

METALLIC CLUSTERS IN ZEOLITES

By

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Zeolites have been used to prepare metal supported catalyst. The present paper reviews the literature on the preparation of metal clusters in zeolites, on the characterization of the dispersion and of the physicochemical properties of the metal particles.

Introduction

Highly dispersed metals are known as catalysts for several chemical reactions. They are usually supported on a stable inorganic carrier, in many cases alumina. The role of the carrier is not merely that of a dilutant, but it is essential for obtaining a high degree of dispersion and for preventing sintering of the metal phase at high temperatures.

When synthetic zeolites became available in large quantities, their usefulness as a carrier for highly dispersed metals was rapidly recognised [1—4]. By their high cation exchange capacity it is possible to incorporate an important amount of various metals, dispersed as single ions. Although it turned out afterwards to be more complicated, it was postulated that upon reduction the metal remained highly dispersed inside the pore system of the zeolites.

After these early works zeolites loaded with noble metals, especially platinum have been developed into practical catalysts for important industrial processes. Hydrocracking and reforming of hydrocarbons are the most important reactions carried out on an industrial scale making use of zeolite catalysts. Metal loaded zeolites have exquisite properties for these reactions: they act as polyfunctional catalysts, they add to the system a selectivity which is due to the molecular dimensions and the shape of their pores. They make a very efficient use of the costly noble metals by maintaining them in a state of high dispersion. Such catalysts exhibit a remarkable resistance against sulfur and nitrogen bases present as impurities in the hydrocarbon feed [5—13].

It is not the intention to give here an exhaustive review of the use of metal containing zeolites in catalysis. An excellent review on this subject was published by MINACHEV and ISAKOV [14]. It covers the literature till 1973.

The aim of this paper is to review critically the preparation of metal particles in zeolites, to discuss the mechanism of formation of reduced metals in zeolites and

the factors which influence the dispersion. In some systems the zeolite framework participates in redox reactions with transition metal ions. Residual charges on the metal particles influence the stability of the dispersion. In most cases the metal phase is polydisperse, and the methods generally used to measure the degree of dispersion on other substrates are not necessarily applicable to metals on zeolites.

Preparation

Metals can be introduced into zeolites in various ways. The most common technique is that of ion exchange and subsequent reduction using a suitable reducing agent. Adsorption from the gas phase of metal containing compounds (carbonyls) and of metal vapours have also been reported, as well as inclusion of elements during the synthesis of the zeolite. The most interesting elements for catalysis are the transition metals, especially group VIII and group Ib and IIb elements to which this review will restrict itself. Most of the work has been performed on zeolites with the faujasite structure, mainly the synthetic zeolite Y, while other zeolites (A, morde-nite) were less extensively studied.

Ion exchange

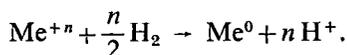
Introduction of transition elements by ion exchange is an easy technique but care must be taken of the chemical properties of the elements. For the more common ions (Ni^{++} , Co^{++} , Cu^{++} , ...) aqueous solutions of the hydrated ions can be used.

The fundamental data on the ion exchange of the transition metals are not very abundant [15—19]. Ion exchange studies are usually carried out in very dilute solutions (0.1 N—0.02 N). Since the solutions of transition metal ions are acidic, partial exchange of protons occurs but this is not so important for the reduction afterwards. More important is the fact that excess transition metals can precipitate due to the basic reaction of the zeolite. This was investigated in detail by SCHOONHEYDT ET AL. [21]. They showed that an important excess of Ni^{++} and especially of Cu^{++} can be fixed on the zeolites Y and even more on X. This excess was present as complex ions when an acetate buffer was used, or as a finely divided hydroxide species probably incorporated in the zeolite pores when the pH of the solution was not controlled. To avoid this complication it is recommended to carry out the ion exchange in dilute solution (<0.05 N), in dilute suspensions (<5%) and at ambient temperature.

One can also exchange transition elements as stable cationic complexes. This is the appropriate procedure for noble metals (Pt, Pd, Ru) which are commonly exchanged as stable amine complexes, but other ions can also be exchanged under complexed form [20]. For the more common ions it is usually attempted to introduce a large amount of metal. Due to the cost, the noble metals are usually exchanged only to a minor fraction of the ion exchange capacity.

