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Zeolite Inclusion Complexes as Detoxicating Catalysts

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New synthetic methods for the preparation of zeolites with included transition metal chelates are reported, together with data on the characterization and catalytic properties of such systems with respect to CO oxidation and NO reduction.

Detoxification of pollutants originating from industrial flue gases and automobile exhausts is usually carried out with extremely low concentrations of toxic components in N_2 and O_2. Increasingly stringent emission standards have also prompted catalysis researchers to seek more active catalysts. It is important that they exhibit almost complete selectivity in order to prevent the formation of more toxic substances *e.g.* in the chlorination of potable water. Some 'eco-catalysts' are required to work at high temperatures (*e.g.* in exhaust converters), and in multicomponent steam–gas mixtures. The characteristics required of eco-catalysts are thus very specific.

For most eco-processes, the reactions are of an oxidation–reduction type, terminating in the formation of 'naturally' harmless products *i.e.*, water, nitrogen and carbon dioxide. In this respect, synthetic and natural zeolites which meet the requirements mentioned above are of great interest. In fact,

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these crystalline alumino-, iron-, boron- *etc.* silicates are well known to exhibit pronounced molecular sieve effects as well as good thermal and chemical resistance. These features of zeolite materials are due to the strict regularity of the internal voids whose dimensions vary from 0.3 up to 1.8 nm depending on the structural type. The zeolite pore structure not only imposes a sieving action upon substrate molecules approaching active sites but also a concentration effect, owing to the high adsorption potential inside the narrow zeolite pores. However, heterogeneous catalysts do not display as great a selectivity or stability as homogeneous ones. Therefore, the design of a new family of catalysts by supporting the complex molecules inside the pore structure of zeolites offers a promising improvement in catalytic activity. We now report synthetic pathways for preparing zeolites with included transition metal (TM) chelates. Data on the characterization and catalytic properties of such systems in CO oxidation and NO reduction are also discussed. These two reactions play a key role in the removal of these pollutants from effluents.

The synthesis of neutral metallocomplexes included within zeolite structures was carried out by us in 1976[1] and later reproduced by Schulz-Ekoff *et al.*,[2] Herron[3] and recently by Kimura *et al.*[4] In principle, there are two ways to include metallocomplexes inside the large cavities of zeolites. These are based on (*i*) cationic forms of zeolites containing TM cations and (*ii*) zeolite materials with preadsorbed labile π-complexes of TM (*e.g.* carbonyl complexes). In both cases, the target complex molecules could be prepared by treating the zeolite sample with the appropriate chelating reagent. In refs. 1–4 the authors used dicyanobenzene (DCB), four molecules of which form the highly stable phthalocyanine (Pc) macroligand, which chelates a TM atom inside the zeolite cage. The resulting PcM complex molecule cannot escape because of its physical dimensions, and is consequently encapsulated. In this case, the formation of a second PcM molecule inside a particular region of the cage is improbable owing to the space restriction. The application of method (*i*) is limited by the effectiveness of ion exchange with aqueous solutions of TM cations, so that some tri- and tetra-valent TM ions cannot be introduced into zeolite structures. This method of synthesis was, however, applied to Ni^{II}, Co^{II}, Fe^{II} and Cu^{II} phthalocyanines in zeolite-Y using the corresponding cationic forms of the zeolite matrix as starting materials[1–4] and DCB vapour at 250–350 °C as a complexing agent. Method (*ii*) seems more viable and its application is limited only by the availability of a volatile or soluble precursor compound and its molecular dimensions. This synthetic pathway avoids the tedious procedure of ion exchange. It has been used to produce bivalent PcNi, PcFe and PcCo as well as Pc-complexes of trivalent Ru, Os and Mn in zeolite-Y,[5–8] mono- and poly-nuclear carbonyl complexes and π-complexes, using cyclopentadienyl and mixed ligands as precursors. The temperatures used for the synthesis were usually between 150–340 °C, although these can be substantially decreased when an unstable precursor such as iron pentacarbonyl is used.

