

ASPECTS OF METAL AND METAL COMPLEX CONTAINING ZEOLITES

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ABSTRACT

Unambiguous informations on the location and structure of metal particles exceeding super cage size in faujasite matrices are summarized. Current ideas on the possible nucleation and growth mechanisms are presented. The structures of encaged chelates are illustrated by means of the examples nickel dimethylglyoxime and cobalt phthalocyanine with regard to requirements and expectations for the catalytic activity of zeolite encapsulated metal complexes. Established applications, prospective uses and promising reactions of metal-containing zeolites in catalysis are regarded exemplarily.

METAL PHASES WITHIN THE ZEOLITE MATRIX

Zeolites, namely X and Y type faujasites are suitable supports for the preparation of well defined monodispersed metal phases, i.e. metal phases located exclusively within the framework of the faujasite matrix.

Narrow particle size distributions can be achieved due to the restrictions imposed by the zeolite channels and cages on the growth of the metal agglomerates. In most cases monodispersed metal phases are found within the supercages [1-6] and a number of excellent tools have been developed and adapted for the study of the physical properties of such highly dispersed metals, of their location and of their interactions with the zeolite support and with suitable probe molecules.

The location of charged clusters of silver atoms [7,8] and of Pd atoms [9,10] on the lattice sites in Y zeolites has been determined from single crystal and powder X-ray diffraction data. Fraissard et al. [11-13] applied the nuclear magnetic resonance of adsorbed Xe to the investigation of Pt dispersions and demonstrated the capability of the method to detect Pt particles consisting of fewer than 10 atoms within the supercages of Y zeolites. Small angle X-ray scattering (SAXS) has been used to determine the size distributions of Pt crystallites in Y zeolites [14,15] and impressive results could be obtained from evaluating the radial electron

distribution from X-ray diffraction data, e.g. the changes of interatomic distances in 1 nm Pt particles supported in Y zeolites upon the adsorption of molecules [14, 16, 17]. Mössbauer spectroscopy in combination with measurements of the spontaneous magnetization has been successfully applied to characterize small iron clusters supported in zeolite A [18,19] and to rule out electron transfer from the metal to the support in this case. Electron deficiency has been observed in other cases, e.g. Pd [9] and Pt [20,21]. This is important information with regard to the role of particle size effects in catalysis. The application of static magnetic methods and of ferromagnetic resonance is restricted to ferromagnetic metals and has been applied especially in the case of Ni-loaded zeolites in order to evaluate the size distribution of the metal particles [22-26]. Curve fitting and the interference of Ni^{2+} -ions in partially reduced samples, however, require the application of complementary methods for reliable interpretations of the experimental data. Direct observation of metal agglomerates of and beyond supercage dimension by electron microscopy is the method suited best to determine size, location and distribution of metal agglomerates supported by zeolites. The existence of 2 nm Pd and Pt particles in Y zeolites was demonstrated by this technique [27,28]. In modern electron microscopes the power of the electron beam can be reduced to a point where modifications of the particle size due to overheating the substrate can be avoided [29].

Recently, metal phases with crystallite sizes by far exceeding supercage dimensions were found to exist within a faujasite X framework for a number of metals, namely Pt [30] , Ru [31-33] , Pd [5,34] and Ni [23,35]. Particle sizes ranging from 3 nm for Pd [5] up to 10 nm for Pt and Pd [34,36] and even 15 nm in the case of Ni [37] were determined mainly by electron microscopy. The location inside the zeolite matrix has been confirmed by XPS measurements [38]. It was shown by electron diffraction from selected areas and single particles in the case of Pd, Pt and Ni [34,36,37] that such aggregates are single crystals. Phase contrast imaging and electron diffraction patterns of the zeolite lattice revealed that the structure of the host lattice is maintained in the neighborhood of the metal crystallites. It was proposed that the growth mechanism of the metal single crystals involves atomic rearrangements of the zeolite lattice in analogy to the process of steam stabilization [37]. A variation of the particle size with the Si/Al ratio of the support can be anticipated. The recrystallization of the zeolite lattice during the growth of the metal phase could be inferred from an increase in the temperature of the lattice breakdown and an increase of the N_2 physisorption capacities [36].

