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Complexes of Transition Metals in Zeolites. Activation of Hydrogenation Functions of Phthalocyanine Fe^{II} Complexes by Zeolites

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The liquid-phase hydrogenation of toluene by dihydrogen in the presence of zeolite-included Fe^{II} phthalocyanine has been studied, (effective energy of activation and pre-exponential factor 28 ± 2 kJ mol^{-1} and 10.3×10^5 g mol^{-1} s^{-1}, respectively) and it has been suggested that the zeolite matrix takes part in the activation of the substrate *via* hydrogen bonding with inner atoms of the large cavity of the zeolite.

It has been reported previously that transition metal complexes of phthalocyanine (MPc) are efficient catalysts for a number of redox systems.[1] They are utilised in gas-phase processes owing to their great stability at high temperatures. However, the catalytic behaviour of MPc in the liquid phase is also of interest. These complexes are known to have limited solubility in the usual solvents, so catalysts supported on a NaY zeolite were prepared by matrix synthesis.[2]

This paper reports on the study of the catalytic properties of Fe^{II} phthalocyanine complexes, topologically included in a zeolite-Y lattice, in the liquid-phase hydrogenation of toluene by molecular hydrogen.

The localization of topologically fixed MPc complexes in zeolites is crucial to their role as inert supports. The introduction of a potential catalyst into the zeolite matrix leads to activation of the catalytic function, which is not realized in homogeneous liquid-phase processes.

Included Fe^{II}Pc (FePc/NaY) was synthesized *in situ* as described previously[3] from Cp_2Fe (Cp = cyclopentadienyl), preadsorbed on NaY zeolite, and phthalonitrile. The reduction of toluene was monitored volumetrically under static conditions by the uptake of H_2 in a glass thermostatted reactor. The products were analysed by GC (Separon column, 3 m × 4 mm i.d., 100 °C).

The molecules of FePc, irreversibly fixed within the zeolite framework, exhibit no covalent interaction with the lattice atoms. After their formation in the large cavities of the zeolite they cannot leave the framework because of steric retention. Nevertheless, co-ordinatively unsaturated Fe atoms of FePc can act as sites for preferential adsorption of toluene or benzene via their π-electron systems.

Our data shows that liquid-phase hydrogenation of aromatic bonds is not activated by either the NaY zeolite or by FePc itself at 30–70 °C. Even in the presence of both FePc and NaY zeolite no catalytic effect is produced in the system.

On the other hand, a sample of zeolite-included FePc shows remarkable catalytic activity in the liquid-phase hydrogenation of toluene with molecular hydrogen. The consumption of H_2 by toluene at different temperatures is shown in Fig. 1. The only product detected of the reduction of toluene was methylcyclohexane. The observed rate of H_2 uptake (W_0) by toluene is linearly dependent upon the mass of the sample of FePc/NaY at constant concentration of the complex [Fig. 2(*a*)] or upon the absolute content of FePc in a sample with constant mass [Fig. 2(*b*)]. These data are consistent with pseudo first-order kinetics for FePc content in the sample and support the suggestion that all molecules of the complex take part in catalysis. Hence, in this case a pseudo-homogeneous regime is realized.

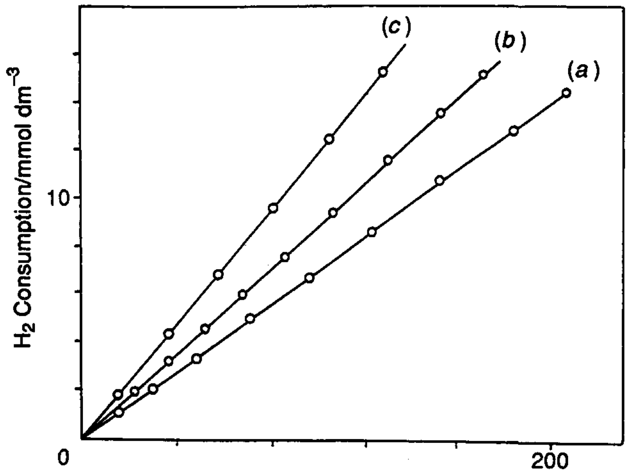

Fig. 1 Consumption of dihydrogen by toluene as a function of time in the presence of 0.025 g of FePc/NaY (0.5 mass % of Fe) at 40(*a*), 50(*b*) and 60 °C (*c*) under total pressure 100 kPa

