; Chromium; Porous materials.

1. INTRODUCTION

Catalytic oxidation in the liquid phase is widely used in manufacture[1] of bulk chemicals and is becoming increasingly important in the synthesis of fine chemicals where tradi-

tional processes involving stoichiometric inorganic oxidants are under considerable environmental pressure[2]. Liquid phase oxidations generally involve the use of soluble metal salts or complexes, preferably in catalytic quantities, in combination with clean, inexpensive oxidants such as O_2, H_2O_2 or RO_2H (R = alkyl, aryl). However, homogeneous catalysts suffer from several disadvantages compared to their heterogeneous counterparts: recovery and recycling is often cumbersome and most organic ligands are unstable towards degradation under oxidizing conditions. Moreover, active oxometal species often undergo dimerization/oligomerization to less reactive μ-oxo species resulting in catalyst deactivation. These problems can be circumvented by site-isolation of active oxometal (M=O) species in inorganic matrices, thus precluding μ-oxo dimer/oligomer formation.

The first example of the successful application of this concept was the Ti(IV)/SiO$_2$ catalyst commercialized by Shell in the 70's for the coproduction of styrene and propylene oxide (SMPO process)[3]. The key step in this process is the epoxidation of propene by (1-phenylethyl)hydroperoxide:

$$\triangle\!\!\!\!\triangle \quad + \quad RO_2H \quad \longrightarrow \quad \triangle\!\!\!\!O \quad + \quad ROH \qquad (1)$$
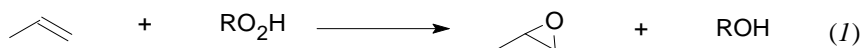
In the mid-eighties Enichem scientists[4] reported the use of titanium silicalite (TS-1) as a catalyst for a variety of selective oxidations including olefin epoxidation with aqueous H_2O_2. This is in complete contrast to the Ti(IV)/SiO$_2$ catalyst which is deactivated by water and, hence, is not active with H_2O_2 as oxidant. TS-1 consists of Ti(IV) isomorphously substituted in the framework of silicalite-1, a highly hydrophobic molecular sieve with a pore size of 5.6×5.3 Å. The hydrophobic nature of its micropores allows for efficient adsorption of hydrophobic substrates, (*e.g.* olefins) even in the presence of large amounts of H_2O. The success of TS-1 led to the expectation that this was perhaps the progenitor of whole families of so-called redox molecular sieves[5] with unique activities, selectivities and stabilities.

Metal ions which catalyze oxygen transfer reactions with H_2O_2 or RO_2H can be divided into two types based on whether the mechanism involves an oxometal or peroxometal pathway[6] (see FIG. 1).
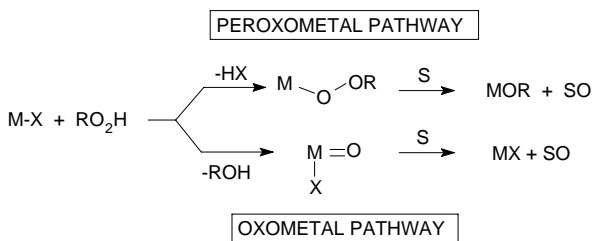

FIG. 1
Oxidation mechanisms

Peroxometal pathways are usually followed by early transition elements with d^0 configuration, *e.g.* Ti(IV). In contrast, late or first row transition elements, *e.g.* Cr(VI), generally involve oxometal pathways. A typical reaction for a peroxometal oxidant is olefin epoxidation. Oxometal species, on the other hand, show a broader range of activities including benzylic and allylic oxidations. Hence, in the ensuing discussion we shall describe the application of both types of redox molecular sieves, *viz.* titanium and chromium-substituted, in catalytic oxidations with H_2O_2 and RO_2H. Of crucial importance for the practical utility of these catalysts is their stability towards leaching of the active metal under reaction conditions[7]. In this paper, the stability and activity of various sieves reported in literature will be evaluated.

2. REDOX MOLECULAR SIEVES

Molecular sieves, unlike conventional supported catalysts, possess a regular microenvironment with homogeneous internal structures consisting of uniform, well-defined cavities and channels of molecular dimensions (4–13 Å). They are commonly referred to as zeolites or zeotypes and are crystalline oxides comprising corner-sharing TO_4 tetrahedra (T = Si, Al, P, *etc*.). Zeolites refer to aluminosilicates (T = Si and Al) and zeotypes to molecular sieves having analogous structures but different elemental compositions, *e.g.* silicates (T = Si), aluminophosphates (AlPOs; T = Al and P) and silica aluminophosphates (SAPOs; T = Si, Al and P).

The pore system in zeolites or zeotypes is well defined and may be one, two or three dimensional[8]. Confinement of the redox active site in these pores can endow the catalyst with unique activities. Moreover, by choosing a molecular sieve with an appropriate size and hydrophobicity, one is able to influence which molecules can readily access the active site on the basis of their size[9] and/or hydrophobic/hydrophilic character. Such materials bear a distinct resemblance to redox enzymes in which the protein mantle plays an analogous role and for this reason these materials have been referred to as mineral enzymes[10].

Until the seventies, attempts to develop redox molecular sieves were mainly limited to the introduction of metal ions into zeolites *via* ion-exchange. A major disadvantage of this approach is the mobility of the metal ion which manifests itself in its facile leaching into solution. This situation changed in 1983, with the discovery of TS-1, which contained metal ions substituted in the framework of silicalite[4]. The success of TS-1 stimulated the development of a variety of redox molecular sieves containing titanium(IV) or other metal ions[5]. Introduction of metals in the framework of silicalites, zeolites, AlPOs or SAPOs generated a diverse family of redox molecular sieves, which can be either neutral or negatively charged (see Fig. 2). Examples are VS-1, CrS-1 (respectively V and Cr in the silicalite framework), VAPOs, CrAPOs, and CoAPOs (V, Cr and Co substituted in the AlPO framework), TAPSO (Ti in SAPO), Ti-ZSM-5 (tita-

nium in ZSM-5) and Ti-BEA (titanium in the framework of zeolite beta). For synthesis methods and terminology, we refer to other publications[8,11].

Another approach, which allows the incorporation of metal complexes rather than metal atoms, is the so-called ship-in-a-bottle concept, which involves the entrapment of a bulky complex inside the cages of (mainly) faujasite zeolites[12]. The classic example is iron-phthalocyanine encapsulated in zeolite Y (ref.[13]). In addition to phthalocyanines, bipyridyls and Schiff-base type ligands, which are easy to assemble through condensation of the starting amine and aldehyde, have been reported in combination with Mn (ref.[14]) and V (ref.[15]) as redox metals.

The discovery, in 1992, of mesoporous (alumino)silicates such as MCM-41 (ref.[16]), inspired the development of additional two methods for metal incorporation. The first involves the grafting of organometallic species to the internal surface of mesoporous molecular sieves. This concept is exemplified by the synthesis of surface-grafted titanium(IV) (ref.[17]) and oxomanganese[18] by reaction of MCM-41 with titanocene dichloride (Cp_2TiCl_2) and $Mn_2(CO)_{10}$, respectively, followed by calcination. The other concept involves tethering a coordination complex *via* a spacer ligand to the wall of the redox molecular sieve. Examples include the tethering of chiral molybdenum complexes to the internal surface of mesoporous ultra-stable zeolite Y (USY) (ref.[19]) and the heterogenization of manganese triazacyclononane complexes on MCM-41 (ref.[20]).