The monodispersed metal phases with narrow particle size distributions could be achieved for Ni as well as for Pd and Pt even though the reduction of ion-exchanged samples follows quite different paths. In the case of Ni the dehydrated ion-exchanged samples were reduced by hydrogen, while Pd and Pt metal phases were

formed by autoreduction of the respective exchanged tetrammine complexes in the course of the dehydration process [39,40].

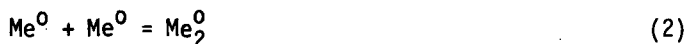
Nucleation in the latter cases must be restricted to the supercages where the big tetrammine complexes are located following the ion-exchange. In the case of platinum a preferred orientation relationship $\langle 100 \rangle_{Pt} // \langle 100 \rangle_{zeolite}$ has been observed [36]. Relatively high metal loadings were required for these investigations. The existence of a preferred orientation of the Pt crystallites can be explained by assuming an orientated growth of the fcc platinum within the cubic faujasite structure starting from an orientation imposed by the geometry of the supercage on the growing nucleus.

The observed orientation of the platinum crystals can in turn be taken as additional proof that the metal crystals must have been grown in an intact zeolite matrix and not in a priori voids formed under steaming conditions, as is stated repeatedly [41]. Nucleation and growth of the metal phases from atomic dispersions of the reduced metal or from preformed clusters seem to be the decisive steps. According to the theory of nucleation [42] nuclei of critical radius r_c are formed at a rate

$$J = B \cdot \exp(-\Delta G_c / kT) \quad (1)$$

per unit volume. The free enthalpy of formation ΔG_c of a nucleus of critical size is proportional to $1/(\Delta\mu)^2$. The super saturation $\Delta\mu$ is assumed to be high at least in the case of noble metals under the experimental conditions used in the preparation of the metal phases. In heterogeneous nucleation B is proportional to the coefficient of surface diffusion of single adatoms and to their density on the surface.

According to Wynblatt [43] no barrier exists for the nucleation of 3-dimensional Pt clusters on the surface of an Al_2O_3 substrate. The formation of metal phases preferentially or even exclusively inside the zeolite matrix indicates that a similar favourable situation for the formation of nuclei should exist within the channels and cages of the zeolite. The zeolite lattice offers a number of singular points, where an existing potential barrier for the formation of a critical nucleus could be lowered or where metal atoms could be trapped. Such centers are non-reducible cations, where the agglomeration of metal atoms results in a reduction of the electrostatic energy. Finer dispersions of the metal phase are often observed if non-reducible transition metal ions, e.g. Cr^{3+} [44], Fe^{3+} [45], Ce^{3+} [6] are present in the zeolite framework during the reduction process, operating as preferred nucleation sites. Other centers for nucleation are ions not yet reduced and available for the formation of charged clusters. Nucleation results from the collision of migrating adatoms and of the two alternatives



the initiating step (3) should be favoured.

The free enthalpy of nucleation will be less for charged as compared to uncharged nuclei. The difference in the free enthalpies of nucleation corresponds to the difference in the enthalpies of formation for the two nuclei. The enthalpy of formation for nucleation step (3) will roughly correspond to the difference of the first and the n th ionization potential, i.e. 5-15 eV for $n = 2$. The formation enthalpy for process (2) will be close to the evaporation enthalpy, i.e. 2-7 eV and is thus smaller.

The nucleation process should therefore be promoted by a high density of transition metal ions populating the migration paths of the metal atoms as collision partners. A nucleus Me_2^{n+} , stabilized in the zeolite framework by electrostatic forces can grow by further collision with Me^0 forming charged clusters, which have been observed in the case of silver exchanged zeolites [46].