Reduction with hydrogen

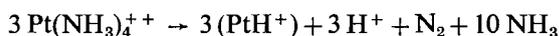
The reduction to the zero valent state is usually done with hydrogen. The overall reaction can be written as follows:



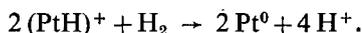
The protons react with the zeolite lattice creating hydroxyl groups. The presence of these hydroxyl groups has been demonstrated with infra-red spectroscopy [30, 31]. They absorb at 3650 cm^{-1} (or in the corresponding OD region), like the acid hydroxyls in HY zeolites. By this acidity the metal loaded zeolites can act as bifunctional catalysts. However, the overall reaction reveals nothing about the fine mechanism of the reduction. Furthermore, slight differences in the reduction procedure may result in quite different degrees of dispersion, an important property of metal catalysts. This reveals that the reduction mechanism is probably complex. Moreover it is not necessarily identical for the different ions or in the different zeolites.

1. Platinum and palladium

Because of its importance for practical catalysis, Pt in Y zeolites has been widely studied and a coherent picture has been developed [20—29]. Thermal decomposition of the $\text{Pt}(\text{NH}_3)_4^{++}$ complex results in the formation of an hydride species (PtH^+). The gaseous decomposition products were analysed by WINKLER ET AL. [25] and contain NH_3 and N_2 . MASHCHENKO ET AL. [27] investigated this decomposition reaction by i.r. spectroscopy and observed a band at 2120 cm^{-1} from which they inferred the presence of a surface platinum hydride. A combination of the observations reported in these two works allows us to write the following reaction scheme for this thermal decomposition at 177°C



The (PtH^+) can be reduced with H_2 to metallic Pt.



The reduced Pt seems to migrate and interact with paramagnetic centers in the zeolite, most probably Fe^{3+} ions [25]. When the $\text{Pt}(\text{NH}_3)_4^{++}$ complex is reduced with H_2 immediately, without previous decomposition, a neutral hydride is formed above 90°C [26]. Its decomposition leads to agglomeration of the platinum.

Oxidation of the amine complex prior to reduction with hydrogen influences the dispersion of the metal phase. It has been proved that after a treatment with oxygen at 300°C most of the platinum is present as Pt^{2+} ions located in the supercages. After oxidation at 600°C the Pt^{2+} ions have migrated into the sodalite cages [28, 29]. In this way, when reduction with hydrogen (under moderate condition) is performed after different oxidative pretreatments, the platinum particles are of different sizes and located at different positions. The situation may be summarized as indicated in Fig. 1 [29].

Hydrogen chemisorption, oxygen chemisorption and hydrogen titration have been applied by several authors [22—26, 29, 76] to determine the degree of dispersion, but the results are not in complete agreement. In the first work on platinum zeolites RABO [22] claimed that atomically dispersed platinum could be obtained and suggested that such an atom could sorb two hydrogen atoms. This explanation is not longer followed. GALLEZOT ET AL. [29] assume that atomic Pt in the supercages does not chemisorb hydrogen. Possible reasons for this are that atomic Pt^0 may not have the properties of metallic Pt, or that H_2 , because of its kinetic diameter of 0.289 nm , does not enter into the sodalite cages.

Palladium behaves in a way similar to platinum. After calcination of the amine complex Pd^{2+} ions are present which can be reduced even at room temperature giving almost atomically dispersed Pd^0 . This was demonstrated using X-ray diffraction [32]. The nature of the Pd^0 was studied by sorption of CO and i.r. spectroscopy

