Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article De Vos, D. E. , Knops-gerrits, P. P. , Vanoppen, D. L. and Jacobs, P. A.(1995) 'Catalytic and physico-chemical properties of new schiff base complexes in zeolites', Supramolecular Chemistry, 6: 1, 49 — 57
To link to this Article: DOI: 10.1080/10610279508032519
URL: http://dx.doi.org/10.1080/10610279508032519

SUPRAMOLECULAR CHEMISTRY, Vol. 6, pp. 49–57
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Catalytic and physico-chemical properties of new schiff base complexes in zeolites

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(Received August 5, 1994)

Adsorption of tetradentate Schiff base ligands on $Mn^{II}NaY$ zeolites yields catalysts for selective oxidation of hydrocarbons with PhIO or tert-butylhydroperoxide (tBHP). The interaction between Mn and the ligands is proved by IR, diffuse reflectance and EPR spectroscopy. Olefin epoxidation with these catalysts suffers from formation of undesirable products when tBHP is used, but reasonable epoxide selectivities are obtained with PhIO. Very active catalysts for alkane oxidation with tBHP are produced by adsorption of the pyridine derived pyren and pyrpn ligands on $Mn^{II}NaY$ (pyren = bis(2-pyridinecarboxaldehyde)ethylenediimine; pyrpn = bis(2-pyridinecarboxaldehyde)propylenediimine). With these catalysts, very high selectivities are obtained for formation of monoketones from alkanes. A relation is proposed between the appearance of low-field features in the Mn(II) EPR spectra and a high activity in hydrocarbon oxidation.

INTRODUCTION

The channels and cages of zeolite lattices are well known to be preferred hosts for transition metal complexes.[1] Numerous ligands have been used for intrazeolitic complexation, going from simple, monodentate ligands (*e.g.* NH_3), to polydentate molecules (*e.g.* the polyamine tetren or the Schiff base $salenH_2$; tetren = tetraethylenepentamine; $salenH_2$ = bis(salicylaldehyde)ethylenediimine). This chemical variability has necessitated the development of diverse synthetic procedures and has lead to a considerable understanding of the ways that complexes may be retained in zeolites.[2] Potential redox applications of these zeolite based materials include reversible oxygen sorption, light energy storage and heterogeneous catalysis. In the latter field, the focus has almost exclusively been on zeolite immobilized phthalocyanines.[3] A major leap forward was the recent discovery of a highly active $[Mn(bipyridine)_2]^{2+}$-NaY alkene oxidation catalyst.[4] By using the Schiff base (SB) $salenH_2$ in a MnNaY environment, Bowers and Dutta pioneered yet another approach in devising a heterogeneous hydrocarbon oxidation catalyst, even if the number of catalytic Mn cycles was rather low.[5]

The strategy of the present paper is to introduce the versatility of Schiff base ligand synthesis into the design of metal-ligand-zeolite supramolecular constructs. The resulting materials are applied as catalysts in oxidation of alkanes or olefins with various oxidants, such as PhIO or tertiary butylhydroperoxide (tBHP). Based on homogeneous catalytic data, ligand structure variation may be expected to influence the electron density of the metal center and its stability towards oxidation.[6] However, as the actual complexation is performed inside the zeolite cages, additional effects of ligand structure on intrazeolitic complex yield and structure are to be expected.[7] Figure 1 presents an overview of the Schiff bases used in this work, together with their acronyms. Apart from these tetradentate ligands, the bidentate dimethylglyoxime ($dmgH_2$) was also used.[8] Though catalysis with Mn was our main objective, we also studied coordination chemistry and oxygen sorption

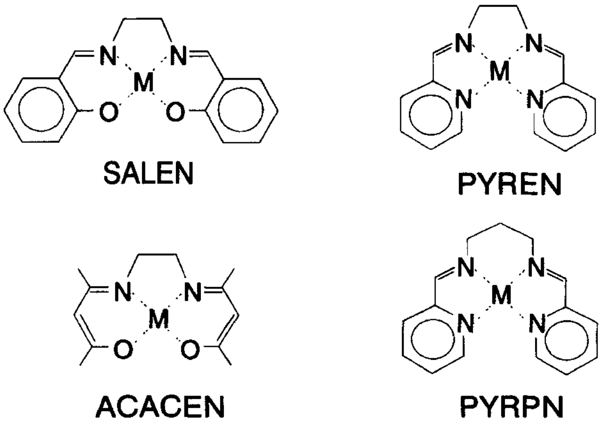

Figure 1 · Metal complexes of some tetradentate Schiff bases; $salenH_2$ = bis(salicylaldehyde)ethylenediimine; $acacenH_2$ = bis(acetylacetone)-ethylenediimine; pyren = bis(pyridinecarboxaldehyde)ethylenediimine; pyrpn = bis(pyridinecarboxaldehyde)ethylenediimine.

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properties of some [Co(SB)] zeolites; these data contribute to a better understanding of the complexation reactions in the zeolites. Similarities or dissimilarities between the heterogenized complexes and their homogeneous counterparts are derived from spectroscopic and catalytic features, and based on these elements, the potential of the new zeolite based materials is outlined.

RESULTS

Synthesis and Spectroscopic characteristics of [Mn(SB)] zeolites. X-band EPR spectroscopy.

In hydrated or dehydrated MnNaY zeolite, a sextet is observed around the free electron value ($g = 2.01 \pm 0.01$; $|A| \cong 95$ G). This spectrum arises from Mn^{2+}, coordinated by the zeolite lattice or by residual water ligands.[9] The spectrum is only slightly changed by adsorption of the $acacenH_2$ and $dmgH_2$ ligands on the dehydrated zeolite ($acacenH_2$ = bis(acetylacetone)ethylenediimine). On the contrary, [Mn(salen)]-NaY, $[Mn(pyren)]^{2+}$-NaY and $[Mn(pyrpn)]^{2+}$-NaY present a spectrum with the following new characteristics (Figure 2): *(i)* a new absorption at $g = 5.2$, *(ii)* a broad shoulder between 1900 and 2900 G, *(iii)* significant broadening of the Mn hyperfine structure. Double integration shows that the overall signal intensity is almost unchanged after ligand adsorption. Even upon removal of excess ligand by soxhlet extraction, the amount of Mn^{2+} remains constant. This evidences that most Mn remains in the + II oxidation state, even after exposure of the sample to ambient air. The Mn signal intensity is decreased after soxhlet extraction only in the case of [Mn(salen)]-NaY and [Mn(acacen)]-NaY; this is clearly related to the presence of dark colored Mn chelates in the extraction solvent.

