

CATALYSIS BY ZEOLITE INCLUSION COMPOUNDS

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ABSTRACT

Zeolite-included transition metal complexes constitute a new type of catalysts which offer advantages of both heterogeneous and homogeneous catalytic systems. Main features of intracrystalline synthesis of zeolite inclusion compound as well as their characterization and catalytic properties are discussed.

INTRODUCTION

Zeolite molecular sieves seem to be almost ideal matrices in designing of guest-host catalytic systems. The synthesis of catalytically active species inside the zeolite cavities that might be carried out on molecular scale is of great interest not only for heterogeneous catalysis but also for enzyme modelling. In this context, the complexes of transition metals (TMC) with organic macroligands appear to be of particular interest since they have much in common with biological catalysts.

However, the TMC's with these ligands can be hardly introduced into zeolite pore system by conventional ion-exchange or adsorption procedures. Therefore, only two ways to prepare the inclusion compounds of the type could be used, i.e., (1) capture of the TMC's during liquid phase synthesis of zeolite crystals (ref.1) and (2) in situ synthesis of TMC's inside cavities of zeolite crystals (ref. 2). The first method is obvious to be limited by solubilities of TMC's. The second way of including the TMC's into zeolite host lattices and physico-chemical properties of systems so prepared are surveyed in present paper.

INTRACRYSTALLINE IN SITU SYNTHESIS OF ZEOLITE-INCLUDED TMC's

The framework charge-compensating cations in zeolites are known to have unsaturated coordination geometry and so they can add some more molecules or ions as ligands. Such complexing occurs un-

less the dimensions of entering potential ligands exceed those of zeolite openings. If so, then treatment of corresponding cationic form of zeolite with appropriate complexing agent could result in a formation of TMC's inside zeolitic cavities. By such a way, the complexes of a variety of TM cations with various amines, dipyridil, dimethylglyoxime and acetylacetone included into zeolite matrices were obtained (ref.3-6).

Meanwhile, it should be noted that the TMC's mentioned are complex cations and consequently are held electrostatically within zeolite cavities. If it is the case, then the zeolite framework plays a role of macroanion to ensure zero charge of a lattice as a whole. Thus, these systems with complex cations are thought to be hardly referred as inclusion compounds, and this term seems to be more proper for neutral molecules captured or in situ formed within zeolite cages. If molecular dimension of such a guest are greater than free diameter of zeolite channels, then the molecule turns out to be entrapped inside the cavity, and it is held there rather topologically.

A few examples of neutral guest molecules included into zeolite host lattices are metal carbonyl clusters, Schiff bases, and transition metal phthalocyanines. These latter were synthesized firstly by us (ref.7) and later by Schulz-Ekloff et al.(ref.8). In what follows, the phthalocyanine complexes of transition metals (PcM) are discussed in details.

The planar molecule of PcM is very stable due to a conjugating of 18 electrons in ligand macrocycle. Its dimension is c.a. 1.4 nm as calculated from X-ray data for the crystalline PoM. The Pc complexes may be obtained from both transition metal salts and pure metals as starting materials by treating the first or the second with phthalonitrile. Therefore, their inclusion into zeolites can be carried out by any of following routes: (1) via transition metal cationic forms of a zeolite, and (2) via zero-valent metal containing zeolite. The (3) possible way should be mentioned: via adsorbed volatile carbonyl complexes in which the labile CO ligands would be readily replaced by far more stronger ones, i.e., the phthalonitriles. All these three synthesis of zeolite-included PcM's were carried out by author and co-workers (refs.7,9-11).

Method 1 (refs.7,11). The Co, Ni, Cu, and Ru cationic forms of Y zeolite were placed into one compartment of two-chamber ampoule, another one was loaded with solid phthalonitrile (c.a. 20% in excess)

After evacuation of zeolite at 300-350°C up to 10^{-2} Pa, the ampoule was sealed, and both compartments were heated at 200-300°C for 25-40 hr (depending on the type of metal). After completion of synthesis, excess of phthalonitrile was removed by warm acetone washings. In addition, non-complexed transition metal ions were re-exchanged with NaCl solution.

Method 2 (ref.9). After thorough evacuation of Na form of Y zeolite at 300°C up to 10^{-4} Pa, vapours of $\text{Fe}(\text{CO})_5$ were allowed to adsorb at 20°C onto the zeolite, the amount of carbonyl adsorbed being c.a. one molecule of $\text{Fe}(\text{CO})_5$ per supercage. Then the zeolite with preadsorbed carbonyl was heated in dry He flow up to 400°C, the CO product releasing being monitored by a catharometer unit. As it was earlier shown by Jacobs et al. (ref.12), under these conditions the adsorbed iron pentacarbonyl transforms quantitatively into metallic iron. Then iron-containing sample was transferred in dry He into one compartment of two-chamber ampoule, and the synthesis of PcFe was carried out at 300°C for 40 hr as described above.