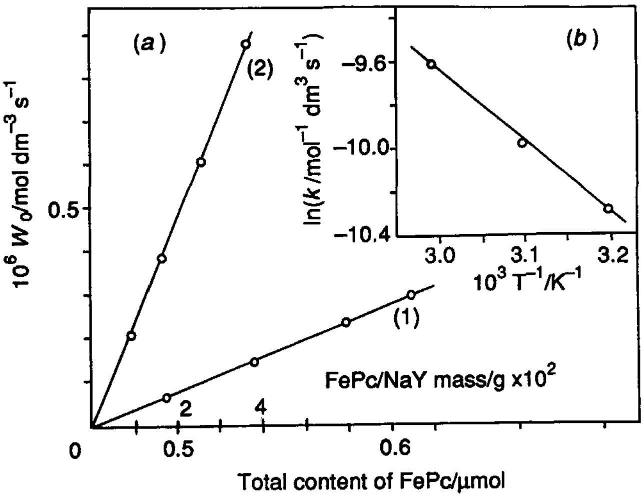

Fig. 2 Dependence of hydrogenation rate of toluene (*a*) upon mass of sample of FePc/-NaY (0.5 mass % of Fe) (1) and upon total content of FePc (in μmol) within NaY zeolite (2) (0.042 g) at 40 °C and total pressure 100 kPa and (*b*) a plot of ln *k vs.* 10^3 T^{-1}

The initial rate of hydrogenation of toluene in the presence of FePc/NaY appears to follow a second-order kinetic law overall, according to eqn. (1),

$$W_0 = k[\mathrm{FePc}]P_{H_2} \qquad (1)$$

where k = observed rate constant, [FePc] = absolute content of complex in sample and P_{H_2} = partial pressure of H_2 in the gas phase. The activation energy and pre-exponential factor used to determine the rate constant for toluene hydrogenation were 28 ± 2 kJ mol^{-1} and 10.3×10^5 g mol^{-1} s^{-1} respectively.

It should be noted that no reaction takes place when benzene is used as a substrate. This indicates the different behaviour of benzene and toluene for hydrogenation. Thus, the activation effect of the zeolite matrix for reduction with molecular hydrogen applies only for toluene.

It is unlikely that the activation effect is of an energetic nature since the enthalpies of formation of methylcyclohexane and cyclohexane (401.7 and 407.9 kJ mol^{-1} respectively[4]) are very similar. This conclusion is supported by the negligible catalytic effect observed for these reactions in the presence of FePc adsorbed on the outer surface of NaY zeolite from solution in dimethylformamide (DMF). The activation of the hydrogenation function of the zeolite lattice probably results from the specificity of fixation of the complex as a result of the

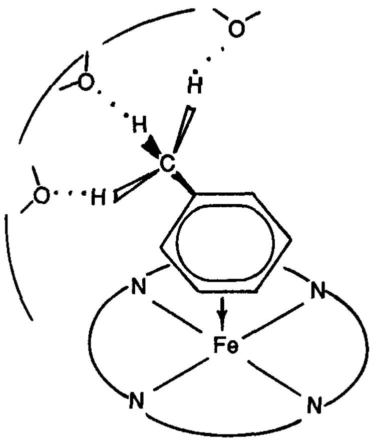

Fig. 3 Possible mode of toluene coordination in a large cavity of a zeolite containing included FePc

template synthesis. This is suggested by the very low value of the effective energy of activation for the hydrogenation.

On the other hand, the non-energetic nature of the self-activation of the catalyst for related reactions with similar enthalpies may be attributed to the influence of stereochemical factors operating when a molecule of the complex is placed in the spherical force field of a zeolite cavity.

The topological retention of a molecule of FePc determines its only possible mode of localization in the zeolite supercage as shown in Fig. 3. A molecule of substrate within the crystal localized in the vicinity of an active FePc centre may be influenced by the unsaturated Fe atom and the force field of the inner atoms of the spherical surface of the large cavity. The multi-centred nature of coordination of the substrate molecule *via* a coordinatively unsaturated Fe atom and donor atoms of the internal spherical surface of the cavity appears to be dominated by competition for the adsorbate. In this respect the H-bonding is likely to be favourable for toluene through the H atoms of the methyl group. The benzene molecule has no substituent and, stereochemically, is less available for H-bonding with the donor atoms of the framework. In this context, the benzene molecule is obviously being attacked by the hydrogenating agent in a less favourable stereochemical arrangement than toluene. The lower rate of hydrogenation for benzene appears to be a result of a decrease in the entropy factor of the observed rate constant. Furthermore, by multi-centred coordination topology the aromatic system of toluene is distorted according to the Rice–Teller principle of minimal rearrangement in the transition state.[5]

According to Kobozev[6] recuperation and transfer of the energy of a reaction to a catalytic centre occurs in biological systems by means of a matrix. However, for the hydrogenation of benzene and toluene the zeolite matrix can play another role which depends on its specific influence on the coordinated substrate *via* the cooperative effects of the catalyst and the zeolite.

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