Reflectance spectra

In Figure 3, spectra of different [Mn(SB)] zeolites are compared to those of NaY zeolites, on which an equal amount of ligand was adsorbed. It is well known that *d-d* transitions in Mn^{2+} are spin-forbidden.[10] As in our samples most Mn is in the +II oxidation state, the Mn related features of the reflectance spectra must therefore be due to *(i)* charge transfer phenomena, or *(ii)* to deprotonation, for the weakly acidic ligands. Usually the influence of the TMI on the spectrum is strong, yielding *e.g.* yellow ($acacenH_2$) or salmon-pink ($dmgH_2$) colors. For the purple $[Mn(pyren)]^{2+}$-NaY and $[Mn(pyrpn)]^{2+}$-NaY, the intense transitions around 600 nm can be related to the presence of α-diimine groups in the ligand.[11] In the case of [Mn(salen)]-NaY, the very intense ligand transition at 400 nm makes metal-related spectral characteristics difficult to observe.

IR spectra

For uncharged Schiff bases, such as pyren and pyrpn, the interaction with the zeolite hosted metal ions causes only minor shifts of the vibrations of the imine group and the aromatic ring. On the other hand, changes are more dramatic for the hydroxylic ligands.[12] For instance in the case of $salenH_2$, the cheland ionization allows to distinguish between free and chelating ligand.[13] The 1500 cm^{-1} band of free $salenH_2$ disappears upon chelation, and a new "*chelation*" band arises between 1520 and 1560 cm^{-1}. For the particular case of crystalline [Mn(salen)] complexes, reported frequencies of this chelation band are 1525 cm^{-1} (for [Mn(II)salen]) and 1551 cm^{-1} (for $[Mn(III)salen]^+PF_6^-$).[14] For the zeolite entrapped [Mn-(salen)] complex, the chelation band is observed at a clearly different frequency (1540 cm^{-1}). This hints that the structure of [Mn(salen)] may be influenced by zeolite entrapment. The characteristic IR bands of non-chelating $salenH_2$ make it possible to continue the extraction precisely until the material contains exclusively ionized, metal-binding salen (Figure 4). In this respect, our [Mn(salen)]-NaY material is undoubtedly distinct from previously reported samples, which display a strong vibration of free $salenH_2$ at 1500 cm^{-1}.[5]

Analogous IR features are observed for $acacenH_2$ and $dmgH_2$ loaded zeolites.[12] The presence of a transition metal ion (such as Mn or Co) greatly raises the retention

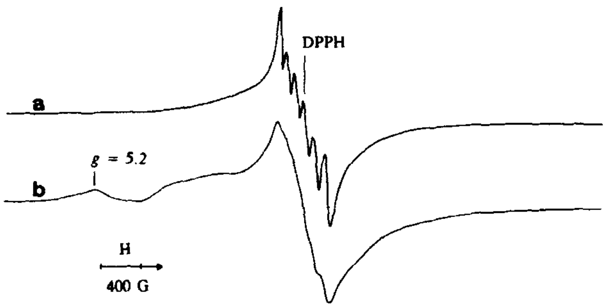

Figure 2 X-band EPR spectra at room temperature of (a) [Mn(acacen)]-NaY, (b) $[Mn(pyren)]^{2+}$-NaY (samples before soxhlet extraction).

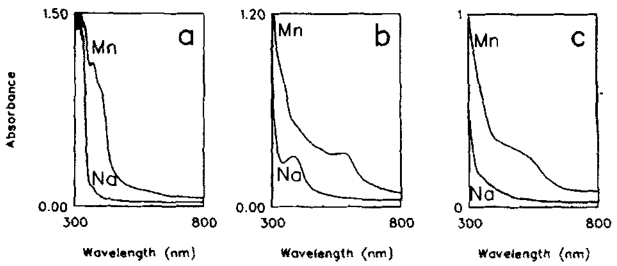

Figure 3 Reflectance spectra of MnNaY and NaY zeolites, after adsorption of ligands. (a) [Mn(acacen)]-NaY and $acacenH_2$-NaY, (b) $[Mn(pyren)]^{2+}$-NaY and pyren-NaY, (c) $[Mn(dmgH)_2]$-NaY and $dmgH_2$-NaY.

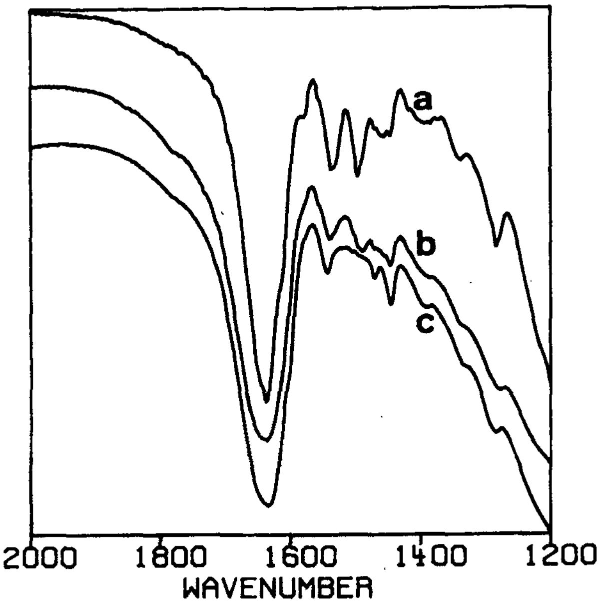

Figure 4 IR spectra of [Mn(salen)]-NaY, (a) before soxhlet extraction, (b) after 5 h of dichloromethane extraction, (c) after 15 h of dichloromethane extraction. The 1500 cm^{-1} band of free salenH$_2$ disappears upon extraction, while the 1540 cm^{-1} chelation band subsists.

of the ligand on the zeolite during the soxhlet treatment: after ligand loading and equal extraction times, the MnNaY zeolite still contains appreciable amounts of ligand, while the NaY zeolite presents a blank spectrum. Vibrations which are typical for the free ligand, and metal-related bands, can clearly be distinguished; this facilitates the total removal of free ligand by extraction. However, there is only partial agreement between the spectra of the zeolite entrapped complexes and those of the free complexes, especially in the case of acacenH$_2$.[15]

Oxidation catalysis with [Mn(SB)] zeolites

Products of selective oxidation were only obtained with PhIO or tBHP. Use of aqueous hydrogen peroxide resulted in a vigorous oxidant decomposition, which was also significant for dehydrated MnNaY zeolites.