Method 3 (ref.10). On investigating the decomposition of adsorbed $\text{Fe}(\text{CO})_5$ within zeolite by temperature-programmed reaction method, we observed that the release of first carbonyl ligands occurs at temperatures 100-150°C lower than that of intracrystalline synthesis of PcM 's by methods 1 and 2. The phthalonitrile vapour pressures at these temperatures were, meanwhile, great enough to ensure a reasonable rate of substitution of carbonyl ligands for phthalonitrile ones. Keeping this in mind, we adsorbed Fe or Ni carbonyls onto degassed NaY zeolite (two-chamber ampoule) and heated the sample at 70-115°C for 15-50 hr in phthalonitrile vapours.

All the preparations thus obtained were greenish-blue in color.

CHARACTERIZATION OF IN SITU SYNTHESIZED TMC'S

It is obvious that on obtaining the included guest moiety via intracrystalline synthesis, a problem of its identification turns out to be of crucial importance. In the case of zeolite host lattice, the extraction of guest species encapsulated in cavities for subsequent routine identification (e.g., by spectral techniques) is evident to be impossible unless the host lattice were destroyed. Fortunately, when the PcM 's are zeolite-included compounds, there is rather unique solvent, i.e., concentrated sulphuric acid which destroys readily the zeolite matrix but only dissolves phthalocyanine component of a cata-

lyst. This method was successfully applied in (refs.8,9) to identify the in situ formed Pc complexes of Fe, Co, Ni, and Cu within zeolites X and Y.

Of course, there were numerous attempts of included TMC identification using spectral (UV, VIS, ESR, ESCA etc.) methods in non-destructive mode, i.e., analysing the guest-host systems as a whole. In some particular cases, identification of in situ formed species as inclusion compounds was well definitive. However, due to the fact that these techniques, in general, do not distinguish between TMC's inside host framework and on external surface of a matrix, the proper assignment of spectral bands appears to be somewhat ambiguous.

DISTRIBUTION OF TMC'S IN MATRIX

The problem of the distribution of TMC's between outer surface of zeolite crystallites and their intracrystalline volume is of obvious importance. Indeed, the trend of zeolite exchange cations as well as of metal atoms to migrate onto external surface and to aggregate there is known to be well pronounced. If so, then it would be quite reasonable to assume that complexing agents might facilitate an extraction of metals from zeolite bulk onto its surface and, then, form TMC's on this surface. In this respect, some information can be drawn from our results (ref.11) on ESCA and chemical analysis estimations of transition metal concentration in cationic forms as well as in PcM containing samples of Y zeolites. These data are given in Fig.1. It may be seen that as a rule there is no enrichment of zeolite surface with transition metals when it was treated in phthalonitrile vapours to form Pc complexes (except for one low Ni concentration sample). Here the in situ synthesis via cationic forms of zeolite was used. The same results were obtained also with PcFe/NaY samples which were synthesized via iron carbonyl complexes (refs.9, 10). In this latter case, double extraction, i.e., firstly, with DMFA solvent which dissolves the surface TCM's only and then with H_2SO_4 was used to determine the "outer" and the "inner" phthalocyanines.

It should be mentioned that our conclusions made on the basis of the data just described are not in line with those of Schulz-Ekloff et al. (ref.8) who found only a few percent of zeolite-encaged PcM's as compared to total PcM contents in X and Y zeolites. Although it is not yet fully understood, this difference could be due to a concentration effect of phthalonitrile reactant during a synthesis.

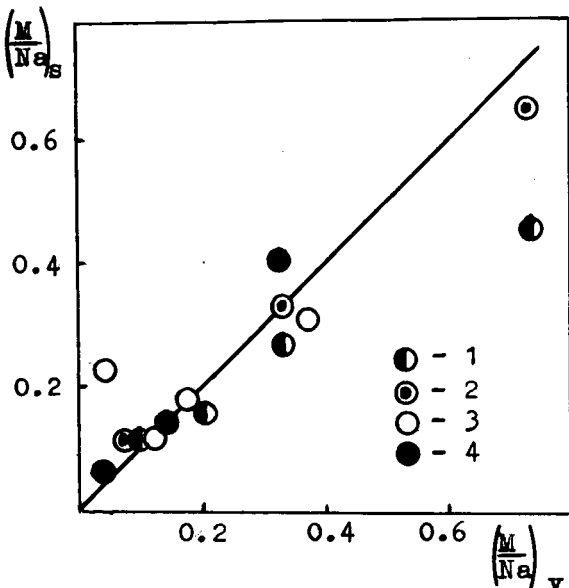


Fig.1. Correlation between relative M to Na concentrations on surface (s) and in volume (v): 1 - NiY, 2 - CoY, 3 - PcNi/NaY, 4 - PcCo/NaY.

