Topological anchoring of metal complexes on zeolites

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The supporting of copper(II) benzoylacetonate on a NaY zeolite by means of 'anchor fragments' (derivatives of benzidine, benzophenone or anthraquinone) sterically retained within supercages of the crystal framework is reported.

The supporting of metal complexes on zeolites is of growing interest due to the catalytic properties the co-ordination compounds exhibit for a number of reactions.[1–4] Steric retention based on the difference between the sizes of the complex molecule and the entrance into the supercage of the zeolite crystal structure was shown[1] to be the most effective way of arranging this support. The topologically-encapsulated metal complexes operate as pseudohomogeneous catalysts owing to the molecular stochastic dispersion throughout the bulk of the crystallites. It is evident, however, that the introduction of metal complexes into the zeolite pores inhibits diffusion through the canals of the support. The catalytically-active metal centres appear to be screened by the zeolite lattice, *i.e.*, they become inaccessible for the substrate molecules which usually leads to an apparent decrease in the effective rate constant of the reaction.

This paper reports the supporting of copper(II) benzoylacetonate on the external surface of the NaY zeolite *via* anchor fragments providing a topological linkage between the chelate and the solid.

The problems connected with the zeolite sieve effect are surely complicated by introducing 'guest' molecules into the large cavities of the 'host' framework. The number of metal complex molecules actually operating as catalysts decreases drastically for those species which are localized in the 'inner' supercages, remote from the external surface of the crystallites.

Taking into consideration the fact that the 'external' metal complexes are those that actually operate as catalysts, this work reports the synthesis of samples in which, with the aim of eliminating the diffusion hindrances, the metal centres of the complexes are dragged out of the zeolite pores on to the external surface in contact with the bulk of the reaction medium. At the same time, this retains the topological cohesion with the support *via* a sterically hindered segment of the ligand.[5]

The same effect is known[6] to take place by supporting the metals by means of the branch functional groups of the solid. Polymer materials, silica gels and some oxides bearing surface OH groups are usually used as supports in these cases. However, there are no examples showing the use of the alkaline forms of zeolites for these aims. At the same time, based on their chemical and physico-mechanical properties, the crystal silica–alumina supports are in no way inferior to, but in fact exceed the polymers, silica gels and oxides in terms of swelling restriction in organic media, wetting, stability at elevated temperatures, and so on. Moreover, surface functionalization can lead to changes in the properties of the solid material.

Figure 1 shows schematically the mode of support of the metal complex **C** by means of the fragment **A** which plays the role of an anchor providing irreversible retention on the zeolite. The fragment **A** is evidently sterically entrapped by the supercage **B** of the NaY zeolite so that the external part of the catalyst molecule containing the metal centre is also supported on the solid.

The anchoring obviously becomes possible under the same conditions that are required for the steric retention. However, there is a significant difference between the steric retention and the topological anchoring.[5] Steric retention is known to be achieved for those species for which all dimensions exceed the effective diameter of the supercage entrance *b*. At the same time, such species which possess only one parameter which exceeds the value *b*, *i.e.*, possess pronounced non-spherical shape, are available for the topological anchoring. Thus, a linear-chain precursor can be used for the topological anchoring. The anchor precursor should consist of roughly cylinder-shaped particles with an effective base diameter a_1 less than that of the entrance into the NaY supercage and with the length a_2 more than the value *b*, *i.e.*, $a_1 < b < a_2$ (see Figure 1).

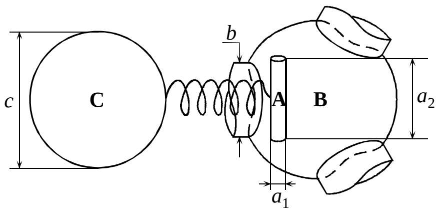


Figure 1 Topological anchoring of the complex **C** with effective diameter *c* in the NaY zeolite supercage **B** (effective diameter of the entrance is *b*) by means of the cylinder-shape anchor **A** (conventional dimensions are a_1 and a_2).

In order that a molecule can be the precursor for the anchoring of the metal complex by providing the topological linkage with the zeolite, the above conditions should be obeyed with one additional requirement. The precursor has to bear an appropriate functional group in the middle of the molecular chain to form a cross linkage with the ligand.

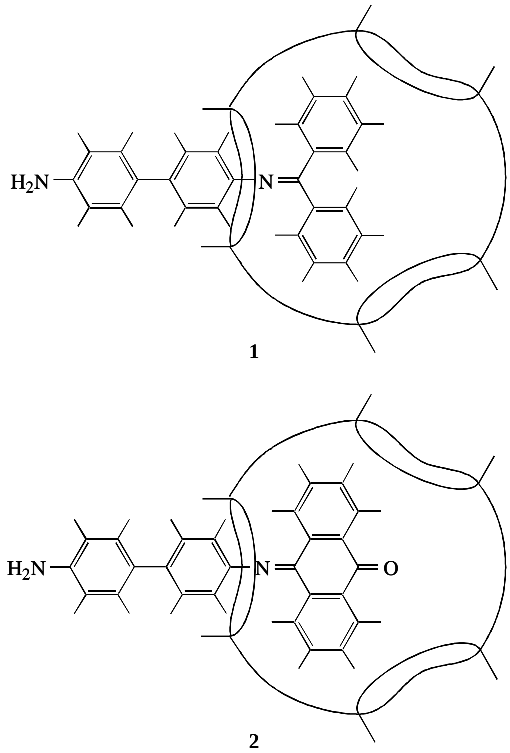
The molecules of benzophenone and anthraquinone clearly meet the above requirements. These compounds can penetrate the large cavities of the NaY zeolite owing to their asymmetric shape in the direction of their main axes. However, they are unable to leave the zeolite supercages by a route perpendicular to the same axis of the molecule.