Alkane oxidation

A number of [Mn(SB)]-zeolites were screened as catalysts of cyclohexane oxidation (Table 1). The only reaction products were the alcohol and the ketone. Catalysts extracted with dichloromethane or with acetone displayed a more or less comparable activity. With pyren, pyrpn or dmgH$_2$ containing catalysts, diffusion of Mn into solution could not be demonstrated by elemental analysis nor by spectrophotometry. However, Mn leaching occurred for neutral complexes such as [Mn(acacen)]-NaY and [Mn(salen)]-NaY, especially when a dichloromethane extracted catalyst was used in acetone. Nevertheless, if acetone is replaced by a less polar solvent, such as cyclohexane, one can work in truly heterogeneous catalytic conditions, even for the complexes with anionic ligands. For these reactions in cyclohexane, Mn turnover numbers are comparable to

Table 1 Screening of Mn Schiff base zeolites as cyclohexane oxidation catalysts

					Products		*Oxidant*
		Extraction		*Reaction*	*(mol per mol Mn)*		*Efficiency*[16]
	Catalyst	*Solvent*	*Oxidant*	*Solvent*	*Alcohol*	*Ketone*	*(%)*
1	MnNaY	–	PhIO	Acetonitrile	< 0.02	< 0.02	< 0.5
2	[Mn(salen)]-NaY	Acetone	"	"	0.55	0.50	6
3	[Mn(pyren)]$^{2+}$-NaY	Acetone	"	"	0.65	0.46	8
4	MnNaY	–	tBHP	Acetone	< 0.02	0.02	~12
5	[Mn(salen)]-NaY	CH_2Cl_2	"	"	1.88	5.00	36
6	[Mn(salen)]-NaY	Acetone	"	"	0.98	4.15	41
7	[Mn(acacen)]-NaY	CH_2Cl_2	"	"	0.16	0.48	23
8	[Mn(acacen)]-NaY	Acetone	"	"	0.20	0.49	40
9	[Mn(pyren)]$^{2+}$-NaY	CH_2Cl_2	"	"	3.15	7.70	43
10	[Mn(pyren)]$^{2+}$-NaY	Acetone	"	"	5.20	10.60	33
11	[Mn(pyrpn)]$^{2+}$-NaY	Acetone	"	"	2.43	7.30	34
12	[Mn(dmgH)$_2$]-NaY	Acetone	"	"	0.44	0.64	34
13	MnNaY	–	tBHP	Cyclohexane	0	0	0
14	[Mn(salen)]-NaY	Acetone	"	"	2.77	5.80	38
15	[Mn(acacen)]-NaY	Acetone	"	"	1.83	1.50	21
16	[Mn(pyren)]$^{2+}$-NaY	Acetone	"	"	3.40	4.80	29
17	[Mn(pyrpn)]$^{2+}$-NaY	Acetone	"	"	3.58	5.35	35
18	[Mn(dmgH)$_2$]-NaY	Acetone	"	"	0.33	0.58	12

Reaction conditions: *(entries 1 to 12)* 0.1 g of zeolite, soxhlet extracted with dichloromethane or with acetone; 2.5 mmol of cyclohexane; 1 mmol of PhIO or 2 mmol of aqueous tBHP; 2 ml of solvent; 293 K; 10 h; *(entries 13 to 18)* same conditions, except for oxidant (1.5 mmol of 80% tBHP in dimer) and solvent (2 ml of cyclohexane).

those obtained in acetone, even if the cyclohexane concentration is much higher (*Table 1, entries 14 to 18*).

From the preliminary tests in Table 1, [Mn(salen)]-NaY, [Mn(pyren)]$^{2+}$-NaY and [Mn(pyrpn)]$^{2+}$-NaY emerge as the most active catalysts. In order to evaluate catalyst stability and to optimize peroxide efficiency, reactions were performed with gradual addition of the peroxide. In Figure 5, conversion, cyclohexanone selectivity and peroxide efficiency are plotted *vs.* time for cyclohexane oxidation with tBHP. [Mn(salen)]-NaY is rapidly deactivated, but with the pyridine derived ligands, conversions up to 24% can be obtained. This corresponds to minimal Mn turnover numbers of 150.[16] Peroxide efficiencies attain a minimum immediately after completion of tBHP addition, and vary between 20 and 40%. With [Mn(pyren)]$^{2+}$-NaY and [Mn(pyrpn)]$^{2+}$-NaY, the ultimate cyclohexanone selectivity exceeds 90%; products of further oxidation, such as diones, diols or acids, are absent. n-Hexane oxidation reveals similar trends (Table 2). Final conversions amount to 0.8 and 8.6% for [Mn(salen)]-NaY and [Mn(pyren)]$^{2+}$-NaY respectively. Only products of mono-oxidation are found in the reaction mixture. The C-2/C-3 oxidation ratio was 1.14 for [Mn(pyren)]$^{2+}$-NaY and 1.04 for [Mn(salen)]-NaY. Data for adamantane oxidation are also included in Table 2. The relative reactivity of tertiary *vs.* secondary hydrogen atoms varies between 8.9 and 10.5.