Summarizing, if we exclude ion-exchange from our discussion we can distinguish four modes of incorporation: framework substitution (a); grafted complexes (b); tethered complexes (c); ship-in-a-bottle complexes (d) as schematized in Fig. 3.

2.1. Activity of Titanium Substituted Molecular Sieves.

The variety in titanium-substituted molecular sieves reflects the various tunable properties of redox molecular sieves: (i) pore size, (ii) hydrophobicity, and (iii) acidity. In Table I, a list of selected examples of titanium-containing molecular sieves is given in chronological order.
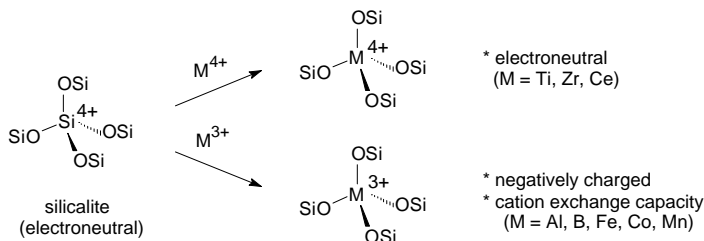

FIG. 2
Isomorphous substitution of silicon in the silicalite framework by other elements

TS-1 is an excellent catalyst for the oxidation of small molecules with H_2O_2. In contrast, TS-1 is not suitable for oxidations with *tert*-butyl hydroperoxide (TBHP), because pore restrictions prohibit the formation of the transition state of oxygen transfer. In the ammoximation of hydroxyacetophenone[29], for example, TS-1 catalyzes the formation of hydroxylamine by oxidation of NH_3 with 30% H_2O_2. The hydroxylamine subsequently reacts with the hydroxyacetophenone in the bulk solution.

The rates of TS-1 catalyzed epoxidation strongly depend on the structure of the olefin and differ markedly from those observed in homogeneous solution[30–31]. Even relatively unreactive electron-poor olefins such as allyl chloride are smoothly epoxidized under mild conditions[31] (see Table II). In contrast, cyclohexene is completely

TABLE I
Titanium-containing molecular sieves

Pore size, Å	Material	Template	Year	Discoverer
5.6×4.4	Ti-silicate (TS-1)	(Pr)₄NOH	1983	Taramasso *et al.*[4a]
5.5×5.1	Ti-silicate (TS-2)	(Bu)₄NOH	1990	Ratnasamy *et al.*[21]
7.4×7.4	Ti-Y	post-synthesis modification	1990	Kouwenhoven *et al.*[22]
7.6×6.4	Ti-Al-beta	(Et)₄NOH	1992	Corma *et al.*[23a]
5.4×5.1	Ti-ZSM-48	$H_2N(CH_2)_8NH_2$	1992	Davis *et al.*[24]
6.7×7.0	Ti-Al-Mor	none	1993	Cho *et al.*[25]
7.3×7.3	Ti-APSO-5	$C_6H_{11}NH_2$	1994	Tuel *et al.*[26]
>40	Ti-MCM-41	$C_{16}H_{33}(CH_3)_3NOH$	1994	Corma *et al*[27], Pinnavaia *et al.*[28]
>40	Ti-HMS	$C_{12}H_{25}NH_2$	1994	Pinnavaia *et al*[28]

Framework-substituted
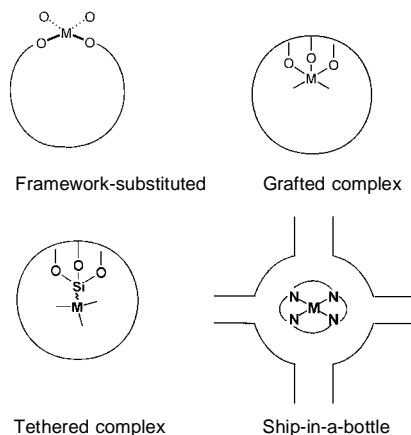
Grafted complex

Tethered complex

Ship-in-a-bottle

FIG. 3
Modes of incorporation of metal active sites in molecular sieves

unreactive, owing to the steric restrictions of the TS-1 pores (5.5 Å). Methanol is the most effective solvent and this is assumed to be a result of coordination of alcohol solvent to the titanium hydroperoxide species forming a five-membered peroxyacid-like species, in which oxygen transfer is facilitated.

To overcome pore size restrictions in TS-1, several research groups synthesized Ti molecular sieves with larger pores such as Ti-beta, TAPSO-5 and Ti-MCM-41. In Table III, the activity of Ti-beta is compared to that of TS-1 for the epoxidation of cyclohexene and 1-hexene with H_2O_2.

With the larger pore Ti-Al-beta cyclohexene and 1-hexene exhibited roughly the same activity. The major product, however, was the corresponding glycol monoether resulting from acid-catalyzed ring opening of the epoxide with the methanol solvent. We showed that this could be suppressed by using Ti-beta in which Brønsted acid sites were neutralized by ion exchange with alkali or earth alkaline metal ions or by perfor-

TABLE II
TS-1 catalyzed epoxidations with 60% aqueous H_2O_2[a,b]

Olefin	T, °C	Time, min	H_2O_2 conversion, %	Epoxide selectivity, %
Propene	40	72	90	94
1-Hexene	25	70	88	90
1-Octene	45	90	81	91
Allyl chloride	45	30	98	92
Cyclohexene	25	90	10	[c]

[a] Adapted from ref.[31]. [b] Olefin/H_2O_2 molar ratio 5 : 1; MeOH solvent. [c] Not defined.

TABLE III
Ti-beta catalyzed epoxidation with 35% aqueous H_2O_2[a,b]

Olefin	Catalyst	H_2O_2		Product selectivity, %	
		conversion, %	selectivity, %	epoxide	glycol ether
Cyclohexene	TS-1	<5	–	100	
1-Hexene	TS-1	98	80	96	4
1-Hexene	Ti-Al-beta[c]	80	80	12	80[d]
Cyclohexene	Ti-Al-beta[c]	80	83	0	100

[a] Adapted from ref.[23b]. [b] Olefin/H_2O_2 (35%) molar ratio 12 : 1, olefin/catalyst w/w *ca* 2, MeOH solvent, 25 °C, products after 3 h. [c] 4% Ti, Si/Al *ca* 200. [d] 8% of diol was also formed.

ming the reaction in a weakly basic solvent such as acetonitrile[32]. Aluminium free Ti-beta has also been used as an epoxidation catalyst with H_2O_2 (ref.[33]). Even though this material should not contain Brønsted acid sites it was, nevertheless, necessary to use weakly basic solvents, such as acetonitrile, to suppress the ring opening of the epoxide[32,33]. Similar effects were observed with TBHP as the oxidant[32a]. The Brønsted acidity in a titanium-substituted zeolite can also be an asset, *e.g.* Ti-beta functions as a bifunctional catalyst in the one-step conversion of 2,3-dimethylbutenes to 3,3-dimethyl-butan-2-one with aqueous H_2O_2 (ref.[34]).