In case a barrier of nucleation does not exist [43] singular points will still act as centers for nucleation. The rate of nucleation, however, will not be affected by the exponential term in equation 1. The number of nuclei formed will be proportional to the number of centers and to the number of metal atoms. A high density of nucleation centers exists in calcined platinum exchanged faujasites [5] and a high density of metal atoms can be expected in calcined Ni exchanged faujasites undergoing reduction with atomic hydrogen [47]. High dispersities of the metal within the zeolite matrix were obtained as a consequence. The generally observed bi-dispersities in the case of Ni-loaded faujasites, i.e. large fractions of reduced nickel at the outer surface and another fraction of smaller aggregates inside the zeolite crystal could be due to a relatively low ion density in the migration path of Ni^0 and a small density of metal atoms due to a low rate of reduction.

In the case of the autoreductive decomposition of Pd-tetrammine complexes within a faujasite X an almost linear correlation between the degree of ion exchange and the number of Pd crystallites formed has been established from the evaluation of a large number of electron micrographs (Table 1) [48].

Table 1: Number of Pd crystallites within a faujasite X matrix in dependence on the degree of ion-exchange

Pd content wt%	mean diameter of Pd crystallites (nm)	number of Pd crystallites per g catalyst $\times 10^{-16}$
14,7	10	2,34
4,4	10	0,71
2,4	10	0,38

Under constant experimental conditions the density of metal atoms should be proportional to the degree of ion exchange, determining the rate of nucleation rather than the rate of growth.

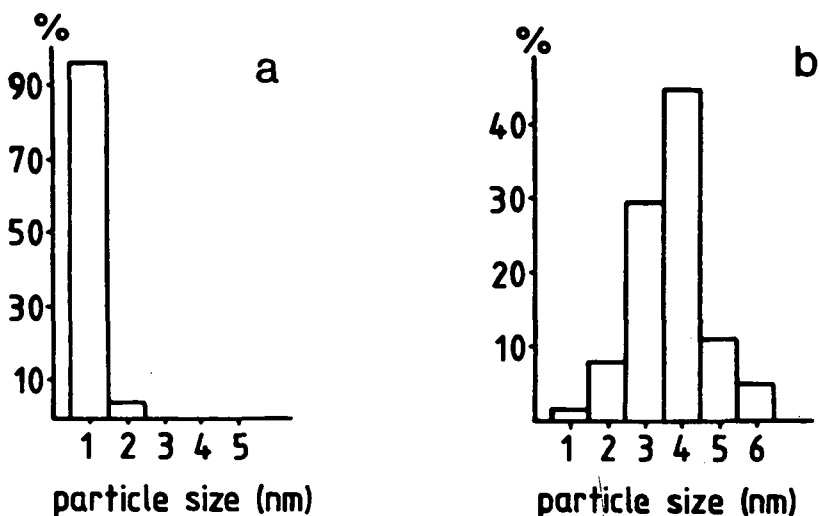


Fig. 1. Platinum particle size distribution by decomposition of $\text{Pt}(\text{NH}_3)_4\text{X}$ in oxygen (a) or in argon (b)

Under precise experimental conditions monodisperse metal phases with narrow particle size distribution can be grown on a zeolite support (Fig. 1). Promising systems can be obtained for the study of the effects of metal particle size and of metal-support interactions on selectivity in catalyzed reactions. The possibility to modify the properties of the crystalline support by controlling the Si/Al ratio, the acidity and by co-exchanging non-reducible cations add another advantage to the system.

On the other hand, fundamental studies regarding the activity of the metal phase are not straightforward due to the catalytic activity of the support itself.

FAUJASITE ENCAGED METAL COMPLEXES

The field of transition metal complexes in zeolite matrices has been reviewed repeatedly [49-52]. The following section will focus on some aspects relevant to the catalytic activity of metal chelates incorporated in a zeolite framework. Limitations in the catalytic application of such complexes with space filling ligands have been pointed out by Lunsford [49].