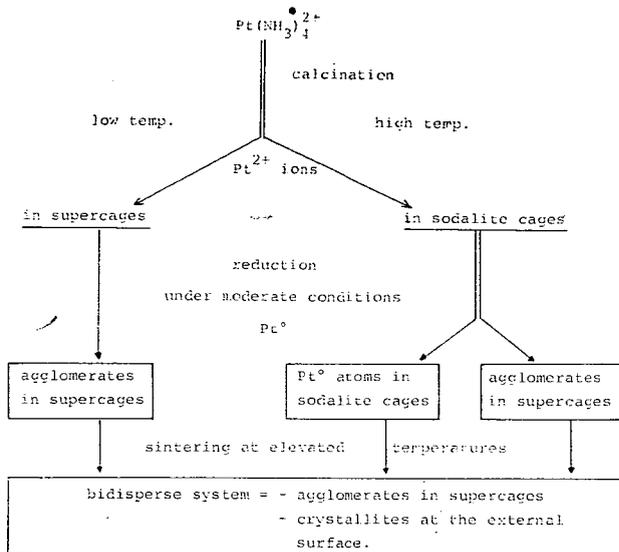


Fig. 1. Reduction scheme of $\text{Pt}(\text{NH}_3)_4^{2+}$ in zeolite Y.

[33]. The Pd atoms are electron deficient: this was derived from the frequency of the CO vibration, and was explained by assuming that the Pd atoms are associated with Lewis acid sites. Pd is very sensitive to sintering. Reduction at 200°C produces metal crystallites outside the zeolite [33].

2. Other transition metal ions

The reduction of a series of transition metal ions of different nature in zeolite Y was reported by YATES in 1965 [34]. In this early paper it was reported already that during reduction the metal phase can leave the zeolite. Cd, Zn, Ni and Ag crystallites were proved to exist outside the zeolite. It was also shown that metals with a high vapour pressure (Hg, Zn, Cd) could distill out of the zeolite during the reduction.

RIEKERT [35] investigated the interaction between hydrogen and Ni^{++} , Cu^{++} and Ag^+ ions in zeolites T and Y. He treated the stoichiometry of the reaction as an intracrystalline equilibrium between Ni^{2+} and Ni^0 inside the zeolite, following nearly the mass action law. He also observed a slow recrystallization of reduced Ni into larger crystals outside the zeolite.

Of all transition metal ions other than Pt and Pd, Ni has received most attention [36—45]. This is probably because of the usefulness of Ni in practical catalysis, but also because of the applicability of a variety of physicochemical methods to characterize the state of the metal phase. Most authors agree that after reduction the nickel

migrates to the external surface where it agglomerates into relatively large particles. ROMANOVSKII [36, 37] has derived a partition function of nickel particles from magnetization experiments. After reduction at 370 °C there were still particles with dimensions smaller than the diameter of the supercages in zeolite X, but a sintering at 400 °C produced particles too large to be accommodated in the supercages. Reduction of Ni^{++} into Ni^0 accompanied with sintering was reported at temperatures as low as 350 °C for zeolite NiNaA [43, 44], 350–400 °C for zeolite NiNaX [34, 43, 44], 300–440 °C for zeolite NiY [40, 42, 44] and 360 °C in mordenite [44]. All the papers in which quantitative data on the extent of the reduction were reported, agree on the fact that the reduction of nickel is incomplete (except for small Ni contents [40]).

In a recent paper BAGER, VOGT AND BREMER [45] recognize the complex nature of the reduction and of the sintering of nickel in a zeolite Y in which other cations were incorporated (Na, Ca, Ce and NH_4). They investigate the samples by different techniques including chemical analysis, XPS, electron ferromagnetic resonance and electron microscopy. They reported (in NiNaY and NiCaY) a rapid reduction at low temperature (below 350°).

Another part of the nickel contained in these samples was reduced only when the temperature was raised above 420 °C. In NiCeY and NiNH_4Y significant reduction of the nickel occurred only at temperatures above 420 °C. These authors made the important observation that the nickel produced at low reduction temperatures sintered easily and agglomerated outside the zeolite, whereas the nickel reduced at higher temperatures remained in a state of high dispersion. In the NiNH_4Y sample nickel crystallites could never be detected outside the zeolite. The result of the physicochemical determinations were confirmed by catalytic activity measurement for dehydrogenation of cyclohexane to benzene.

Recently [77] the preparation of Ru^0 in several zeolites was reported. The Ru was exchanged into the zeolite as trivalent ions and reduced with hydrogen. Particle sizes are derived from hydrogen sorption. A rather small average crystallite size is found on zeolites X, Y and M. The authors conclude that on these zeolites a large fraction of the metal is inside the zeolite. The samples were good catalysts for benzene hydrogenation.