Titanium-substituted MCM-41 is less active and less stable than Ti-beta and TS-1 (the MCM-41 structure was found to collapse[35]) in oxidations with H_2O_2 but reasonable results were obtained with RO_2H as the oxidant[27]. These mesoporous (alumino)silicates consist of a regular array of one-dimensional pores with diameters in the range 15–100 Å and have properties intermediate between those of amorphous SiO_2 and Al_2O_3 and microporous sieves. Aero- and xerogels can be envisaged as special examples of meso-porous molecular sieve materials and it is interesting, therefore, to compare the activity of Ti-MCM-41 with those of titanium substituted aero- and xerogels[36,37].

The synthesis of titania-silica aerogels, containing up to 20% titanium[36], involves low-temperature drying with supercritical CO_2, leading to a high-surface area (500 m^2/g) and a mesoporous structure with a high degree of Ti–O–Si linkages. These materials resemble the Shell Ti(IV)/SiO_2 catalyst, albeit with ten times as much titanium, leading to a higher activity per gram of catalyst as shown in Table IV.

Titania-silica xerogels, on the other hand, are prepared using a conventional drying procedure[37]. The resulting materials contained up to 17% Ti and also had high surface areas (*ca* 400–500 m^2/g) and a narrow pore size distribution (effectively 6.5–7.7 Å) comparable with large-pore zeolites. They were shown to be effective catalysts for the epoxidation of linear and cyclic alkenes with TBHP, with activities comparable to the

TABLE IV
Comparison of titanium catalysts in the epoxidation of cyclohexene with RO_2H^a

Catalyst	TiO_2, %	Temperature °C	Activity g/g/h	Conversion %	Selectivity %	Ref.
20 LT Aerogel	20	60	32	50	100	Baiker *et al.*[36]
Xerogel	3	90	1.2	26	97	Maier *et al.*[37]
TiO_2/SiO_2(Shell)	2	60	5.9	80	100	
Ti-Beta	1–2	50	0.1	34	99	Corma *et al.*[23]
Ti-MCM-41	1–2	60	0.01	14	93	Corma *et al.*[27]
TiO_2/MCM-41	1–2	40	10	50	95	Thomas *et al.*[17]

^{a} RO_2H refers to the use of either *tert*-butyl hydroperoxide or cumyl hydroperoxide.

Shell catalyst (Table IV). Ti-beta and Ti-MCM-41, in contrast, showed rather low activities. Titanium grafted MCM-41 (ref.[17]) (designated as TiO_2/MCM-41) exhibited an enhanced activity compared to isomorphous substituted Ti-MCM-41 which is attributed to the better accessibility of the titanium sites[38], *i.e.*, in Ti-MCM-41 the titanium is embedded in the wall, whereas grafted titanium is located at the surface.

Both the titanium aerogels and xerogels described above are hydrophilic in nature and, analogously to the Ti(IV)/SiO_2 catalyst, are not effective catalysts for aqueous epoxidations with H_2O_2. More recently, Maier and coworkers have described the synthesis of hydrophobic xerogels from mixtures of $MeSi(Et)_3$ and $Si(OEt)_4$ in combination with $Ti(OPr-i)_4$ (ref.[39]). The hydrophobicity index of these materials was shown to approach that of TS-1. Unfortunately, the epoxidation of cyclohexene was used as a model reaction to compare reactivities of these materials with TS-1 in oxidations with H_2O_2 (ref.[39]). As noted earlier, TS-1 is not an effective catalyst for the epoxidation of cyclohexene. Hence, the catalytic properties of these new materials need to be evaluated with a more suitable substrate, *e.g.* 1-hexene.

As a model for the Ti–$(OSi)_x$ structure present in titanosilicates, titanium-silsesquioxanes have been studied[40] (Fig. 4). It was shown, that at least three Ti–O–Si bonds are necessary for stability towards solvolysis. This situation is extant in TS-1, where the mechanism of oxidation most likely involves conversion of a Ti–O–Si or Ti–O–H group to Ti–OOR (R = H, alkyl) which is still bonded to three siloxane groups. These Ti-silsesquioxanes are active homogeneous catalysts for epoxidation (with alkyl hydroperoxides)[40], whereas homogeneous titanium complexes generally exhibit low activities due to oligomerization to unreactive μ-oxo complexes (see above).

2.2. Stability of Chromium Substituted Molecular Sieves

Incorporation of chromium(VI) into silicalite or aluminophosphate-5 and -11 produces materials which catalyze a variety of oxidations with TBHP or O_2 as the terminal oxi-
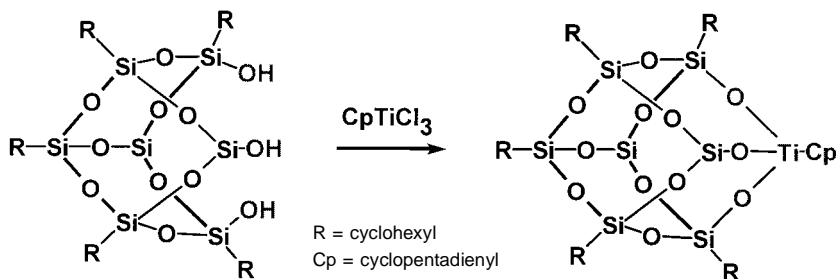

Fɪɢ. 4
Titanium-silsesquioxanes

dant[2b,41]. The as-synthesized materials contain chromium(III) which is probably iso-morphously substituted for Si or Al. On calcination, the chromium is oxidized to the hexavalent chromyl (CrO_2^{2+}) state which is attached to the framework by only two metal–oxygen bonds and, hence, cannot be isomorphously substituted.

As noted earlier, chromium(VI) typically catalyzes oxidations *via* an oxometal mech-anism, in which Cr(VI)=O is the active oxidant. Hence, Cr-APO-5 was shown to cata-lyze reactions typical of oxometal oxidants, *i.e.* benzylic and allylic oxidations and (cyclo)alkane oxidations[2b,41]. The catalytic cycle is assumed to involve reoxidation of Cr(IV) to Cr(VI)=O by TBHP or, in the case of reactions with O_2, by the hydroperoxide derived from (chromium-catalyzed) autoxidation of the substrate.

We chose the allylic oxidation of α-pinene[42] (Eq. (*2*)) as a model reaction to investi-gate the catalyst stability. To test for leaching, we filtered the catalyst (CrAPO-5) after 30 min, which corresponded to *ca* 20% α-pinene conversion, and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (80 °C) in order to avoid possible readsorption of solubilized chromium on cooling. Indeed, we found that after hot filtration the filtrate (mother liquor) reacted further at roughly the same rate as that observed when the catalyst was not filtered. In contrast, when the mixture was allowed to cool to room temperature before catalyst filtration, the proce-dure generally followed when testing for leaching, some further reaction was observed. On the basis of these results we concluded that chromium is leached from the catalyst and that the observed catalysis is due to homogeneous chromium.