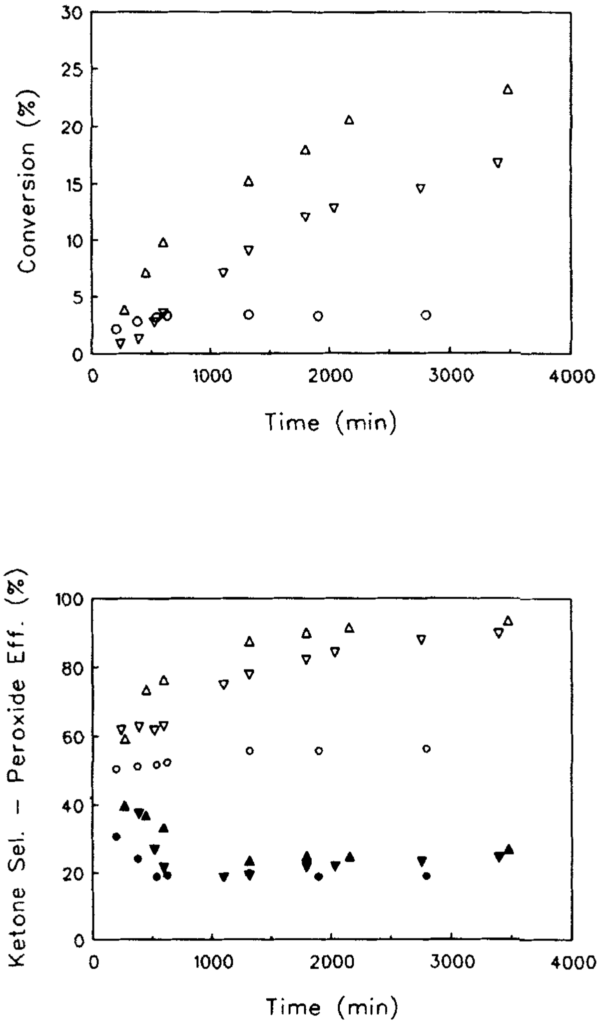

Figure 5 *(Top)* Conversion *vs.* time for the oxidation of cyclohexane (50 mmoles) with aqueous tBHP (80 mmoles, added linearly over 10 h) in 50 ml of acetone. Catalysts were [Mn(salen)]-NaY (○), [Mn(pyren)]$^{2+}$-NaY (△), [Mn(pyrpn)]$^{2+}$-NaY (▽); *(Bottom)* same reactions; oxidant efficiencies for [Mn(salen)]-NaY (●), [Mn(pyren)]$^{2+}$-NaY (▲), [Mn(pyrpn)]$^{2+}$-NaY (▼); Ketone selectivities for [Mn(salen)]-NaY (○), [Mn(pyren)]$^{2+}$-NaY (△), [Mn(pyrpn)]$^{2+}$-NaY (▽).

Olefin oxidation

Results are summarized in Table 3. In the batch oxidation of cyclohexene, the main products were cyclohexene oxide, 1,2-cyclohexanediol, cyclohex-2-en-1-one and (cyclohex-2-enyl)(*t*-butyl)peroxide. With [Mn(SB)] zeolites and PhIO, reasonable selectivities for oxidation of the double bond were obtained (*entries 16 and 17*); tBHP mainly yielded allylic oxidation products (*entries 19 and 20*). Attempts were made to increase the epoxide yield by addition of pyridine. At pyridine : Mn ratios between 2 and 60, no improvement of the (epoxide + diol) yield was observed. In an alternative approach, an axially coordinating base was inserted into the salenH$_2$ and acacenH$_2$ ligands, yielding respectively smdptH$_2$ (bis(salicylaldehyde)methylnitrilodipropylenediimine) and amdptH$_2$ (bis(acetylacetone)methylnitrilodipropylenediimine). With the resulting [Mn(smdpt)]-NaY and [Mn(amdpt)]-NaY catalysts, Mn turnover numbers were less than one; the main reaction product was still the allylic peroxide.

Styrene

oxidation products were styrene oxide, phenyl-1,2-ethanediol and benzaldehyde. Together these products account for over 95% of styrene conversion. For reactions performed in acetone and in cyclohexane comparable conversions are obtained; but as in the latter case anhydrous peroxide is applied, the oxirane ring opening is suppressed.[17]

Coordination and oxygen sorption on [Co(pyren)]$^{2+}$-NaY and [Co(pyrpn)]$^{2+}$-NaY zeolites

The reflectance spectra of these samples closely resemble those of the corresponding Mn and Ni zeolites, with dominant low-energy charge transfer bands. However, the EPR spectra give detailed information concerning the Co^{2+} coordination. There seem to be at least two coordination types around Co^{2+}. At room temperature and under an oxygen atmosphere, Co superoxo species are present. Maximum concentrations amount to 9 ± 1 mmol.g^{-1} for [Co(pyren)]$^{2+}$-NaY and 4 ± 1 mmol.g^{-1} for [Co(pyrpn)]$^{2+}$-NaY (the total Co concentration is 150

Table 2 Oxidation of n-hexane and adamantane over [Mn(SB)] zeolites

	Substrate	Catalyst	Time(h)	Products (mol per mol Mn)			
				2-ol	*2-one*	*3-ol*	*3-one*
1	n-hexane	[Mn(salen)]-NaY	25	0.19	1.17	0.26	1.03
2	"	$[Mn(pyren)]^{2+}$-NaY	25	1.55	13.3	1.88	11.2
				1-ol	*2-ol*	*2-one*	$H^{3°}/H^{2°}$
3	adamantane	[Mn(salen)]-NaY	3	1.93	0.46	0.16	9.4
4	"	[Mn(salen)]-NaY	14	3.46	0.75	0.41	8.9
5	"	$[Mn(pyren)]^{2+}$-NaY	3	8.07	1.71	0.77	9.8
6	"	$[Mn(pyren)]^{2+}$-NaY	5	10.61	1.93	1.10	10.5

Reaction conditions: *(entries 1 and 2)* 0.5 g of acetone extracted catalyst; 50 mmoles of n-hexane; 80 mmoles of aqueous tBHP, added linearly over 10 hours; 50 ml of acetone; 293 K; *(entries 3 to 6)* 0.3 g of acetone extracted catalyst; 15 mmoles of adamantane; 60 mmoles of tBHP (80% in dimer), added linearly over 10 hours; 30 ml of dichloromethane; 293 K.

mmol.g^{-1}). Much higher intensities are observed for a second species, which gradually appears upon cooling under N_2 or O_2. This growing-in phenomenon must be ascribed to a Co^{2+} high spin $\rightleftharpoons$ low spin transition. Estimated concentrations of low-spin Co^{2+} at 110 K are 26 ± 1 mmol.g^{-1} for $[Co(pyren)]^{2+}$-NaY and 20 ± 1 mmol.g^{-1} for $[Co(pyrpn)]^{2+}$-NaY. The signal is typically that of a pseudo-octahedral, low-spin Co complex; all three *g* values fall between 2.30 and 2.00, which compares well to the parameter set of *e.g.* $[Co(terpy)_2]^{2+}$.[18] The superimposition of the superoxo and the low-spin species is illustrated in the EPR spectrum of Figure 6.