Howe and Lunsford [53,54] and Schoonheydt and Pelgrims [55] synthesized complexes of Co(II) with ethylenediamine and could demonstrate the formation of the

superoxo adduct, i.e. the catalytic activation of molecular oxygen. The complex exhibited, however, the tendency to form the coordinatively saturated tris-ethylenediamine variant. The ligand ethylenediamine is obviously so strong that the octahedral coordination is favoured and that only a small fraction of the planar low-spin complex is formed. Fully coordinated complexes, however, are of little importance in catalysis and it would therefore be of interest to find and to synthesize complexes exhibiting free coordination sites, which cannot be occupied by the chelate ligands. Furthermore, a distortion of such a stable chelate by partial coordination to zeolite lattice sites [55], which might be favourable for the catalytic activity of the complex, should be expected. These requirements will be met, first of all, by the class of planar complexes. $[\text{CoX}_4]^{2+}$ and $[\text{NiX}_4]^{2+}$ low-spin compounds with neutral ligand systems, forming planar-quadratic complexes, will be favourable candidates [56,57,58]. Especially the $[\text{CoX}_4]^{2+}$ system with D_{4h} symmetry should be of interest, because of its unpaired electron in the ground state. Octahedral complexes with a high tendency for tetrahedral distortion might also be taken into consideration. Such complexes can be formed with the ions Fe^{3+} and Co^{2+} , if different ligands of similar and relatively weak field strength are used.

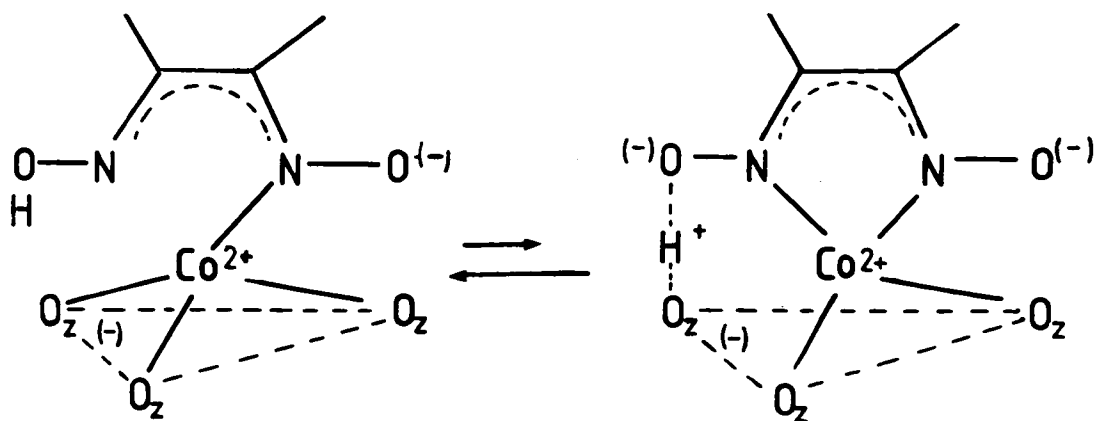


Fig. 2. Possible tetrahedral intermediate in the formation of zeolite encaged cobalt dimethylglyoxime .

The most straightforward way to prepare complexes with planar coordination is the use of four-dentate ligands, like tetrapyridyl, porphyrine or bis-dimethylglyoxime. The large ligands might be incorporated into the zeolite framework either by diffusion or by in situ synthesis from smaller molecules. Charged complexes can be stably fixed to the carrier by strong electrostatic interactions with the zeolite lattice.

Neutral complexes with weak van der Waals interactions with the zeolite can be stably fixed to the carrier only by steric hindrance. This means that the chelate complex should have diameters exceeding those of the super cage window. In this case, the in situ preparation of the ligand within the cavities is the method to be chosen.

Faujasite encaged bis-dimethylglyoximate complexes were obtained by dehydration of Ni^{2+} and Co^{2+} exchanged zeolites and gas phase diffusion of dimethylglyoxime into the cavities of the support [59-61]. $\text{Ni}[\text{dmgH}]_2$ is directly formed in this way in the super cages as a planar-quadratic complex. In the cobalt exchanged faujasite, however, intermediate tetrahedral complexes with C_{3v} and C_{2v} distortion are formed (Fig. 2) [61,62].