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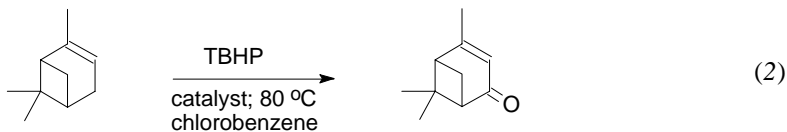
In a second test for leaching we studied the allylic oxidation of α-pinene with a bulky triphenylmethylhydroperoxide (TPMHP) and of a bulky olefin 5,6-dimethyl-8-isopropenylbicyclo[4.4.0]dec-1-ene (valencene) with TBHP (Eqs (*3*) and (*4*), respec-tively)[43].

$$\text{(3)}$$

$$\text{(4)}$$
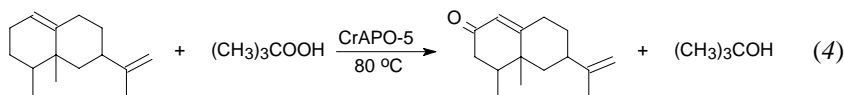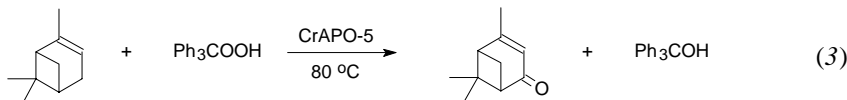
If the reaction was occurring within the micropores one would expect to observe no reaction in both cases, since both TPMHP and the bicyclodecene are too bulky to access the pores. However, we observed facile conversion of the latter one with TBHP but virtually no conversion of α-pinene with TPMHP. The only explanation which is consistent with these observations is that soluble chromium is responsible for the observed catalysis and that *it is leached by reaction with the hydroperoxide*. That this is the case was confirmed in experiments where CrAPO-5 was pretreated with TBHP, filtered, and α-pinene added to the mother liquor resulting in facile oxidation. Analysis of the filtrate showed that 0.3% of the 0.88% chromium (*i.e.* 0.0026% of the total catalyst weight) present in CrAPO-5 was leached under the above mentioned conditions[43]. This corresponds to a substrate/catalyst (S/C) ratio of 17 000 or *ca* 1 ppm Cr in the filtrate.

Analogous experiments with CrAPO-11 and samples of CrS-1 prepared by different procedures showed that the extent of chromium leaching varied between 0.3 and 34% and increased markedly with decreasing crystallite size. Furthermore, we showed that if the filtrate was allowed to cool to room temperature, the chromium was reduced to the trivalent state. Subsequent experiments, in which pyridinium dichromate, $(C_5H_6N)_2Cr_2O_7$, was used as a homogeneous catalyst (at a S/C ratio of 17 000) in the TBHP oxidation of α-pinene afforded the same rate as that observed in the CrAPO-5 catalyzed reaction. In contrast, when $Cr(acac)_3$ (acac = acetylacetonate), *i.e.* trivalent chromium, was used as a catalyst, long induction periods (*e.g.* 5 h at S/C = 10 000) were observed. In short, these results unequivocally demonstrate that the observed catalysis with CrAPO-5, CrAPO-11 and CrS-1 is homogeneous in nature due to chromium leached from the catalyst. They also show that conventional cooling of the reaction mixture prior to catalyst filtration could lead to erroneous conclusions. Moreover, we showed that in homogeneous catalysis by chromium(VI) the relationship between the reaction rate and catalyst concentration is nonlinear: turnover frequencies increased with decreasing catalyst concentration suggesting possible dissociation of dimeric or oligomeric chromium species in solution. Here again, this could lead to erroneous conclusions in comparison of homogeneous with "heterogeneous" catalysts.

Similarly, a careful study of the CoAPO-5 catalyzed aerobic oxidation of cyclohexane to adipic acid[44] revealed that the activity was entirely due to low concentrations of Co(II) leached by the acetic acid solvent. Separate studies of catalysis by (homogeneous) Co(II) showed that a sharp maximum in the catalytic activity was encountered at [Co(II)] = 0.17 mmol dm^{-3} which was explained on the basis of catalyst–inhibitor conversion at higher cobalt concentrations[1].

Generally speaking one can distinguish three different scenarios for heterogeneous catalysts in liquid phase oxidations:

A. The metal does not leach and the observed catalysis is truly heterogeneous, *e.g.* TS-1.

B. The metal leaches to form an active homogeneous catalyst (see above for CrS-1 and CrAPOs).
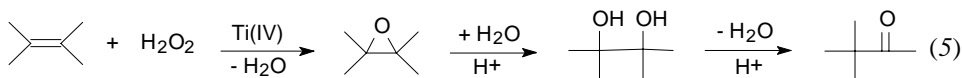
C. The metal leaches but is not an active homogeneous catalyst; this is the case in, *e.g.*, Ti-MCM-41 when reacted with H_2O_2, because homogeneous titanium is not an active catalyst.

3. EVALUATION OF ACTIVITY AND STABILITY OF OTHER REDOX MOLECULAR SIEVES

3.1. TAPSO-5

SAPO-5 is a 12-membered ring silicoaluminophosphate molecular sieve with a one-dimensional micropore system[45]. Depending on the synthesis procedure, the fraction of Si incorporated (Si/(Si + Al + P)) could be varied from 0.01 up to 0.9 (ref.[46]). ^{29}Si MAS NMR showed[47] for low Si contents that Si^{4+} is substituted preferentially for framework P^{5+}, creating an acidic site. With increasing Si content, also Al^{3+} is replaced, leading to silica domains in the AlPO framework[48]. When a transition metal is incorporated in the framework of SAPO-5, so called MeAPSO-5 (ref.[49]) is obtained. A typical example of a MeAPSO-5 is the titanium-substituted SAPO-5, TAPSO-5, which was found to be active in the epoxidation of cyclohexene with H_2O_2 and TBHP (ref.[26]). Hence, we investigated this potentially interesting material in more detail. On following the reported synthesis procedure we failed to obtain the described white TAPSO-5. Instead, a grey material was obtained which consisted in its most favourable composition of about 90% of coffin-shaped crystals with the AlPO-44 structure (probably TAPSO-44) and 10% of cauliflower-shaped crystals with the AlPO-5 structure (TAPSO-5). In some cases pure samples of TAPSO-44 were obtained. This imperfection in the literature procedure could be overcome by decreasing the amount of Si in the synthesis gel. In this way the amount of TAPSO-44 could be, in the most favourable case, reduced to 10%. The purity of this material could be further improved by making use of the difference in density of the SAPO-44 crystals compared to SAPO-44 in a sedimentation experiment.