contents (M = Cu, Co, and Ni). From all these results, we suggested that the PcM guest molecules do form inside the zeolite host lattice. Thus, these systems could be regarded as a new family of inclusion compounds.

CATALYSIS BY ZEOLITE INCLUSION COMPOUNDS

Zeolite-included TMC's are rather unique heterogeneous catalytic systems with no disadvantages of common catalysts. First of all, there is no question as to what is an active moiety of a catalyst since the nature of it is well known in advance. Moreover, even a concentration of virtually active species in catalysts could be calculated before catalytic experiment and what is far more substantial independently of it. These advantages offered by heterogenized TMC's would expect to be very useful in solving many important problems of theoretical and practical catalysis.

However, on heterogenizing the TMC's two questions arise, i.e., (1) whether they retain the peculiarities characteristic of their homogeneous analogs, and (2) if so, then how do environmental aspects of a matrix influence the TMC molecules as active centers of

A substantial excess of complexing agent (up to two-fold) was applied in (ref.8), the phthalonitrile and zeolite being thoroughly mixed before synthesis. In contrast, we used separate compartments of a reaction vessel to place the reactants as it was described above and thereby the formation of PcM's inside supercages would be favoured by higher concentration of complexing agent within the cavities than at outer surface. In addition, consistent with the notion of preferential formation of the PcM's inside zeolitic supercages is our observation that the adsorption capacities of PcM/NaY samples toward H₂O, O₂, N₂, and CO are linear functions of total PcM

catalyst?

For many cases of heterogenized TMC's investigated up to now, the first question could be answered rather positively. In fact, these systems were shown to catalize, for example, H_2O_2 decomposition (ref.3), oxidation of various substrate by molecular O_2 (refs.4, 5, 13), hydrogenation and dehydrogenation (refs.5, 13), dehydration (ref.5), dehydrothiolation (ref.13), hydroformylation (ref.14) etc. which have been well known for homogeneous TMC catalysts.

As to zeolite-included TMC's, they appear to behave very similarly to their analogs in solutions. In particular, they exhibit the most characteristic and important feature of complex catalysts that is the drastic dependence of activity and selectivity on the nature of ligand environment (ref.3). For example, as it was shown in (ref. 5), in cyclohexene epoxide conversion using various zeolite-included chelate of Cu as catalysts the selectivity patterns were strikingly inverse with different ligands, namely, when reacted on PcCu/NaY, the epoxide yields 100% of cyclohexadiene whereas on enCu/NaY (en = ethylenediamine ligand) it forms benzene only.

Fig.2 shows the data obtained for liquid phase oxidation of cystein by molecular O_2 catalyzed by PcCo/NaY (ref.13). The bell -

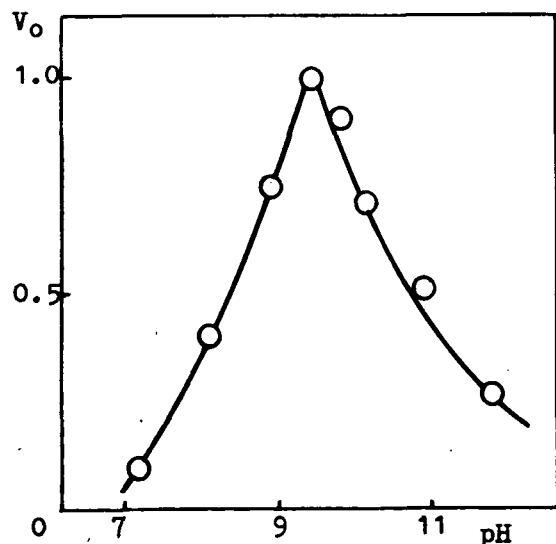


Fig.2. pH dependence of initial rate (arb.units) of cystein oxidation in solution on PcCo/NaY catalyst at $20^\circ C$.

shaped dependence of the reaction rate on pH value of solution which zeolite-included PcCo exhibits is also typical for homogeneous catalysis by transition metal complexes.