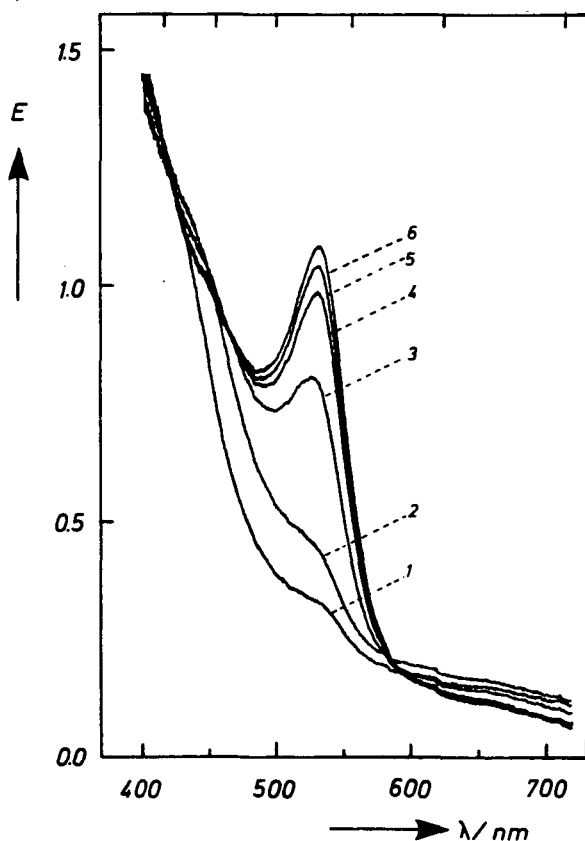


Fig. 3. Bathochromic shift of the 524 nm band of zeolite encaged nickel dimethylglyoxime during the uptake of water

Different coordination properties of the transition metal ions might result in different strengths of interaction between the chelate compounds and the zeolite lattice. Another type of interaction between the faujasite framework and the chelates which is due to the space filling property of the ligand system can be demonstrated in the case of encaged and hydrated nickel bis-dimethylglyoxime. Hydration of the yellow $\text{Ni}[\text{dmH}]_2 \cdot \text{X}$ leads to a bathochromic shift of the growing and characteristic

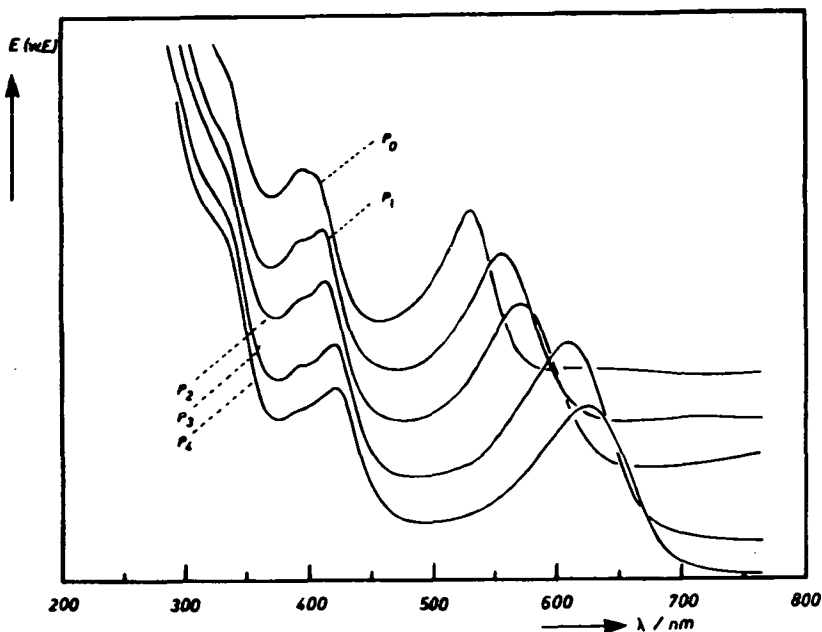


Fig. 4. Bathochromic shift of the 524 nm band of a nickel dimethylglyoxime film in a high pressure diamond-anvil cell ($P_0 - P_4 \cong 0.1 \text{ MPa} - 3.1 \text{ GPa}$)