Experiments were reported to document the influence of the pretreatment [45, 46], the nature of the charge compensating cations [40, 45] and the nature of the zeolite [47] on the reduction and the state of dispersion of the metallic phase after reduction. Despite of the large number of papers, it is difficult for the moment to make general conclusions on the different parameters which influence the reduction of transition metal cations.

Preparation of metal clusters using adsorption of neutral compounds

Zeolites, previously dehydrated, can be loaded with metals by adsorption and subsequent decomposition of neutral compounds containing metals. Preparations with metacarbonyls, acetylacetonates, alkyl derivatives and others have been reported and patented [66, 67]. The procedure has been "rediscovered" recently. GALLEZOT ET AL. [68] and DEROUANE ET AL. [69] report loading of zeolite Y with Mo, Re, Ru [68] and Ni [99] by adsorption of metal carbonyls and subsequent thermal decomposition. These recent papers use X-ray diffraction, i.r. spectroscopy and ^{13}C -NMR to describe the procedure and the properties of the final product. A definite characterization of the system obtained by this method has not been obtained yet.

Dispersion of the metals in the zeolites

It is obvious from the foregoing that most of the effort was directed to the preparation of a stable nickel phase highly dispersed inside the zeolite system. The major problem to overcome is the existence of bidisperse systems. The particles inside the zeolite have necessarily dimensions smaller than the diameter of the cages. Metal crystallites observed at the outside of the zeolites have dimensions which are greater by almost an order of magnitude.

The adsorption of H_2 , of O_2 and the so-called hydrogen titration are now standard methods to determine the dispersion of metals on classical substrates like alumina and silica. The application of this method to metals on zeolites is questionable. Indeed, if the zeolites are treated under such conditions that a bidisperse system exists, the adsorption experiments estimate an average size which does not correspond to reality. This was demonstrated by KUBO ET AL. [48] for Pt zeolite and by LAWSON ET AL. [42] for Ni zeolites. In their experiments electron microscopy revealed the existence of small and large particles, while H_2 adsorption produced an average value. If the zeolite contains only ultra small particles inside the cavities, the gas adsorption methods might eventually measure the correct order of magnitude. However, not enough attention has been given to the perturbing effect of steric hindrance. It is also questionable whether the adsorptive properties of ultra small particles are the same as those of real metals.

Other physical methods have been used to determine the particle size. Electron microscopy [23, 42, 48, 49] is of course very suitable to determine particle size distributions. However, the ultrafine particles inside the zeolite pores are outside the range of resolution of most of the electron microscopes presently in use.

X-ray diffraction line broadening is another method frequently used [31, 32, 34, 42, 44]. The lower limit of this method reaches only particles of 20–30 Å, and hence it also gives no insight in the state of the metal phase inside the zeolite pores.

Magnetic measurements have been used to characterize the metal phase in the case of Ni zeolites. Susceptibility measurements and ferromagnetic resonance experiments were reported [36, 37, 40, 45]. Again, the appearance of superparamagnetic or ferromagnetic properties was ascribed to larger particles outside the zeolite cages. BAGER ET AL. [45] combine O_2 adsorption with their physicochemical methods (XR, electron microscope, EFR) in order to determine the particle size of intracrystalline Ni^0 particles.

Recently the method of temperature programmed reduction followed by temperature programmed oxidation was proposed by JACOBS ET AL. [50] as a method to distinguish between particles inside and outside a zeolite. The method consist in a reduction with hydrogen, or an oxidation with oxygen in a small volume reactor in which the gas consumption can be followed by measuring the pressure drop. After suitable pretreatments of the samples (outgassing *etc.*) the temperature of the sample was increased at a linear rate of $5^{\circ} \cdot \text{min}^{-1}$, and condensable gases were trapped out continuously. The rate of gas uptake (first derivative of gas consumption) was determined every 90 seconds and plotted as a function of the temperature. Example of the curves obtained is given in Fig. 2 for CuY zeolite, and in Fig. 3 for NiY zeolite. The temperature at which the peaks occur is indicative of the chemical reaction which goes on, and the intensity of the peaks, since it is proportional to the amount of gas consumed, allows a quantitative estimate. Thus in Fig. 2 the curve r_1 represents

the reduction of CuY. The low temperature peak at about 150 °C is due to the reduction Cu^{++} to Cu^+ , the high temperature peak at 420 °C reflects the transformation Cu^+ to Cu^0 . Temperature programmed reoxidation of this sample results in a peak around 180 °C, which is ascribed to the reoxidation to the Cu^{++} state of all the