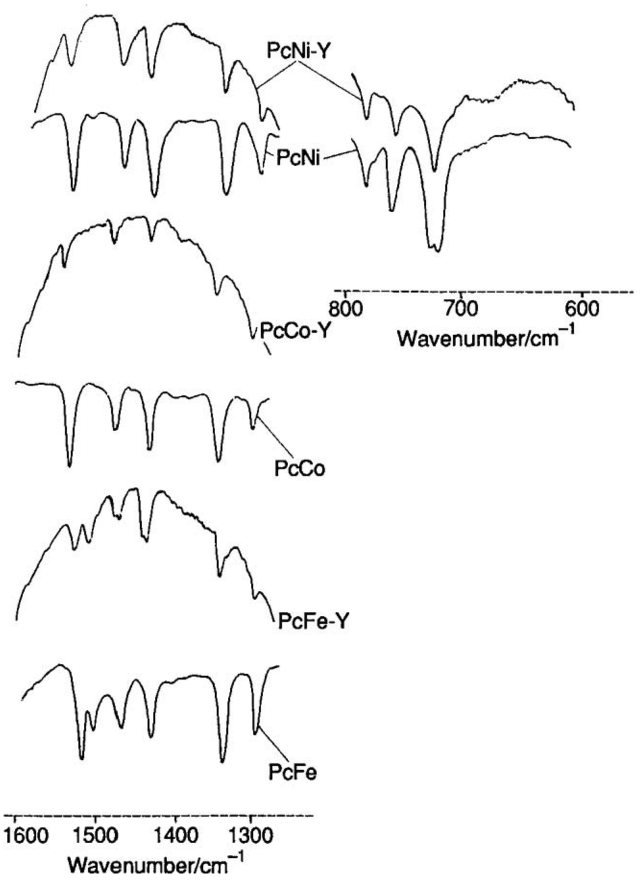

Fig. 1 FTIR spectra of free PcM and zeolite-included PcM-Y samples

One of the main problems in such a matrix-synthesis of inclusion complexes is the identification of the species formed inside the zeolite cages. From the coincidence not only of the band frequencies in the FTIR spectra but also from the closeness of intensity ratios for the samples synthesized

Table 1 Characteristics of supported Pc-complexes in zeolite-Y

No.	Sample[b]	Temperature of synthesis /°C	[M]/[N] (XPS)	Degree of complexation (%)	{[M]/[Si]} × 10^3 XPS	{[M]/[Si]} × 10^3 CA[a]
1	PcNi-Y	250	0.12	100	6.2	5.0
2	PcNi-Y	250	0.12	100	55.0	40.0
3	PcFe-Y	250	0.12	100	3.0	2.2
4	PcFe-Y	250	0.14	89	25.0	20.0
5	PcCo-Y	250	0.80	16	9.0	7.8
6	PcCo-Y	340	0.14	89	8.0	8.3
7	PcRu-Y	150	0.50	25	14.0	7.7
8	PcRu-Y	250	0.14	89	10.0	10.0
9	PcOs-Y	250	0.12	100	23.3	–
10	PcOs-Y	250	0.14	89	7.2	–

[a] CA: chemical analysis. [b] Metallocenes Cp_2Ni, Cp_2Ru, Cp_2Fe and carbonyls $Fe(CO)_5$, $Co_2(CO)_8$, $Os(CO)_{12}$ and $CpMn(CO)_3$ were used as precursors.

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Table 2 Binding energies for zeolite-included and free PcM's

Sample	M $2p_{1/2}$/eV	M $2p_{3/2}$, eV
PcNi	872.0	854.7
PcNi-Y	872.1	854.8
PcCo	796.4	781.0
PcCo-Y	796.4	781.1
PcFe	722.3	709.8
PcFe-Y	722.4	709.9

(PcM-Y) and for the free PcM complexes, of the species formed within the zeolite matrix could be tentatively identified as phthalocyanine molecules (see Fig. 1).

Based on the results of XPS experiments, the percentage conversion of the complex precursors can be evaluated, using experimental metal-to-nitrogen ratios estimated by XPS and the theoretical value of 0.125 (see Table 1). The XPS data show that the formation of PcM's from more labile π-complexes can proceed in up to 100% yield.†

The molecular dimensions of the starting polynuclear Co and Os carbonyls hinder their entry into the narrow zeolite channels and thereby the large cases. The question thus arises as to how these PcM species can be formed inside the voids. We propose a sophisticated explanation connected with the predissociation of the large carbonyl complexes into smaller mononuclear $M(CO)_x$ fragments on the outer surface of the zeolite crystals. Our suggestion of the formation of PcM species within the cavities where only one molecule of this complex can be entrapped, was based on the agreement between the superficial concentration of PcM (by XPS technique) and total amount of PcM (chemical analysis). The data are given in Table 1 as $\{[M]:[Si]\} \times 10^3$ ratios.