While pyren is a 2-2-2 ligand,[19] the 2-3-2 pyrpn ligand is surely large enough to allow a planar ligand disposition. Four coordinate, planar Co complexes should have at least one *g*-value > 2.40.[20] However, there is no spectral evidence for the presence of such square complexes with a planar ligand organization.

DISCUSSION

For all [Mn(SB)] zeolites, the interaction between Mn and the ligand is proved by IR, reflectance or EPR data. Changes of the EPR spectra are most pronounced after adsorption of salenH_2, pyren or pyrpn. Based on the

Table 3 Olefin oxidation with Mn Schiff base zeolites

	Catalyst	Substrate	Oxidant	Products (mol per mol Mn) PhCOH			
				epoxide	*1,2-diol*	*PhCOH*	
1	MnNaY	Styrene	PhIO	1.73	—	2.80	
2	[Mn(salen)]-NaY	"	"	13.34	—	1.11	
3	$[Mn(pyren)]^{2+}$-NaY	"	"	9.80	—	4.00	
4	MnNaY	Styrene	aqueous tBHP	0	< 0.02	0.50	
5	[Mn(salen)]-NaY	"	"	1.50	1.07	4.43	
6	[Mn(acacen)]-NaY	"	"	1.16	< 0.02	1.80	
7	$[Mn(pyren)]^{2+}$-NaY	"	"	1.04	0.63	3.88	
8	$[Mn(pyrpn)]^{2+}$-NaY	"	"	3.23	0.57	6.27	
9	$[Mn(dmgH)_2]^{2+}$-NaY	"	"	3.27	< 0.02	4.23	
10	MnNaY	Styrene	anhydrous tBHP	0.23	—	0.87	
11	[Mn(salen)]-NaY	"	"	3.03	—	3.70	
12	$[Mn(pyren)]^{2+}$-NaY	"	"	2.68	—	2.53	
13	$[Mn(pyrpn)]^{2+}$-NaY	"	"	2.53	—	3.63	
14	$[Mn(dmgH)_2]^{2+}$-NaY	"	"	2.30	—	2.33	
				epoxide	*1,2-diol*	*enone*	*peroxide*
15	MnNaY	Cyclohexene	PhIO	0.23	< 0.02	2.16	—
16	[Mn(salen)]-NaY	"	"	3.48	< 0.02	1.10	—
17	$[Mn(pyren)]^{2+}$-NaY	"	"	1.40	< 0.02	1.03	—
18	MnNaY	Cyclohexene	aqueous tBHP	<0.02	0.06	0.13	1.67
19	[Mn(salen)]-NaY	"	"	0.20	< 0.02	2.48	12.07
20	$[Mn(pyren)]^{2+}$-NaY	"	"	0.47	< 0.02	2.07	10.84

Reaction conditions: 0.1 g of MnNaY or 0.1 g of acetone extracted [Mn(SB)]-NaY catalyst; 2.5 mmol of olefin; 1 mmol of PhIO, 2 mmol of aqueous tBHP or 1.5 mmol of anhydrous tBHP; 2 ml of solvent (1–3, 15–17: acetonitrile; 4–9, 18–20: acetone; 10–14: cyclohexane); 293 K, 10 h. Abbreviations: enone = cyclohex-2-en-1-one; peroxide = (cyclohex-2-enyl)(t-butyl)peroxide.

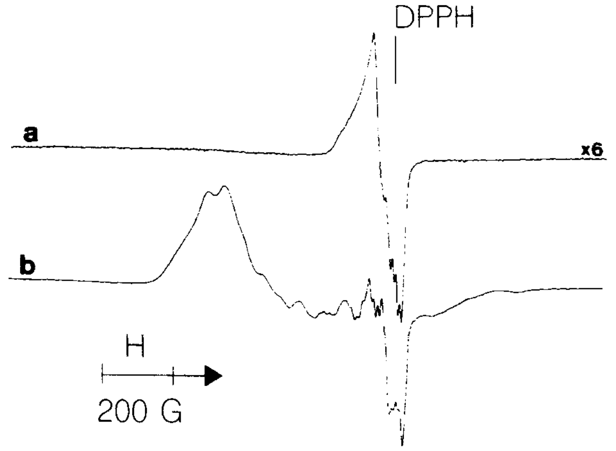

Figure 6 X-band EPR spectra of $[Co(pyrpn)]^{2+}$-NaY; *(top)* room temperature, 1000 mbar of O_2; *(bottom)* 110 K, 1000 mbar of O_2. At 110 K, the low spin Co(II) signal is superimposed on the superoxosignal of the upper spectrum.

concepts developed by Dowsing *et al.*,[21] it can be stated that these ligands cause a major part of Mn^{2+} to depart substantially from the original regular tetrahedral or octahedral environment. The air-stability of the Mn +II state in the zeolite supported complexes is a direct consequence of the complex immobilization, and contrasts sharply with solution chemistry, where oxidative conditions lead to formation of different polynuclear Mn species.[22]

In the presence of MnNaY reference catalysts, product formation is sometimes observed, especially when PhIOis used. This result agrees with the known catalytic-activity of many transition metal salts in oxidations with PhIO.[23] However, conversions and oxidant efficiencies (*e.g.* in cyclohexane oxidation, see Table 1) or product selectivities (*e.g.* in reactions with olefins, see Table 3) clearly establish the effect of chelation on the catalytic activity of Mn. While unchelated Mn does not impede the application of PhIO or tBHP, its presence may be the cause of the pronounced decomposition of hydrogen peroxide on all [Mn(SB)] zeolites. An alternative explanation would involve the known catalase activity of [Mn(SB)] complexes;[24] however such reactions require participation of binuclear SB complexes, which seems unlikely for the monomolecularly dispersed intrazeolitic Mn complexes. In order to permit the use of H_2O_2 in analogous systems, free Mn should be minimized by increasing complexation time, as was demonstrated recently for $[Mn(bpy)_2]^{2+}$-NaY (bpy = 2,2'-bipyridine).[4] However, this approach does not apply to Schiff bases, in view of the limited thermal stability of these ligands.