TAPSO-5 is in principle a bifunctional catalyst, as it contains titanium sites and Brønsted acid sites. As a model reaction to test for this bifunctionality, we studied the TAPSO-5 catalyzed epoxidation of 2,3-dimethylbut-2-ene with H_2O_2 to 2,3-dimethyl-2,3-epoxybutane, the ring-opening of which affords 2,3-dimethylbutan-2,3-diol (pinacol). The latter is expected to undergo acid-catalyzed rearrangement to 3,3-dimethylbutan-2-one (pinacolone) with loss of a water molecule (Eq. (5) epoxidation of 2,3-dimethylbut-2-ene). We also studied the epoxidation of cyclohexene using H_2O_2 or TBHP as the oxidant as was described in the original publication[26,50].

$$\diagdown\!\!=\!\!\diagup \;+\; H_2O_2 \;\xrightarrow[-\,H_2O]{Ti(IV)}\; \text{epoxide} \;\xrightarrow[H^+]{+\,H_2O}\; \text{diol} \;\xrightarrow[H^+]{-\,H_2O}\; \text{ketone} \qquad (5)$$

Ti-Al-beta, which is also known to be a bifunctional catalyst[34,51] (see above), was compared with TAPSO-5. The Ti-Al-beta catalyzed epoxidation of 2,3-dimethylbut-2-ene with H_2O_2 in dioxane gave after 6 h at 65 °C a moderate diol yield of 25% (Table V). Under the same conditions, TAPSO-5 showed no activity. Similarly, in the TAPSO-5 catalyzed epoxidation of cyclohexene with H_2O_2 or TBHP, no or low substrate conversions and only traces of products were observed. Our results are at variance with the literature report[26] that TAPSO-5 is an active epoxidation catalyst. However, closer inspection of the reported results reveals that only poor product yields of 7 and 14% were observed with H_2O_2 and TBHP, respectively, and reaction times were not mentioned.

3.2. Zr- and Ti-Hexagonal Mesoporous Silicas

Various metals, *e.g.* Ti (ref.[51]), V (ref.[52]) and Cr (ref.[53]) have been reportedly incorporated in MCM-41 and the resulting materials were found to be effective catalysts for the oxidation of bulky substrates. However, V and Cr catalytic activity is most likely due to traces of leached metal[43,54]. In the case of Ti the catalytic activity is without any doubt heterogeneous in nature. One major problem of Ti-MCM-41 is, however, its instability under the conditions of catalytic oxidation with H_2O_2 (ref.[35]), which results in the collapse of the structure and, hence, in titanium leaching. In principle, the stability of the lattice could be improved by shifting to the more robust HMS material which contains a pore wall thickness of 30 Å (ref.[55]) compared to the maximum of 16 Å (ref.[56]) for MCM-41.

The synthesis of both Ti-HMS and Zr-HMS has been described in the literature[57]. In particular Zr-HMS was reported[57] to be a very active catalyst for oxidation reactions with both H_2O_2 and TBHP. The synthesis of Zr-HMS and Ti-HMS is relatively straightforward, involving room temperature mixing of a metal alkoxide containing tetraethyl

TABLE V
Epoxidation of 2,3-dimethylbut-2-ene and cyclohexene catalyzed by TAPSO-5

Substrate	Oxidant	Catalyst	Yield, %[a]	Ref.
2,3-Dimethylbut-2-ene	H_2O_2	Ti-Al-beta	25[b]	34
2,3-Dimethylbut-2-ene	H_2O_2	TAPSO-5	0	this article
Cyclohexene	H_2O_2	TAPSO-5	7[c]	26
Cyclohexene	H_2O_2	TAPSO-5	0	this article
Cyclohexene	TBHP	TAPSO-5	14[d]	26
Cyclohexene	TBHP	TAPSO-5	0	this article

[a] Yield = conversion × selectivity (epoxide + diol). [b] 100% Selectivity to diol. [c] 59% Selectivity to diol, no epoxide is observed. [d] 9% Selectivity to diol, 79% selectivity to epoxide.

orthosilicate solution with a hexadecylamine solution in ethanol. The obtained gel was mixed and left overnight under static conditions. The template was removed from the obtained white material by Soxhlet extraction and subsequent calcination. The catalytic activity of the obtained materials was tested in olefin epoxidation and the oxidation of aniline and was compared with the originally reported data (Table VI).

We observed essentially no activity with Ti-HMS and Zr-HMS in the epoxidation of 2,3-dimethylbut-2-ene with H_2O_2 or the epoxidation of cyclohexene with H_2O_2 or TBHP. In the case of the Ti-HMS catalyzed epoxidation a low conversion was observed with formation of some polymeric material. On the other hand, it was reported[57] that in the epoxidation of cyclohexene catalyzed by Ti-HMS and Zr-HMS product selectivities of 64 and 89% were obtained, respectively. However, we note that a very low oxidant/substrate ratio of 0.05 was employed which corresponds to a maximum of 5% substrate conversion based on the oxidant added. Hence, relatively small losses of cyclohexene have a significant effect on the measured conversion and product selectivities based on the amount of the oxidant added rendering the reliability of the reported results questionable. Furthermore, Ti-HMS and Zr-HMS were reported to catalyze the epoxidation of norbornene with TBHP (results not shown). However, we note that norbornene (and cyclooctene) react readily at slightly elevated temperatures with dioxygen to form the epoxide. Hence, if the reaction is not carried out under an inert atmosphere, which it probably was not, the observed results may be the result of free radical autoxidation.

A second reaction which was studied was the oxidation of aniline to azobenzene and azoxybenzene (Eqs (6)–(8)). In this case the reported results and our results agree. In both cases high yields of the products were observed. The reaction involves three steps. The first step is the oxidation of aniline to nitrosobenzene, which occurs instantaneously after the addition of H_2O_2. It should be stressed that this instantaneous reaction proceeds in the absence of any catalyst and consumes most of the H_2O_2. The second step is the condensation of nitrosobenzene with aniline to azobenzene. Finally, the azobenzene is oxidized to azoxybenzene with the remaining H_2O_2.

$$\text{C}_6\text{H}_5-\text{NH}_2 \ + \ 2\,\text{H}_2\text{O}_2 \ \longrightarrow \ \text{C}_6\text{H}_5-\text{N}=\text{O} \ + \ 3\,\text{H}_2\text{O} \qquad (6)$$

$$\text{C}_6\text{H}_5-\text{NH}_2 \ + \ \text{C}_6\text{H}_5-\text{N}=\text{O} \ \longrightarrow \ \text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5 \ + \ \text{H}_2\text{O} \qquad (7)$$

$$\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5 \ \longrightarrow \ \text{C}_6\text{H}_5-\overset{\displaystyle}{\underset{\text{O}}{\text{N}}}=\text{N}-\text{C}_6\text{H}_5 \ + \ \text{H}_2\text{O} \qquad (8)$$
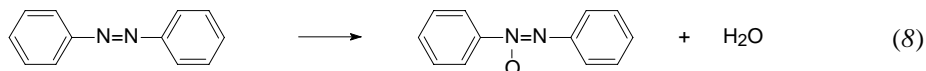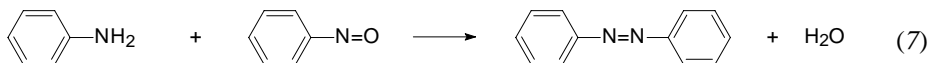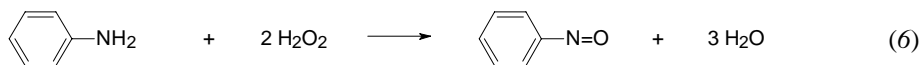
The second and third step also occur without a catalyst as the blank gives a full conversion and high selectivity within 24 h. Nevertheless, the Zr-HMS shows catalytic activity in this reaction resulting in a 100% conversion in 30 min. In filtration experiments, the filtrate exhibited a rate similar to that observed for the blank reaction, demonstrating the heterogeneous character of the catalyst, even though the catalyst lost about 5% of its zirconium during four cycles (from ICP data). The reaction was also carried out with a homogeneous zirconium catalyst (zirconium propoxide) and showed a similar profile to the blank. Hence, the incorporation of isolated zirconium atoms in the framework has a beneficial effect on the catalytic activity, as was reported for titanium substituted molecular sieves.