Similarly, the pyridine base preadsorbed on the PcM's in zeolite matrices was shown to enhance the ability of metallic centers to fix molecular O_2 as well as their activities in CO oxidation, dehydrogenation of cyclohexane and isopropanol (ref.5).

The most probable explanation for these observations is that Py molecule situated trans to a substrate species may exert a considerable influence on

the reactivity of latter.

It is noteworthy that the very fact of enhancing influence of preadsorbed Py on the zeolite-included TMC's provides good evidence of molecular or near-molecular dispersity of these in matrix. One should recall that the trans effect is a characteristic feature of homogeneous catalysis by transition metal complexes in solutions.

Finally, even the turn-over numbers (TN) found for supported and not-supported PCM's do not differ substantially as it is seen from the following data:

TN ^a in oxidation by molecular O ₂ of cystein ^b of carbon monox. ^c	Individual PcCo	Supported PcCo/NaY
	7.7	20.7
	2.8	8.4

a: arbitrary units; b: (ref.13); c: (ref.5).

On the other hand, one might expect that molecular sieve properties of zeolite host lattice could be accounted for some peculiarities of guest species as catalytically active centers. Thus, in liquid phase hydrogenation of olefins using the zeolite-encapsulated Rh complexes as catalyst, rather "anomalous" sequence of reactivities was found (ref.15), i.e., 1-butene > 1-hexene > 1-octene. This series is different from that obtained with SiO₂ matrix where the reaction rates were comparable for the olefins.

At all probabilities, this is due to the strong spatial restrictions imposed by zeolite framework on molecules of olefin entering pores, or of intermediate forming within cavities, or of product leaving supercages.

Another example of specific influence of surroundings on the zeolite-encapsulated TMC's is provided by our findings that the high adsorption potential inside supercages where the complexes reside could promote reagent concentrations and hence higher reaction rates. This effect seems to account for negative temperature coefficient below 0°C of reaction rate in CO oxidation by molecular O₂ on PCM/NaY catalysts (ref.5) as well as for 3-fold increase in TN's on going from individual PCM to included one.

CONCLUSION

The synthesis and the study of zeolite-included guest molecules is a relatively new area of zeolite catalysis. But it is every ground to say that these systems as already outlined could be very promising in the molecular level designing of active centers within

solid matrices and thereby in the building-up of catalysts with foreseen functions. Of course, from a practical viewpoint, there are a number of questions to answer, e.g., the way in which an activity of the TMC's is governed by the environment of the species included what is not yet clear and the diffusional phenomena etc.

REFERENCES

1. Weisz P.B., Frillette V.J., Maatman R.W., Mover E.B., *J.Catal.* 1, 307 (1962).
2. Klier K., Ralek M.J., *J.Phys.Chem.Solids*, 29, 951 (1968).
3. Mochida J., Takeshita K., *J.Phys.Chem.*, 76, 1653 (1974).
4. Howe R.F., Lunsford J.H., *J.Am.Chem.Soc.*, 97, 5156 (1975).
5. Zakharov V.Yu., Cand.Diss., Moscow Univ., 1978.
6. Winskorn J.C., Lubitz W., Diegruber H., Möseler R., In *Metal Microstructures in Zeolites*. Stud. in Surf. and Catal., Elsevier Sci. Publ.Co., Amsterdam, 1982, p.15.
7. Zakharov V.Yu., Romanovsky B.V., *Vestn.Mosk.Univ., Ser.Khim.*, 20, 94 (1979).
8. Meyer G., Wöhrle D., Mohl M., Schulz-Ekloff G., *Zeolites*, 4, 80 (1984).
9. Korol'kova T.V., Zakharov A.N., Romanovsky B.V., *Vestn.Mosk.Univ., Ser.Khim.*, 25, 362 (1984).
10. Zakharov A.N., Romanovsky B.V., *J.Incl.Phcn.*, in press.
11. Gudkov S.V., Romanovsky B.V., Shpiro Ye.S., Antoshin G.V. Minachev Kh.M., *Izv.Akad.Nauk SSSR, Ser.Khim.*, 2448 (1980).
12. Bein Th., Jacobs P.A., Schmidt F., In *Metal Microstructures in Zeolites*. Stu. in Surf. and Catal., Elsevier Sci. Publ.Co., Amsterdam, 1982, p.111.
13. Zakharova O.M., Cand.Diss., Moscow Univ., 1982.
14. Céntola P., Terzaghi G., Del Rosso R., Pasquon I., *Chim.Ind.(Milano)*, 54, 775 (1972).
15. Huang Tai.Nang, Schwartz J., *J.Am.Chem.Soc.*, 104, 5244 (1982).