A crucial point is whether or not one is dealing with *heterogeneous* catalysis. Intrazeolitic formation of metallosalen complexes is sometimes described as an (irreversible) "ship-in-a-bottle" process. Nevertheless, in his original paper, Herron proved by ESCA that salenH_2 treatment, followed by extraction, caused Co^{2+} depletion in the outer zone of CoNaY.[25] Our data confirm this trend. For instance, if [Mn(salen)]-NaY is extracted with the apolar dichloromethane instead of with acetone, and subsequently used in a reaction in acetone, the liquid phase turns a dark color. However, Mn turnover numbers are not noticeably influenced by the polarity of the extraction solvent, which indicates that the eventual contribution of the dissolved complexes is negligible. Nevertheless, the following measures were taken to minimize Mn losses during reaction: (*i*) soxhlet extraction with a polar solvent, and extension of the extraction beyond its apparent completion, (*ii*) use of neutral ligands (such as pyren or pyrpn), resulting in electrostatic complex retention, (*iii*) application of a less polar reaction medium, *e.g.* an anhydrous hydrocarbon solvent. As a consequence, the Mn chelates (and their catalytic activity) can be totally confined to the solid phase.

When one considers *the influence of ligand structure on initial catalytic activity* in hydrocarbon oxidation (Table 1), it is striking that the highest activities are generally obtained with the salenH_2, pyren and pyrpn ligands, which are precisely those ligands that cause the previously discussed changes in the Mn^{2+} EPR spectra (Figure 2). This empirical relationship was checked for the $[Mn(pyren)]^{2+}$-NaY catalyst by adding tBHP to the zeolite and recording again the EPR spectrum. The low-field features of Schiff base coordinated Mn(II) disappeared after reaction with the oxidant; in the spectrum, only zeolite coordinated Mn(II) remained visible. This hints that activation of the [Mn(II)(SB)]-NaY catalyst occurs by oxidation of Schiff base coordinated Mn to the tri- or tetravalent state.[6]

[Mn(SB)] zeolites in general catalyze *olefin oxyfunctionalisation with PhIO*, which confirms an earlier result for [Mn(salen)]-NaY.[5] Styrene oxidation with our systems yields a considerable amount of epoxide, while Bowers and Dutta reported formation of phenylacetaldehyde.[5] This selectivity difference probably stems from the attempted re-exchange of Mn^{2+} with Na^+, which generates acid sites.[5,26] It has indeed been reported that epoxide to aldehyde rearrangement is catalyzed by acid zeolites.[27] Less valuable side products of olefin oxidation include benzaldehyde (from styrene) and allylic oxidation products (from cyclohexene). However, it is generally observed that the ratio (epoxide + diol) / (undesirable oxidation products) is significantly raised by the use of the Schiff base ligands.

As turnover numbers with PhIO are low, tBHP may be a more active alternative. In reactions of styrene with tBHP, benzaldehyde has often been reported to be the main product,[28] but nevertheless significant epoxide selectivities are obtained with our systems (*Table 3*, *entries 5 to 9 and 11 to 14*). Cyclohexene oxidation, however, mainly gives the (cyclohex-2-enyl)(t-butyl)peroxide. In the homogeneous oxidation of cyclohexene with $[Mn(salen)]^+$ and tBHP, cyclohexene oxide yields can be improved by axial coordination of a Lewis base on the five-coordinated [Mn(salen)(OOtBu)].[14] For [Mn(salen)]-NaY, such a *trans* effect on the Mn-O-O structure could not be established, though the zeolite cage is undoubtedly large enough to host [Mn(salen)(pyridine)].[29] A possible explanation is that intrazeolitic [Mn(salen)] has a *cis* conformation instead of the usual *trans* form. The *cis* form is expected to be favored by the properties of the zeolite surface as a ligand. Whereas zeolite Y can of course act as a bi- or polydentate ligand, its concave surface is not at all capable of binding as a monodentate ligand on square planar complexes, as we proved recently for the square planar [Co(acacen)] complex.[7] The transformation of a transient *cis* complex into *trans* is therefore probably retarded in zeolite Y. This trend is confirmed by our spectroscopic data for the $[Co(pyrpn)]^{2+}$-NaY sample. Though the pyrpn ligand is sufficiently large for a *trans* complex to be formed, one fails to observe the well-known characteristics of a planar complex. The implication of a non-planar ligand arrangement is that development of a ***heterogeneous***, ***chiral*** epoxidation catalyst based on [Mn(SB)]-zeolites may not be feasible; indeed in Jacobsen's chiral [Mn(SB)] catalysts, the aromatic rings are coplanar, and the substrate is oriented at the chiral diamine moiety of the ligand.[30]

Perspectives in alkane oxidation with peroxides are much better. While the screenings reveal little distinction between the $salenH_2$, pyren and pyrpn based systems, the long term stability of the latter two is remarkable. The fast deactivation of [Mn(salen)]-NaY is probably of an oxidative nature, as *(i)* the neutral salen complexes are expected to be more loosely associated with the zeolite and may oxidize each other, and *(ii)* the phenolic groups of salen are less resistant towards oxidation than pyridine rings.[31] For cyclohexane oxidation over $[Mn(pyren)]^{2+}$-NaY, 2.4 g of product is obtained per g of catalyst—which is as good as with zeolite Y occluded Fe-phthalocyanines ([Fe(Pc)]-NaY).[3c] On the other hand, remarkable selectivities for mono-oxidation are observed with $[Mn(pyren)]^{2+}$-NaY for all alkanes tested, while at comparable conversions mixtures of oxidation products are obtained with [Fe(Pc)]-NaY.[3d] The activity of $[Mn(pyrpn)]^{2+}$-NaY is slightly inferior to that of $[Mn(pyren)]^{2+}$-NaY. This parallels the observations with Co, and may simply reflect that complexation with the finely crystalline pyren is more efficient than with the sticky pyrpn oil, which is not as easily mixed with the zeolite in a homogeneous way. The reaction over $[Mn(pyren)]^{2+}$-NaY has a strong preference for oxidation at position 1 of adamantane. This confirms that the active species in Mn centered alkane oxidations are of a radical nature.[6,32] In n-hexane oxidation, the slight preference for reaction at C-2 may be the consequence of shape selectivity exerted by the zeolite framework. However, it may be impossible to check this, as the $[Mn(pyren)]^{2+}$-NaY has, strictly speaking, no homogeneous counterpart. In any case the effect is rather small to be of practical use.