green band at 524nm which refers to an electron transition perpendicular to the plane of the molecule (Fig.3) [63]. In zeolites a maximum shift of about 10 nm could be observed for the hydrated complex. This shift can be simulated by a pressure of 0.74 kbar exerted on a film of $\text{Ni}[\text{dmgH}]_2$ [64] using a high pressure diamond-anvil cell (Fig.4) [65,66]. The spectroscopic properties of the encaged complexes lend support to the conclusion that chemical interactions within the zeolite framework proceed under high pressure. Such a hypothesis was already put forward by Fraissard [67].

The distortion of the symmetry, which chelates incorporated in the zeolite framework can suffer, leads to the expectation that these complexes might exhibit enhanced catalytic activities and selectivities in the cavities of the support. This hypothesis might be studied exemplarily for a class of chelates having rigid

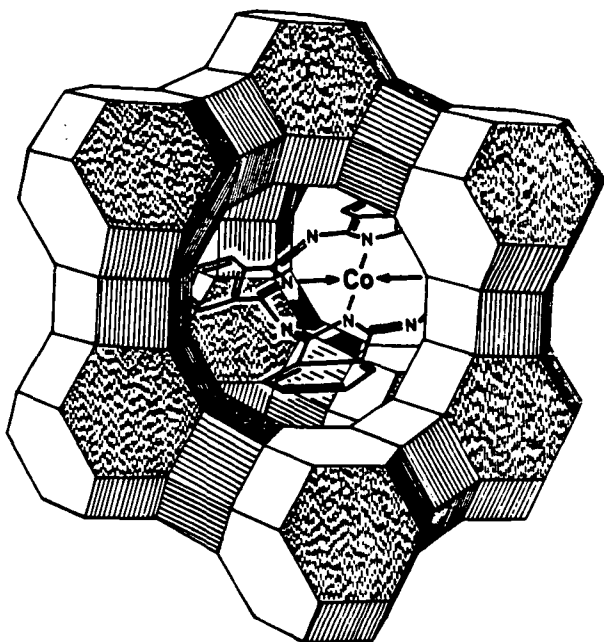


Fig. 5. Scheme of a faujasite encaged cobalt phthalocyanine molecule

planar structures of high stability. The metal phthalocyanines are favourable candidates for such investigations due to the strongly conjugated π -electron system of these compounds. The phthalocyanine molecule is larger than the opening of the super cage window, so that it cannot be incorporated by diffusion (Fig.5). However, the *in situ* synthesis of these chelates could be achieved [68,69] and their location inside the super cages could be proven [70,71]. The distortion, which the zeolite environment exerts on the electronic structure of the phthalocyanine molecule can be observed by means of the band doublet at about 620 and 660 nm, which corresponds to the electronic vibration transition of the macrocycle [63]. The observed shift of this doublet with respect to the band positions of phthalocyanine in a liquid acid solution corresponds to one obtained by a pressure of about 30 kbar imposed on a metal phthalocyanine film [61,72] and a strong influence of the zeolite cages on the electronic structure of the porphyrine type chelates can be inferred.

Romanovsky and co-workers have shown that faujasite supported phthalocyanines exhibit a variety of marked catalytic properties [68]. The encaged chelates are thermally very stable and, therefore, represent an interesting class of immobilized homogeneous catalysts. Since a large number of variants can be derived for the porphyrine type chelates, the properties of which might be modified by incor-

poration into the zeolite matrix, it is worthwhile to evaluate the potential of this system with regard to its catalytic activity still further.