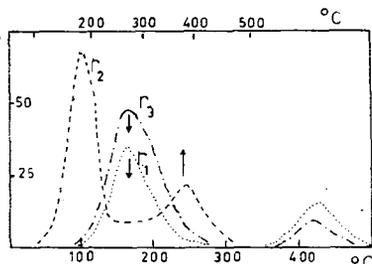


Fig. 2. Rate of gas consumption — $\text{mol g}^{-1} \text{s}^{-1} \times 10^8$ as a function of temperature in TPR/TPO experiment
 r_1 = TPR with hydrogen on CuY
 r_2 = TPO with oxygen on reduced CuY
 r_3 = TPR with hydrogen on reoxidized sample

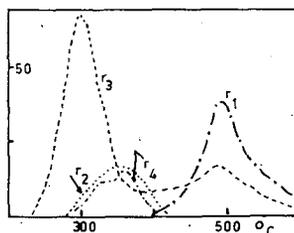


Fig. 3. Gas consumption in $\text{mol g}^{-1} \text{sec}^{-1} \times 10^8$ as a function of temperature in TPR/TPO experiments on NiY zeolite
 r_1 = TPR = rate of reduction on fresh sample
 r_2 = TPO on reduced sample
 r_3 = TPR on reoxidized sample (second cycle)
 r_4 = TPO during second redox cycle

species present inside the zeolite, either as Cu^+ or as ultrasmall Cu^0 particles. A second peak at 400 °C is attributed to the oxidation of large Cu^0 aggregates outside the zeolite which produces a CuO phase. A second TPR of the same sample reveals a peak at 150 °C with a higher intensity than during the first reduction. This is due to the superposition of two phenomena: the transition Cu^{++} to Cu^+ of the copper ions in the zeolite and reduction of a CuO phase outside the zeolite. The high temperature peak at 420 °C has decreased in intensity due to the decrease of the copper content in the zeolite. All these assignments were supported by a detailed characterisation of CuY zeolites during reduction and reoxidation using a variety of physicochemical techniques [51], and by a kinetic study of the reduction and the reoxidation phenomena [52].

Fig. 3 allows a detailed discussion of the behaviour of a NiY. During a first TPR a broad peak at 500 °C appears. An X-ray diffractogram of this sample revealed the presence of a considerable amount of Ni^0 external to the zeolite. TPO on this sample reveals that Ni^0 is completely reoxidised with a maximum in rate at 400 °C. A second TPR on the same sample produces two peaks; the NiO phase formed during the previous TPD is reduced at a lower temperature (300 °C) than the Ni^{++} ions inside the zeolite.

Although the method does not allow a determination of particle sizes, it allows a quantitative distinction between the phases inside and outside the zeolite. Indeed, the total extent of reduction (and oxidation) can be derived from the total gas consumption. The area under the different peaks can be compared to each other and allows conclusions on the relative abundance of the species reduced or oxidized.

Mechanism of the reduction with hydrogen

Reducibility of the cations in zeolites

The formal mechanism of the reduction of the nonnoble transition metals in zeolites has been studied by a few authors [31, 38, 50—56]. For such studies it is important that the zeolite samples are prepared in such a way that the transition metals are only present as exchangeable cations, and that finally divided hydroxide species are avoided [21].