We conclude that Zr-HMS is a much more promising heterogeneous catalyst than TAPSO-5 as it is easy to synthesize and shows genuine heterogeneous activity, albeit in the oxidation of the easily oxidized substrate aniline. A major disadvantage is the leaching of zirconium and deactivation after a few cycles. This deactivation might be caused by clustering of catalytically active isolated zirconium species to catalytically inactive zirconium oligomers during catalysis or recalcination. Moreover, the material showed negligible activity in the more synthetically useful epoxidation.

TABLE VI
Oxidation of some substrates catalyzed by Ti-HMS and Zr-HMS

| Substrate	Oxidant	Catalyst	Ox/S	Conversion %	Selectivity %
2,3-Dimethylbut-2-ene	H_2O_2	Ti-HMS[a]	0.5	low	
2,3-Dimethylbut-2-ene	H_2O_2	Zr-HMS[a]	0.5	0	
Cyclohexene	H_2O_2	Ti-HMS[b]	0.05	?	64[c]
Cyclohexene	H_2O_2	Zr-HMS[b]	0.05	?	89[c]
1-Octene	H_2O_2	Zr-HMS[a]	1	0	
1-Octene	TBHP	Zr-HMS[a]	1	0	
Aniline	H_2O_2	Ti-HMS[b]	0.2	?	100[d]
Aniline	H_2O_2	Zr-HMS[b]	0.2	?	100[d]
Aniline	H_2O_2	Zr-HMS[a]	0.2	100[e]	100[d]
Aniline	H_2O_2	Zr(OPr)$_4$	0.2	100[f]	100[d]
Aniline	H_2O_2	blank	0.2	100[f]	100[d]

[a] This article. [b] Taken from ref.[57], no substrate conversions are mentioned in this paper. [c] Selectivity to cyclohexene oxide and cyclohexanediol. [d] Selectivity to azo- and azoxybenzene. [e] Obtained within 30 min. [f] Obtained within 24 h.

3.3. MoS-1

Molybdenum is known to catalyze the epoxidation of olefins with anhydrous TBHP (ref.[1]). The presence of water leads to strong inhibition due to competition for coordination sites on molybdenum. This is also the reason why molybdenum is not active when the epoxidation is carried out with aqueous H_2O_2 as oxidant. Hence, incorporation of molybdenum in a hydrophobic material such as silicalite could produce an interesting catalyst. The obtained MoS-1 should be able to extract selectively nonpolar substrates and relatively nonpolar H_2O_2 while polar products and water are excluded, as is observed for TS-1 (*vide supra*).

We have devoted considerable effort to the synthesis of MoS-1 (ref.[58]). The parameters which were investigated were: the molybdenum source, the order of addition of the reagents in the gel preparation, carrying out the MoS-1 synthesis out in an alkaline or in a neutral fluoride gel and the effect of static crystallization versus crystallization in a rotating autoclave. The main conclusion from these studies was that the incorporation of a reasonable amount of molydenum was not possible (often below the detection limit of ICP), and that, consequently, the catalytic activity of the materials in the epoxidation of 1-hexene with H_2O_2 was very poor.

However, the synthesis of MoS-1 was very recently described in literature[59] and the material was reported to catalyze the selective oxidation of thioethers to the corresponding sulfoxides with H_2O_2. However, in our hands repeating the reported procedure for the synthesis of MoS-1 with a Si/Mo gel ratio of 100 failed to afford the described crystalline material. Our material contained virtually no molybdenum (Si/Mo ≈ 6 000). Carrying the MoS-1 crystallization out in a rotating rather than a static autoclave did not show any improvement. While waiting for the results of the elemental analysis a catalytic sulfoxidation of thioanisole was carried out in methanol with our MoS-1 sample at room temperature (20 °C, Table VII, Eq. (9)). The first observation was that upon mixing the reagents heat evolved due to an exothermic reaction and that the $t = 0$ sample already contained sulfoxide. The second observation was that our MoS-1, which contained almost no molybdenum, gave about the same results as those reported in the literature for MoS-1 (Si/Mo = 80) at 20 °C, namely, high substrate conversions and a high methyl phenyl sulfoxide selectivity.

$$\text{PhSCH}_3 \quad + \quad H_2O_2 \quad \xrightarrow{\text{MoS-1}} \quad \text{PhS(O)CH}_3 \quad + \quad H_2O \qquad (9)$$
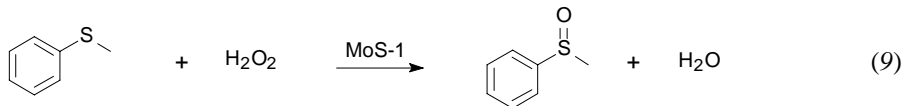
These two observations were strong indications that this reaction does not require a catalyst, which was confirmed by performing the sulfoxidation of thioanisole under the same conditions as described in literature, but, in the absence of a catalyst: 63% thioanisole conversion and 95% selectivity to methyl phenyl sulfoxide was observed. These results once again show, as was the case with vanadium and chromium molecu-

lar sieves, TAPSO-5 and Zr-HMS that the results are less promising than was originally reported and emphasize the need for performing elementary blank experiments.

3.4. Vanadium Ship-in-a-Bottle Complexes

The ship-in-a-bottle approach has recently been applied to the synthesis of a vast number of catalytically active materials. For example, Ru (ref.[60]), Mn (refs[14,61]), Fe (ref.[62]), V (ref.[15]) and Cu (ref.[63]) have been encapsulated in zeolite Y. We checked one of these materials, ([VO(bpy)$_2$]$^{2+}$–Y) (ref.[15a]) for its heterogeneity. [VO(bpy)$_2$]$^{2+}$–Y] was synthesized according to the literature procedure which consisted of ion-exchange of Na–Y with VOSO$_4$·5 H$_2$O followed by drying and incubation with 2,2′-bipyridine at 100 °C. The material was soxhlet-extracted with dichloromethane, to remove uncomplexed ligand, affording a product containing 0.2 wt.% vanadium.