CATALYSIS BY METAL-LOADED ZEOLITES

Established Applications. The application of transition metal-containing zeolites in petrochemical processes, like e.g. cracking, isomerization, hydrocracking or hydrodewaxing, is of high economic importance and has been reviewed repeatedly [73-76]. Zeolite catalysts, which contain non-reducible metal ions, e.g. rare earth metals or rhenium, or reduced metals, e.g. platinum, palladium or nickel, are used for reforming processes. The catalytic function of the transition metal ions consists in the formation of additional Bronsted acid sites, due to the hydrolysis of water molecules [77-79]. Reduced metal phases supported by acidic carriers like zeolites will strongly increase the hydrogenation and dehydrogenation properties of the catalyst by the enhanced formation of olefin intermediates in the isomerization of paraffins [80]. Since the isomerization reaction proceeds via carbenium ion and carbonium ion intermediates on strong Bronsted sites, it should be favored by an increase of the proton activity [81]. Figure 6 depicts a scheme of the polyfunctional reaction including the suggestions of Weisz for a dual site isomerization [82] and of Olah for carbonium ion intermediates in super acids [83].

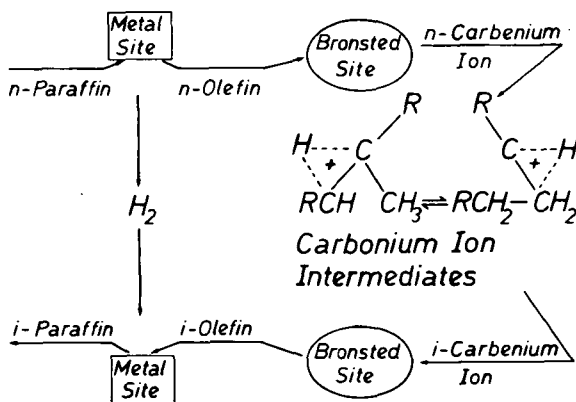


Fig. 6. Scheme of the bifunctional isomerization of paraffins

Zeolite catalysts containing reduced metals generally exhibit reduced rates of deactivation by coke deposition, which might be due to an enhanced hydrogenation of coke precursors, like olefins and aromatics [84]. However, a hydrogenation of hydrocarbons via the activation of molecular hydrogen proceeds on the

strong acid sites of transition metal-free zeolites as well. The non-classical hydronium ion H_3^+ , which has been proposed by Olah [85] might be the hydrogen activating intermediate in this reaction. The relatively rapid deactivation of this hydrogenation route is obvious, since the protons of the strong Bronsted sites are constituents of coke precursors.

Prospective Uses. The direct conversion of synthesis gas in a combined process of Fischer-Tropsch synthesis and shape-selective hydrocarbon conversion to gasoline seems to be very promising [86-88]. This two stage reaction proceeds by converting FT products, like olefins and oxygen-containing compounds, to high-grade gasoline, which is rich in isomers and aromatics. The fraction of aromatics can be enhanced by a factor of three if the two catalyst components are mixed in such a way that they can be used in a one-stage process. In this case, the strong acid sites of the zeolite will be located proximate to the FT sites increasing the probability of the formation of carbenium ions from the α -olefins, primarily formed in the FT reaction. Consequently, the fraction of intermediates entering the route of cyclization, aromatization and disproportionation, respectively, is increased resulting in the formation of light aromatics, which are favoured by the restricted transition state-type selectivity of the zeolite [89].

The synthesis gas to gasoline conversion might favorably be carried out by a one-stage process in the liquid phase, i.e. in a slurry reactor, at temperatures below 300°C where the coking rates are low. A regeneration at low temperatures, around 350°C, seems to be successful and not to affect the FT component [90].

The selective FT synthesis, which has repeatedly been reported for different metal-loaded zeolites and which is characterized by deviations from the Schulz-Flory distribution of the products, might in many cases be referred to a variety of secondary effects, caused by long formation periods, keeping the catalyst far from steady states [91]. Such transient states are, presumably, favoured by the zeolite support. The existence of true selectivity effects, which can unambiguously be referred to the geometric or electronic peculiarities of the zeolite matrix, is still open to discussion in view of the large number of factors, which may effect the properties of a zeolite supported metal, e.g. particle size and geometry, metal reducibility, location of metal, pore structure, strength and activity of Bronsted acid sites, nature and strength of Lewis acid sites, nature and location of additional cations, etc.