CONCLUSION

Variation of the design of Schiff base ligands leads to formation of oxidation-resistant, highly active Mn centers in zeolites. In particular, alkanes can be oxidized with high selectivity to ketones over $[Mn(pyren)]^{2+}$-NaY and $[Mn(pyrpn)]^{2+}$-NaY catalysts.

Our catalysts constitute a new group of the class of "*zeozymes*", the zeolite-based enzyme mimics. The scheme below summarizes the different types of oxidation chemistry achievable with catalysts of this type, and provides evidence that these zeozymes are a valuable alternative for many homogeneous or purely inorganic heterogeneous catalysts.

Catalyst	Oxidant	Substrate	Products	*Reference*
$[Mn(bpy)_2]^{2+}$-NaY	H_2O_2	olefins	epoxides, diols, diketones carboxylic acids	*4*
$[Mn(pyren)]^{2+}$-NaY	tBHP	alkanes	ketones	*this work*
[Fe(Pc)]-NaY	tBHP	alkanes	(di)alcohols, (di)ketones, carboxylic acids	*3c, 3d*

EXPERIMENTAL SECTION

Materials

Following commercial products were used as obtained: adamantane, 1-adamantanol, 2-adamantanol, 2-adamantanone, tBHP (70% in water), cyclohexanone, cyclohexene oxide, 3,3'-diamino-*N*-methyldipropyldiamine, dichloromethane, iodobenzene diacetate, pyridine and $salenH_2$ (all from Aldrich), tBHP (80% in di-tert-butylperoxide) and 1,3-diaminopropane (from Fluka), acetone, benzaldehyde, chlorobenzene, cyclohexane, 1,2-cyclohexanediol, cyclohexanol, cyclohexene, 2-cyclohexen-1-one, dimethylglyoxime, ethylenediamine, n-hexane, 2-hexanol, 2-hexanone, 3-hexanol, 3-hexanone, phenylacetaldehyde, styrene, styrene oxide, $Co(CH_3COO)_2{\cdot}4H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$ (all from

Janssen Chimica), NaY zeolite (from the PQ corporation).

AcacenH_2, amdptH_2, smdptH_2 and pyren were prepared as previously described.[7] Pyrpn was synthesized by adding 2.08 g of 1,3-diaminopropane to 6.00 g of 2-pyridinecarboxaldehyde in 25 ml of absolute ethanol and stirring for 30 minutes. After solvent evaporation, weight control proved that the condensation product, an orange oil, was within experimental error water free. Crystallization attempts were without success. ^{1}H-NMR ($CDCl_3$): 8.66 (d, 2H, ArH), 8.47 (s, 2H, CH=N), 8.06 (d, 2H, ArH), 7.70 (d, d, 2H, ArH), 7.25 (d, d, 2H, ArH), 3.78 (t, 4H, CH_2), 2.14 (m, 2H, CH_2). (Cyclohex-2-enyl)(*t*-butyl)peroxide was identified by the characteristic t-butyl (M/z = 57, 43) and cyclohexenyl (M/z = 81, 80) fragments in the mass spectrum, and by comparison with an authentic sample, prepared by a literature method.[6]

Instrumentation

IR spectra were recorded with a Nicolet 700 apparatus. The UV-Vis-NIR domain was scanned with a Cary 5 spectrometer, equipped with a white reflecting sphere. A Bruker 300 spectrometer was used to record EPR spectra at X-band with a TE_{104} cavity, which could be cooled to 110 K. For quantitative measurements, a calibration curve was constructed with KBr diluted $[Cu(acac)_2]$. ^{1}H-NMR spectra were run on a Bruker AMX 300 at 300 MHz. Gas chromatography was performed on a Chrompack CP-Sil 5 or CP-Sil 88 column, with chlorobenzene as an internal standard. Identifications were performed with a HP 5988A GC/MS systems.

Synthesis of transition metal-Schiff base zeolites

NaY zeolites were partially exchanged with Co^{2+} (0.9 wt %) or Mn^{2+} (1.7 wt %) at pH 5. After drying under N_2 at 473 K, the zeolite was mixed with a double ligand excess (with respect to the transition metal content) and heated for 10 h in a sealed vacuum chamber at 413 K (salenH_2, acacenH_2) or 373 K (pyren, pyrpn, dmgH, smdptH, amdptH). Excess ligand was removed by soxhlet extraction with acetone or CH_2Cl_2. The extraction was continued for 10 h after apparent completion. In cases where characteristic IR bands could be used, extraction was continued until total removal of free ligand.

Reaction procedures

Catalyst screening reactions were performed in closed 4 ml reaction vessels. The reaction mixture consisted of 0.1 g of catalyst, 2.5 mmol of substrate, 1, 1.5 or 2 mmol of the oxidant (PhIO, tBHP in water or in di-tert-butylperoxide) and 2 ml of solvent (acetone, acetonitrile or cyclohexane). Reactions were also performed with gradual addition of the tBHP oxidant. For cyclohexane and n-hexane oxidation, the initial composition of the reaction mixture was 0.5 g of catalyst, 50 mmol of substrate and 30 ml of acetone. 80 mmoles of tBHP were added as a 70% aqueous solution at a rate of 8 $mmol{\cdot}h^{-1}$. For adamantane oxidation, the starting mixture contained 0.3 g of catalyst, 15 mmol of adamantane and 30 ml of dichloromethane. 60 mmoles of tBHP were added as an 80% solution in di-tert-butylperoxide at a rate of 6 $mmol{\cdot}h^{-1}$.

ACKNOWLEDGEMENTS

We are indebted to the Belgian National Science Foundation N.F.W.O. (DEDV and PPKG) and to I.W.O.N.L. (DLV) for fellowships as Research Assistants. We acknowledge IUAP-PAI sponsoring from the Belgian Federal Government. We thank P.J. Grobet and R. Reynders for recording ^{1}H NMR spectra.