The epoxidation of cyclooctene was carried out with [VO(bpy)$_2$]$^{2+}$–Y using TBHP as the oxidant at 70 °C. After 24 h an epoxide yield of 24% was obtained (100% selectivity). A leaching experiment was carried out as was described for CrAPO-5 (ref.[43]) with an incubation time of 1 h (ref.[43]). Filtration of the catalyst at the reaction temperature, followed by heating the filtrate for 24 h, resulted in a 10% yield of epoxide. The results obtained with CrAPO-5 taught us that leaching is not instantaneous, but a rather slow process. Hence, the difference between the catalytic experiment and the leaching experiment can probably be attributed to the difference in contact-time between the catalyst and TBHP (24 *versus* 1 h). A longer incubation period would probably result in a more comparable epoxide yield. In the original publication, [VO(bpy)$_2$]$^{2+}$–Y was described as a heterogeneous ship-in-a-bottle-catalyst for the oxidation of cyclohexene at room temperature. Our results show, however, that the catalytic activity is most likely due to the homogeneous contribution of leached vanadium. Surprisingly, the authors observed ±0.5% leaching of vanadium from [VO(bpy)$_2$]$^{2+}$–Y, but did not attribute the observed catalytic activity to this leached vanadium. They showed that their catalyst could be reused three times without activity or selectivity loss. A simple calculation,

TABLE VII
MoS-1 "Catalyzed" sulfoxidation of thioanisole with H$_2$O$_2$

Catalyst	Temperature, °C	Conversion, %	Selectivity, %
MoS-1 (80)^a	20	93	90
MoS-1 (6 700)	20	85	93
Blank	20	63	95
Blank	30	99	95

^{a} Taken from ref.[59].

assuming 0.5% of vanadium leaching of the original amount of vanadium would mean that the catalyst could be reused two hundred times. The statement that the catalyst could be reused three times is therefore no proof of heterogeneity.

4. CONCLUSIONS AND FUTURE PROSPECTS

In conclusion, the euphoric rush to synthesize new redox molecular sieves, which was stimulated by the discovery of remarkable catalytic properties of TS-1, has not led to many new interesting catalysts. Although the impression is given that, for example, TAPSO-5 and Zr-HMS are interesting materials, the actual catalytic activity is low. Good catalytic activities are only obtained in the oxidation of very easy substrates such as aniline or thioanisole. In the case of MoS-1 catalyzed sulfoxidation of thioanisole the observed catalysis was completely due to the blank reaction. Catalyst filtration in experiments with a vanadium ship-in-a-bottle complex revealed that the catalytic activity was largely due to leached metal. Hence, we suggest that other ship-in-a-bottle complexes need to be subjected to rigorous proof of heterogeneity. Moreover, another problem associated with ship-in-a-bottle catalysts is inherent low activity owing to diffusion limitations. For example, zeolite-encapsulated iron phthalocyanine[64] is described as a very active catalyst in the oxidation of octane where it gives a total of 6 000 turnovers. However, with a turnover frequency of 12 h^{-1} a total reaction time of approximately three weeks is needed to achieve this turnover.

In short, our studies have taught us to be suspicious with regard to literature claims concerning oxidation catalysis by redox molecular sieves and to emphasize the importance of performing appropriate blanks and catalyst filtration experiments. Our attention has been focused on framework-substituted molecular sieves and ship-in-a-bottle type catalysts. As mentioned earlier, other types of heterogeneous oxidation catalysts have been reported, *viz.* mesoporous materials containing metal centres grafted or tethered to the surface and metal-incorporated aero- and xerogels. Some of these materials appear to be promising oxidation catalysts. It is evident, however, that they need to be subjected to a scientifically rigorous evaluation with regard to their stability towards leaching and activity in synthetically relevant oxidations.

REFERENCES

1. Sheldon R. A., Kochi J. K.: *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York 1981.
2. a) Sheldon R. A.: *Chemtech* **1991**, 566; b) Sheldon R. A.: *J. Mol. Catal. A* **1996**, *107*, 75 and references cited therein.
3. Sheldon R. A., van Doorn J. A.: *J. Catal*. **1973**, *31*, 427.
4. a) Taramasso M., Perego G., Notari B.: U.S. 4 410 501 (1983) to Snamprogetti; b) Notari B.: *Stud. Surf. Sci. Catal*. **1988**, *37*, 413.
5. Arends I. W. C. E., Sheldon R. A., Wallau M., Schuchardt U.: *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1144 and references cited therein.

6. Sheldon R. A.: *Top. Curr. Chem*. **1993**, *164*, 21.

7. Sheldon R. A., Wallau M., Arends I. W. C. E., Schuchardt U.: *Acc. Chem. Res*., in press.

8. Meier W. M., Olson D. H., Baerlocher Ch.: *Zeolites* **1996**, *17*, 1.

9. Sciscery S. M.: *Zeolites* **1984**, *4*, 202.

10. Parton P. de Vos D., Jacobs P. A. in: *Zeolite Microporous Solids: Synthesis, Structure and Reactivity* (E. G. Derouane and F. Lemos, Eds), Kluwer, Dordrecht, The Netherlands 1992.

11. a) van Bekkum H., Flanigen E. M., Jansen J. C. (Eds): *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam 1991; b) Szostak R.: *Molecular Sieves*. van Nostrand, New York 1989.

12. a) de Vos D. E., Thibault-Starzyk F., Knops-Gerrits P. P., Jacobs P. A.: *Macromol. Symp*. **1994**, *80*, 157. b) de Vos D. E.; Parton R. F., Weckhuysen B. M., Jacobs P. A., Schoonheydt R. A.: *J. Incl. Phen. Mol. Recogn. Chem*. **1995**, *21*, 185.

13. Herron N.: *J. Coord. Che*m. **1988**, *19*, 25.

14. a) Knops-Gerrits P. P., de Vos D., Thibault-Starzik F., Jacobs P. A.: *Nature* **1994**, *369*, 543; b) Ogunwumi S. B., Bein T.: *Chem. Commun*. **1997**, 901.

15. a) Knops-Gerrits P. P., Trujillo C. A., Zhan B. Z., Li X. Y., Rouxhet P., Jacobs P. A.: *Top. Catal*. **1996**, *3*, 437. b) Arends I. W. C. E., Pellizon Birelli M., Sheldon R. A.: *Stud. Surf. Sci. Catal*. **1997**, *110*, 1031.

16. Beck J. S.; Vartuli J. C., Roth W. J., Leonowicz M. E., Kresge C. T., Schmitt K. P., Chu C. T. W., Olson D. H., Sheppard E. W., McCullen S. B., Higgins J. B., Schlenker J. L.: *J. Am. Chem. Soc*. **1992**, *114*, 10834.

17. Maschmeyer T., Rey F., Sankar G., Thomas J. M.: *Nature* **1995**, *378*, 159.

18. Burch R., Cruise N., Gleeson D., Tsang S. C.: *J. Chem. Soc. Chem., Commun*. **1996**, 951.

19. Corma A., Fuerte A., Iglesisas M., Sanchez F.: *J. Mol. Catal., A* **1996**, *107*, 225.

20. Subba Rao Y. V., Vos D. de, Bein T., Jacobs P. A.: *J. Chem. Soc., Chem. Commun*. **1997**, 355.

21. Reddy J. S., Kumar R., Ratnasamy P.: *Appl. Catal*. **1990**, *58*, L1; b) Bellussi G., Carati A., Clerici M. G., Esposito A., Millini R., Buonuomo F.: Belg. 1,001,038 (1989) to Enichem.