Since we were convinced that the data reported in the literature are often obtained on inhomogeneous samples, we investigated a series of zeolites Y saturated with different cations (Ag^+ , Cu^{++} , Ni^{++} , Co^{++} , Zn^{++}) in very dilute suspensions (zeolite loading of 0.5 g/l) and using a concentration of the transition metal salts (nitrates or chlorides) of 0.005 N. The reducibility of these zeolites was then investigated using the TPR method and by isothermal reduction at different temperatures. AgY can be reduced at very low temperatures ($<100^\circ\text{C}$) [31]. Cu^{++}Y goes to Cu^+Y at low temperature (150°C). Further reduction to Cu^0 goes rapidly at 420°C (TPR) but at 400° several hours were needed to transform 50% of the Cu^+ into Cu^0 [51]. Ni^{++}Y gave a maximum in the rate of reduction (TPR) at 500°C [51]. Under static conditions a temperature of 450°C is needed during several hours to obtain only 36% of reduction. At 350°C reduction proceeded after several hours, to 8% of the total Ni content [57]. Co^{++}Y at 500°C consumed only slight quantities of H_2 corresponding to a degree of reduction of only a few percent, while the CdY, ZnY and MnY could not be reduced at all (unpublished results).

In all these experiments the sample were pretreated by careful outgassing at 500°C . The reducibility could be enhanced by working in the presence of water vapour, or by realising a so-called deep-bed pretreatment.

Table I

Reducibility of metals in zeolites compared to electrochemical potentials and ionisation potentials of the elements

	TPR ^a	Electrochemical potential	Ionisation potential (1st or 2nd) volt
AgY	120°C	0.7996	6.9
CuY	400°C	0.158 (Cu^+)	7.72 (1st) 20.29 (2nd)
NiY	500°C	-0.230	18.15 (2nd)
CoY	b	-0.280	17.05 (2nd)
CdY	b	-0.4026	16.90 (2nd)
FeY	c	-0.409	16.18 (2nd)
ZnY	b	-0.760	17.96 (2nd)
MnY	b	-1.029	15.63 (2nd)

a. Temperature at which maximum occurs in the rate of H_2 consumption in TPR procedures.

b. Reduction not observed.

c. Ref. [78] and [79]—no reduction of $\text{Fe}^{++} \rightarrow \text{Fe}^0$

From these observations we concluded:

(i) The transition metal ions in zeolites have properties which can be compared to the properties of the ions in solution. Indeed, the order of reducibility of the ions follows the electrochemical potentials of the elements as listed in Table I. The reducibility of the metal does not follow the sequence of the ionization potential which is a property of the isolated metal atoms (see also Table I).

(ii) In the previous work reporting a reduction of metal ions which are known to have weak oxidative properties, it is likely that a fraction of the ions was present as a finely divided hydroxyde. The same is probably true for these works where Ni could be reduced at temperatures as low as 300 °C. This remark applies to the experiments on zeolite Y and is not necessarily valid for experiments on other types of zeolite although the precipitation of hydroxydes must still be easier in the zeolites with lower Si/Al ratio (X and A) which give a stronger alkaline reaction than zeolite Y.

These conclusions find support in the observations made by GARTEN [78] and by HUANG AND ANDERSON [79] with Fe^{++}Y zeolites. These authors report that Fe^{++}Y resist reduction with hydrogen. This is in agreement with the position of Fe^{++} on the list of electrochemical potentials. Nevertheless, MORICE AND REES [80] have found that Fe^{3+}CaX could be reduced in hydrogen at 350 °C to give metallic particles.

Mechanism derived from kinetics of H_2 consumption

BEYER ET AL. [31] investigated the kinetics of reduction of AgY at different temperatures. Examples of the H_2 consumption curves are given in Fig. 4. The extent of reduction was dependent on the temperature. Reduction proceeds by another mechanism at low and at high temperature. These results were explained by postulating that the low temperature mechanism applies to the silver ions located in the supercage, while the high temperature reduction affects also the ions in the sites SI. The rate equation for the high temperature mechanism is first order in the concentration of unreduced silver $\left[\frac{dR}{dt} = k[\text{Ag}^+]\right]$ and the activation energy of this mechanism is 97.6 kJ. This is an acceptable value for the activation energy of diffusion of Ag^+ out of the hexagonal prism.