Comparison of the M $2p_{3/2}$ binding energies for zeolite-included Ni, Fe and Co phthalocyanines with the values of E_b for the individual PcM's indicates that the metal atoms are divalent with both axial coordination sites vacant (Table 2).

In contrast, for PcOs (as well as PcRu) we found E_b values characteristic of the III oxidation state of the metal (see Fig. 2). The phthalocyanine complexes with trivalent metals are known to have one extra ligand in the fifth axial position, and therefore they exhibit only one free coordination site. This appears to be the case for zeolite-included PcRu and PcOs, where an OH group of the matrix may fulfill the role of the extra ligand.

The eco-activities of the prepared catalysts were evaluated using the two test reactions: (*i*) low temperature oxidation of CO by molecular dioxygen and (*ii*) reduction of NO by molecular hydrogen and by carbon monoxide.

Oxidation of CO was performed in a static reactor at − 78 to + 60 °C.[9] The carbon dioxide formed was frozen out from the gaseous mixture. Data on the catalytic activities of zeolite-included and free PcCo as well as of Co–zeolite-Y are given in Table 3. Incorporation of a metal atom into the chelate increases its efficiency by two to three orders of magnitude. The inclusion of Pc complexes results in an additional rise in activity which one could attribute to the substrate concentrating effect. This suggestion is supported by the high catalytic activity of PcCo-Y in CO oxidation even at − 78 °C. The kinetics of the reaction are best described as first order in CO and one half in O_2. This result was obtained previously for ethene oxidation over individual PcM's.[10]

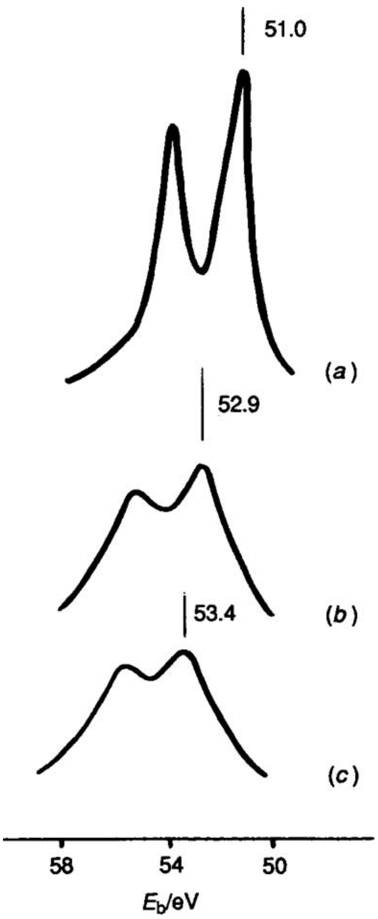

Fig. 2 XP (Os 4f) spectra of the osmium-containing samples: Os^0 (*a*), $Os_3(CO)_{12}$-Y (*b*) and PcOs-Y (*c*)

Self-poisoning of the Pc catalysts by the formation of CO_3^- as intermediates in CO oxidation of O_2 at room temperature was unexpectedly observed. This species is stable at these temperatures and could be destroyed only by prolonged pumping of the spent sample at 200 °C. Interestingly, this effect does not appear when the reaction occurs in the liquid phase in the presence of pyridinium ions.[11] The gas phase oxidation of CO over zeolite-included PcM's is enhanced by preadsorbed pyridine base, presumably as a result of fitting of the Py molecule on one side of the complex. Thus, the zeolite-included TM chelates serve as good low-temperature catalysts for CO oxidation.

Reduction of NO by CO and H_2 over supported PcM was studied using a pulsed technique. The complexes were found to exhibit fairly stable activity toward NO + CO and NO + H_2 reactions at 200–300 °C. The catalytic activity of the zeolite-included PcM depends on the nature of the metal (Table 4). The variation in activity can be rationalized in terms of the electronic structures. The out-of-plane atomic orbitals of

Table 3 Catalytic activities of zeolite included and free PcCo

Turnover number/h^{-1}		
PcCo-Y	PcCo	Co-Y
6.84	2.16	0.0054

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† *XPS measurements*: the C 1s line (E_b = 285 eV) and the Si 2p line (E_b = 103 eV) were used for energy calibration.