22. Kouwenhoven H. W., Ferrini C.: *Stud. Surf. Sci. Catal*. **1990**, *55*, 53.

23. a) Camblor M. A., Corma A., Martinez A., Perez-Pariente J.: *J. Chem., Soc. Chem. Commun*. **1992**, 589; b) Corma A., Camblor M. A., Esteve P., Martinez A., Perez-Pariente J.: *J. Catal*. **1994**, *145*, 151.

24. Serrano, D. P., Li H. X., Davis M. E.: *J. Chem. Soc., Chem. Commun*. **1992**, 745.

25. Kim G. J., Cho B. R., Kim J. H.: *Catal. Lett*. **1993**, *22*, 259.

26. Tuel A.: *Zeolites* **1995**, *15*, 228.

27. Corma A., Navarro M. T., Perez-Pariente J.: *J. Chem. Soc., Chem. Commun*. **1994**, 147.

28. Tanev P. T., Chibwe M., Pinnavaia T. J.: *Nature* **1994**, *386*, 239.

29. Le Bars J., Dakka J., Sheldon R. A.: *Appl. Catal., A* **1996**, *36*, 69.

30. Bellussi G., Rigutto M. S.: *Stud. Surf. Sci. Catal*. **1994**, *85*, 177.

31. Clerici M. G., Ingallina P.: *J. Catal*. **1993**, *140*, 71.

32. a) Sato T., Dakka J., Sheldon R. A.: *J. Chem. Soc., Chem. Commun*. **1994**, 1887; b) Sato T., Dakka J., Sheldon R. A.: *Stud. Surf. Sci. Catal*. **1994**, *84*, 1853.

33. van der Waal J. C., van Bekkum H.: *J. Mol. Catal., A* **1997**, *124*, 137.

34. van Klaveren M., Sheldon R. A.: *Stud. Surf. Sci. Catal*. **1997**, *110*, 567.

35. Rhee C. H., Lee J. S.: *Catal. Lett*. **1996**, *40*, 261.

36. Hutter R., Mallat T., Baiker A.: *J. Catal*. **1995**, *135*, 177.

37. a) Maier W. F., Martens J. A., Klein S., Heilman J., Parton R., Vercruysse K., Jacobs P. A.: *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 380; b) Klein S., Martens J. A., Parton R., Vercruysse K., Jacobs P. A., Maier W. F.: *Catal. Lett*. **1996**, *38*, 209.

38. Oldroyd R. D., Thomas J. M., Maschmeyer T., MacFaul P. A., Snelgrove D. W. Ingold K. U., Wayner D. D. M.: *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2787.

39. Klein S., Maier W. F.: *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2230.

40. a) Abbenhuis H. C. L., Krijnen S., van Santen R. A.: *J. Chem. Soc., Chem. Commun.* **1997**, 331; b) Maschmeyer T., Klunduk M. C., Martin C. M., Shephard D. S., Thomas J. M., Johnson B. F. G.: *Chem. Commun.* **1997**, 1847.

41. a) Chen J. D., Sheldon R. A.: *J. Catal.* **1995**, *153*, 1; b) Sheldon R. A., Chen J. D., Dakka J., Neeleman E.: *Stud. Surf. Sci. Catal.* **1994**, *82*, 515; c) Sheldon R. A., Chen J. D., Dakka J., Neeleman E.: *Stud. Surf. Sci. Catal.* **1994**, *83*, 407.

42. a) Lempers H. E. B., Sheldon R. A.: *Stud. Surf. Sci. Catal.* **1997**, *105*, 1061; b) Lempers H. E. B., Sheldon R. A.: *Appl. Catal., A* **1996**, *143*, 137.

43. Lempers H. E. B., Sheldon R. A.: *J. Catal.* **1998**, *175*, 62.

44. Belkhir I., Germanin A., Fajula F., Fache E.: *J. Chem. Soc., Faraday Trans.*, in press.

45. Lok B. M., Messina C. A., Parton R. L., Gajek R. T., Cannan T. R., Flanigen E. M.: U.S. 4440871 (1984).

46. Martens J. A., Mertens M, Grobet P. J., Jacobs P. A.: *Stud. Surf. Sci. Catal.* **1988**, *37*, 97.

47. Chao K. J., Leu L. J.: *Stud. Surf. Sci. Catal.* **1989**, *46*, 19.

48. Wang X., Liu X., Song T., Hu Qui J.: *Chem. Phys Lett.* **1989**, 87.

49. Wilson S. T., Flanigen E. M.: *ACS Symp. Ser.* **1989**, *398*, 329.

50. Tuel A., Ben Taarit Y: *J. Chem. Soc., Chem. Commun.* **1996**, 651.

51. Corma A., Iglesias M., Sanchez F.: *J. Chem. Soc., Chem. Commun.* **1995**, 1635.

52. a) Zhang W., Wang J., Tanev P. T., Pinavaia T. J.: *J. Chem. Soc., Chem. Commun.* **1996**, 979. b) Reddy K. M., Moudrakovski I., Sayari A.: *J. Chem. Soc., Chem. Commun.* **1994**, 1059.

53. Ulayappan N., Rao C. N. R.: *J. Chem. Soc., Chem. Commun.* **1996**, 1047.

54. Haanepen M. J., Elemans-Mehring A. M., van Hooff J. H. C.: *Appl. Catal., A*: **1997** 152, 203.

55. Tanev P. T., Pinnavaia T. J.: *Chem. Mater.* **1996**, *8*, 2068.

56. Coustel N., di Renzo F., Fajula F.: *J. Chem. Soc., Chem. Commun.* **1994**, 967.

57. Tuel A., Gontier S., Teissier R.: *J. Chem. Soc., Chem. Commun.* **1996**, 651.

58. a) Dakka J.: Unpublished results; b) Plyuto Y.: Unpublished results.

59. Raghavan P. S., Ramaswamy V., Upadhya T. T., Ramaswamy A. V., Sivasanker S.: *J. Mol. Catal., A* **1997**, *122*, 75.

60. a) Liu C.-J., Li S.-Y., Pang W.-Q., Che C.-M.: *J. Chem. Soc., Chem. Commun.* **1997**, 65; b) Balkus K. J., Eissa M., Lavado R.: *Stud. Surf. Sci. Catal.* **1995**, *94*, 713.

61. de Vos D., Meiershagen J. L., Bein T.: *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2211.

62. a) Parton R. F., Bezoukhanova C. P., Grobet J., Jacobs P. A.: *Stud. Surf. Sci. Catal.* **1994**, *83*, 371; b) Liu C., Ye X., Wu Y.: *Catal. Lett.* **1996**, *36*, 263.

63. Weckhuysen B. M., Verberkmoes A. A., Fu L., Schoonheydt R. A.: *J. Phys. Chem.* **1996**, *100*, 9456.

64. Parton R. F., Uytterhoeven L., Jacobs P. A.: *Stud. Surf. Sci. Catal.* **1991**, *59*, 395.