After sorption on the zeolite, the precursor molecules located in the large cavities undergo reaction with benzidine to give the T-shaped products of condensation as shown in Scheme 1. Having been formed *in situ* the condensation products will become topologically retained within the supercages of the NaY zeolite owing to the rigidity of the benzidine molecule. They cannot be drawn out from the zeolite without destruction of the crystal network. For the same reason, the condensed T-shape derivatives also cannot be drawn into the zeolite void space more than by the depth of one supercage.

Thus, after being formed in the zeolite, the anchor compounds **1** and **2**[†] (see Scheme 1) seem to be irreversibly entrapped by the crystal lattice. As these compounds bear one functional group which is located aside the external surface of the crystallite, they can react with other substances. The amino group of benzidine susceptible to reaction is accessible for the reagents from solution or gas phases outside the zeolite.

The samples of NaY zeolite containing the anchor compounds

[†] 1 g of the NaY zeolite (SiO_2:Al_2O_3 = 4.1) calcined in air at 550 °C for 4–5 h was treated with benzophenone or anthraquinone vapour. Excess of a solution of benzidine in chloroform was added and the mixtures were refluxed for 30–40 min. The samples were extracted with warm chloroform followed by removal of excess solvent *in vacuo* at 50–60 °C. The products were identified by IR-spectroscopy and elemental analysis.



1

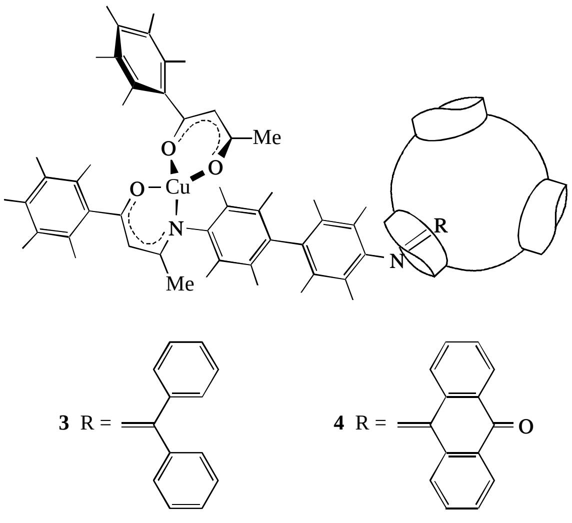
2

Scheme 1

1 and **2** were extracted with chloroform to remove unreacted substances and were treated with a solution of copper(II) benzoylacetonate. The resulting samples formulated as **3** and **4**[‡] (see Scheme 2), respectively, do not lose colour after subsequent extraction with the solvent. This observation provides indirect but important evidence in favour of the irreversible support of the copper(II) chelate molecules on the zeolite. Indeed, the molecules of copper(II) benzoylacetonate are too large to enter into the supercages of the NaY zeolite and, therefore, could be adsorbed only on the external surface of the crystallites. If this were the case, the subsequent extraction with boiling solvent would result in total removal of the sorbate from the zeolite. On the contrary, if the copper(II) chelates do react with functional NH_2 groups, the metal centres are chemically fixed and the metal complexes remain on the support even after solvent extraction.

Thus, the samples **3** and **4** containing the resulting complexes anchored by the fragment of benzidine appear to be topologically supported on the NaY zeolite. According to the SEM data, the external surface concentration of copper(II) is quite comparable with the amount of precursor adsorbed on the zeolite, which is indicative that the condensation of benzophenone or anthraquinone with benzidine takes place more rapidly than desorption from the zeolite.

It should be noted that the topological anchoring of the metal complexes on porous supports reveals pronounced advantages in comparison with the intracrystalline synthesis. The catalytically-active centres are not hidden within the silica–alumina skeleton but are localized in the phase in contact with the zeolite. They are therefore accessible to any substrate from the side of the reaction medium independently of its shape and dimensions. This method of support eliminates the influence of the intrapellet diffusion gradients which results in an increase in the observed rate constant. Moreover, the topological anchoring allows support of complexes of various shapes and sizes which cannot be geometrically situated at all in the supercages of the zeolite.



Scheme 2

According to the diffuse reflectance spectra for **3** and **4**, the nature of the anchor fragment of the ligand hidden in the zeolite framework is not reflected on *d–d* transitions of the copper(II) complex and, therefore, does not affect the chelate catalytic activity.[7] This enables us to use different precursors with respect to the character and features of the zeolite without undesirable changes in the catalytic properties of the coordination compound.

The matrix synthesis of metal complexes is known to be hindered in the presence of solvent molecules which compete for the adsorption sites in the large cavities of the zeolite. In the case of topological anchoring, the filling of supercages with the solvent molecules surprisingly favours the retention of the anchor segment by the solid and, at the same time, does not inhibit the reaction between the metal complex and the amino group on the external surface of the zeolite crystallites. This feature permits the reaction between the metal complex and the zeolite-encapsulated anchor to proceed in solution rather than *in vacuo*.

Thus, topological anchoring provides for the development of zeolite-supported systems and allows an expansion of the application of chelate metal complexes to the solution of catalytic problems.

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Received: Moscow, 24th December 1997
Cambridge, 9th March 1998; Com. 8/00166I

[‡] The samples **1** and **2** were treated with excess solutions of copper(II) benzoylacetonate under reflux in ethanol for 1 h. The resulting products **3** and **4**, respectively, were loaded into an extractor for removal of excess reagents and unreacted substances with warm ethanol. The excess of the solvent was then removed *in vacuo* at 70 °C. The samples **3** and **4** were characterized by elemental analysis and SEM, and FTIR-spectroscopy.