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Table 4 Degree of NO conversion (a_{NO}) and composition of nitrogen-containing products at 275 °C

	$NO + H_2$ Products/mol %				$NO + CO$ Products/mol %		
Catalyst	a_{NO}/mol %	N_2O	N_2	NH_3	a_{NO}	N_2O	N_2
PcCo-Y	100	19	25	56	66	80	20
PcFe-Y	68	48	34	18	31	65	35
PcNi-Y	22	5	5	90	9	40	60
PcRu-Y	–	–	–	–	15	67	33
PcOs-Y	–	–	–	–	9	68	32

Co^{2+} and Fe^{2+} (d_{z^2}) are unfilled, enabling them to participate in substrate activation. In contrast, this AO for Ni^{2+} is fully occupied. On the other hand, different abilities of Co^{2+} and Fe^{2+} atoms for back-donation onto the antibonding π-MO of NO appear to account for their different catalytic behaviours. The low catalytic activity displayed by the Ru and Os complexes is obviously connected with their coordination state.

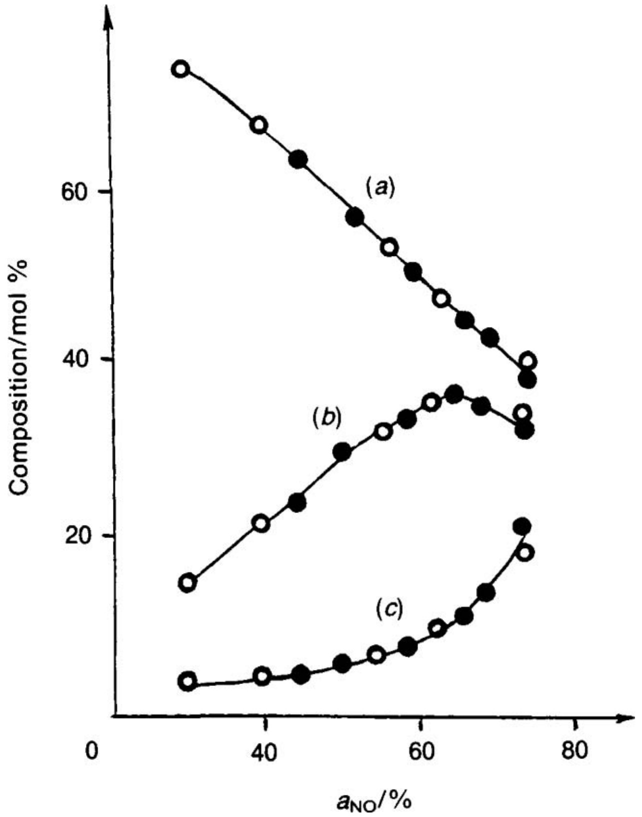

Fig. 3 Product composition in NO reduction by CO *vs.* conversion of NO over PcCo-Y: (●) temperature variation; (○) contact time variation; (*a*) NO, (*b*) N_2O, (*c*) N_2

The product compositions for the NO + CO reaction are shown in Fig. 3. The curves representing N_2O yield *vs.* total NO conversion have a pronounced maximum. Therefore one could suggest that the reduction of NO to N_2 proceeds *via* N_2O intermediates. Interestingly, the formation of N_2O as an intermediate in NO reduction by CO has been reported previously for metal and oxide catalysts where molecules of both N_2 and N_2O are likely to form *via* the dual-site mechanism. Nevertheless, it is apparent that the latter is not required for dinitrogen species formation, which can occur during NO reduction since the zeolite-included PcM complexes are dispersed in the matrix.

The zeolites, when hosting TM complexes, may be considered as true inclusion compounds where bulky species, generated *in situ*, are topologically included in the matrix cavities owing to pore diameter restrictions. On the other hand, this very feature of superfine channel system of zeolites explains their ability to concentrate harmful components from the gas phase. The behaviour of some zeolite-included TM chelates toward the catalytic oxidation of CO and reduction of NO provides evidence supporting the use of these inclusion compounds as prospective ecocatalysts.

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