The aromatization of ethane on a metal-containing shape-selective zeolite is of interest, because it offers a method for obtaining valuable products from a readily available lowcost feedstock. The metal, e.g. platinum, enhances the dehydrogenation of the ethane to ethene, which can enter the route of cyclization and aromatization [92].

The catalytic production of high-grade fuel from biomass compounds by shape-selective catalysis [93] is promising in view of the increasing demand to improve the utilization of rapidly growing amounts of wastes and sewage sludges. Platinum-loaded shape-selective zeolites, which exhibit lower coking rates as compared to the hydrogen forms, might favourably be used, if they are not affected by volatile metals, like Zn, Cd or Hg, which might be evolved in the pyrolysis of the refuse derived biomass.

The use of platinum group metals incorporated in zeolites for the oxidative cleaning of exhaust gases might be expected in the future with respect to the lower amount of precious metals, which is needed for the oxidation of carbon monoxide and hydrocarbons on this type of catalyst. Presumably, the catalytic activity is favourably influenced by the strong Bronsted acidity of the support [94] resulting in a synergistic action of the catalyst.

Promising Reactions. Rhodium and iridium exchanged zeolites were found to show interesting catalytic activities for the carbonylation of methanol to methylacetate [95-100]. The zeolites exhibited more stable activities than other inorganic or polymer type carriers or carbon. Cations in lower oxidation states seem to be the active sites in parallel to the homogeneously catalyzed reaction. Catalyst deactivation by reduction to zero valent metal occurs around 250°C.

Also the hydroformylation of olefins has repeatedly drawn attention [101-103]. Presumably, only ethene can be hydroformylated in the pores of the zeolite matrix [103]. A scheme of this metal ion catalysed reaction is depicted in Figure 7.

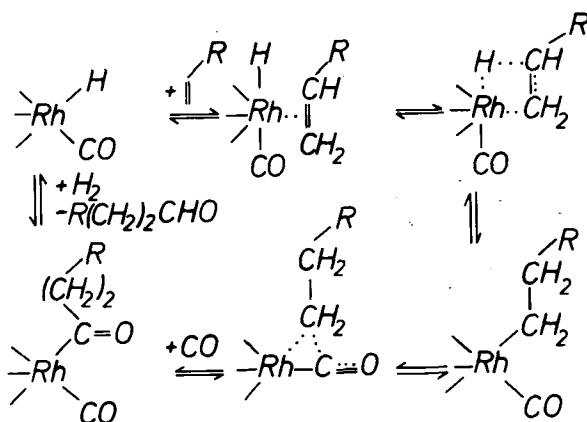


Fig. 7. Scheme of the hydroformylation of olefins by rhodium complexes

The low temperature water gas shift activity of ruthenium zeolites [104] is proposed to proceed on Ru(I) intermediates [105]. The water gas conversion extends to the Kölbel-Engelhardt reaction, if the metal component is reduced to a finely dispersed metal phase, which hydrogenates chemisorbed carbon monoxide [104,106]. The latter reaction requires elevated temperatures ($> 330^{\circ}\text{C}$), likely, in order to avoid the formation of deactivating surface carbide layers on the metal phase.

Many of the promising reactivities of metal-containing zeolites are based on the property of the microporous matrix to act as a solid solvent for transition metal complexes resulting in heterogenized homogeneous catalysts. Most of these catalysts are based on the faujasite-type zeolites, because of their relatively large internal free space and the three-dimensional pore arrangement. Moreover, the matrix can act as a polydentate ligand and provides discrete domains where distinct steric and electronic configurations can be formed. The zeolite matrix affords the highest metal ion dispersion in comparison with other supports and high stabilization for cations in low oxidation states. The reactions can be carried out at much lower pressures than those required by other homogeneous catalysts in liquid phase. These unique properties will draw continuous future attention to the structures and reactivities of zeolite supported metals and metal complexes.

ACKNOWLEDGEMENT

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