REFERENCES

1 Ozin, G.; Gil, C. *Chem. Rev.* **1989**, *89*, 1749.
2 De Vos, D.; Thibault-Starzyk, F.; Knops-Gerrits, P.; Parton, R.F.; Jacobs, P.A. *Makromol. Chem., Macromol. Symp.* **1994**, *80*, 157.
3 (a) Herron, N. *J. Coord. Chem.* **1988**, *19*, 25. (b) Romanovsky, B.V.; Gabrielov, A.G. *J. Molec. Catal.* **1992**, *74*, 293. (c) Parton, R.F.; Uytterhoeven, L.; Jacobs, P.A. *Stud. Surf. Sci. Catal.* **1991**, *59*, 395. (d) Thibault-Starzyk, F.; Parton, R.F.; Jacobs, P.A. *Proc. 10th Int. Zeolite Conference*, page 1419, **1994**, Eds. Weitkamp, J.; Karge, H.G.; Pfeifer, H.; Hölderich, W., Elsevier.
4 Knops-Gerrits, P.P.; De Vos, D.; Thibault-Starzyk, F.; Jacobs, P.A. *Nature* **1994**, *369*, 543.
5 Bowers, C.; Dutta, P. K. *J. Catal.* **1990**, *122*, 271.
6 Srinivasan, K.; Michaud, P.; Kochi, J.K. *J. Am. Chem. Soc.* **1986**, *108*, 2309.
7 De Vos, D.E.; Feijen, E.J.; Schoonheydt, R.A.; Jacobs, P.A. *J. Am. Chem. Soc.* **1994**, *116*, 4746.
8 For a study of dimethylglyoxime adsorption on Co^{2+} and Ni^{2+} zeolites, see: Strutz, J.; Diegruber, H.; Jaeger, N.; Möseler, R. *Zeolites* **1983**, *3*, 102.
9 Tikhimirova, N.; Nikolaeva, I.; Demkin, N.; Rosolovskaya, E.; Topchieva, K. *J. Catal.* **1973**, *29*, 500.
10 Lever, A. "Inorganic Electronic Spectroscopy", 2nd edition, *Studies in Physical and Theoretical Chemistry, 33*; Elsevier: Amsterdam, 1984.
11 De Wilde, W.; Peeters, G.; Lunsford, J.H. *J. Phys. Chem.* **1980**, *84*, 2306.
12 The IR data set for acacenH_2 loaded samples is available as supplementary material.
13 De Vos, D.; Jacobs, P. *Proc. 9th Int. Zeolite Conference*, II-615, Eds. von Ballmoos, R.; Higgins, J.; Treacy, M.; Butterworth-Heinemann: Boston, 1993.
14 Srinivasan, K.; Perrier, S.; Kochi, J.K. *J. Molec. Catal.* **1986**, *36*, 297.
15 Ueno, K.; Martell, A. *J. Phys. Chem.* **1955**, 998.
16 Turnover numbers in alkane oxidation are calculated on product basis, *i.e.* ((cC6ol + 2 * cC6one) / total Mn). As only part of the Mn is catalytically active, turnover values are minimum estimates. Oxidant efficiencies were calculated as ((cC6ol + 2 * cC6one) / oxidant consumed). Oxidant consumption = PhI or tBuOH production.
17 Oxidation of the cyclohexane solvent was strongly suppressed in the presence of styrene; the concentration of cyclohexane

oxidation products was always at least twenty times lower than that of styrene oxidation products.

18 Kremer, S.; Henke, W.; Reinen, D. *Inorg. Chem.* **1982**, *21*, 3013.

19 The three digits refer to the number of carbon atoms between the ligand donor atoms.

20 Nishida, Y.; Kisa, S. *Coord. Chem. Rev.* **1979**, *27*, 275.

21 (a) Dowsing, R.; Gibson, J.; Goodgame, D.; Goodgame, M.; Hayward, P. *Nature* **1968**, *219*, 1037. (b) Dowsing, R.; Gibson, J.; Goodgame, M.; Hayward, P. *J. Chem. Soc. (A) Inorg. Phys. Theor.* **1969**, 187.

22 While EPR provides evidence that Mn in a salen loaded zeolite is mainly divalent, cyclic voltammetry seems to favour the trivalent state: Gaillon, L.; Sajot, N.; Bedioui, F.; Devynck, J.; Balkus, K.J. *J. Electroanal. Chem.* **1993**, *345*, 157. However, with cyclic voltammetry only the complexes in the outer rim of the zeolite are observed, while EPR spectroscopy is essentially a bulk technique.

23 VanAtta, R.; Franklin, C.; Valentine, J. *Inorg. Chem.* **1984**, *23*, 4123.

24 Larson, E.; Pecoraro, V. *J. Am. Chem. Soc.* **1991**, *113*, 7809.

25 Herron, N. *Inorg. Chem.* **1986**, *25*, 4714.

26 A supplementary drawback of the re-exchange procedure is the hydrolysis of salenH_2, which produces detectable amounts of salicylaldehyde.

27 Hoelderich, W.; Goetz, N. *Proc. 9th Int. Zeolite Conference*, II-309, Eds. von Ballmoos, R.; Higgins, J.; Treacy, M.; Butterworth-Heinemann: Boston, 1993.

28 Sarneski, J.; Michos, D.; Thorp, H.; Didiuk, M.; Poon, T.; Blewitt, J.; Brudvig, G.; Crabtree, R. *Tetrahedron Lett.* **1991**, *32*, 1153.

29 Note that even $[Ru(bpy)_3]^{2+}$ and [Co(smdpt)] have been synthesized in a Y supercage; see reference 2.

30 (a) Irie, R.; Noda, K.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* **1991**, *32*, 1055. (b) Lee, N.H.; Jacobsen, E. *Tetrahedron Lett.* **1991**, *32*, 6533.

31 Hamilton, D.; Drago, R.S.; Zombeck, A. *J. Am. Chem. Soc.* **1987**, *109*, 374.

32 (a) Fish, R.; Fong, R.; Vincent, J.; Christou, G. *J. Chem. Soc., Chem. Comm.* **1988**, 1504. (b) Taft, K.; Kulawiec, R.; Sarneski, J.; Crabtree, R. *Tetrahedron Lett.* **1989**, *30*, 5689. (c) Che, C.; Tang, W.; Wong, K.; Wong, W.; Lai, T. *J. Chem. Res. (S)* **1991**, 30.