The low temperature mechanism was expressed by the following rate law

$$\frac{1}{P} \cdot \frac{dR}{dt} = k' \frac{1}{R} - k''$$

in which R is the extent of the reduction at time t . That the rate is inversely proportional to the extent of reduction implies that the reaction products slow down the reaction. In all the samples which were studied only two thirds of the Ag^+ ions,

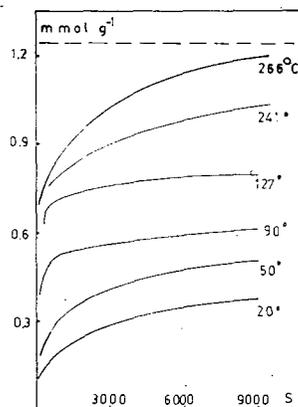
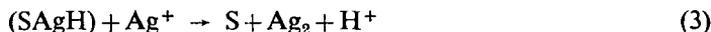


Fig. 4. Hydrogen consumption (in mmol g^{-1}) as a function of time at different temperatures on zeolite AgNaY

normally available in the large cavities for the low temperature mechanism, participate really in the reduction reaction.

BEYER ET AL. [31] further postulate that the reduction is a catalysed process. The hydrogen is activated at some active sites, probably paramagnetic impurities.

The following sequence of reactions accounts for the rate law observed.



in which reaction (3), *i.e.* the regeneration of the active sites, is rate determining. It is assumed that Ag_2 further associated with unreduced silver to form charged clusters Ag_n^+ . From the fact that only two thirds of the silver available in the supercages is effectively reduced in the low temperature mechanism, it was inferred that the silver cluster has an average composition Ag_3^+ , and that such a charged cluster is more difficult to reduce than isolated silver ions.

The assumption that paramagnetic impurities play a role in these processes is supported by a few facts. It has been proved in D_2-H_2 equilibrium experiments that iron impurities can indeed activate hydrogen in zeolites [58]. Pt reduced in zeolites was shown to agglomerate with iron impurities in the zeolite [25]. Furthermore, BEYER and JACOBS [53] were investigating the reduction of Ag^+ in mordenite, and proved that the rate of the reduction was decreased when the level of iron impurities was decreased previously by an extraction of the iron with dithionate. This extraction does not modify the mechanism of the reaction since the activation energy is the same before and after deferration.

There is only indirect proof that charged clusters are created during reduction of silver at least at moderate temperatures. In BEYER's [31, 58] picture the coulombic interactions between the negatively charged zeolite lattice and the positive clusters prevents the escape of the metal from the zeolite and its agglomeration into a bulk phase. Experimental proof to this hypothesis was recently found by H. BEYER (unpublished). A zeolite AgY was reduced at increasing temperatures (50 to 350 °C), and the existence of metallic particles was checked by the appearance of the (III) line in the X-ray diffraction diagrams. The formation of Ag particles of 210 Å was observed after 4 hours of reduction at 350 °C. At temperatures below 150 °C the formation of extra lattice particles did not occur. When the hydrogen was removed by outgassing at 150 °C, the reduced AgY zeolite could be heated to 350 °C for a long time without formation of silver crystallites detectable by X-ray. One can conclude from this experiment that the Ag particles are in the zeolite cages as a stable entity, probably with a residual positive charge, because sintering occurs only when the temperature is raised in the presence of excess reductant.

Reduction kinetics of NiY were investigated by VERDONCK [57]. At 500 °C only 30% of the Ni present could be reduced to the Ni^0 state. The kinetics of the H_2 consumption could be explained on the basis of the mechanism proposed by BEYER [31]. This implies (*i*) activation of the H_2 at some surface sites; (*ii*) diffusion of the nickel ions towards these active sites; (*iii*) the regeneration of the active site is the rate determining step; (*iv*) formation of charged Ni_n^{+} clusters. The results allowed to estimate the average size and charge of the clusters to be Ni_3^+ or Ni_4^+ . However,

due to the high temperature (500 °C) a considerable sintering of the nickel phase is observed which makes such estimates highly speculative. Another complication arising with the reduction of NiY is the dehydroxylation of the OH groups created in the reduction reactions at the temperatures at which reduction is carried out.

A similar mechanistic study on CuY zeolites was much more difficult. The reason is that reduction proceeds by a two step mechanism: at low temperature Cu^{++} is reduced to the Cu^+ state. Reduction of Cu^+ to Cu^0 request temperatures close to 400 °C and higher [51, 52]. The activation energy of the reduction of Cu^+ to Cu^0 is rather low ($25 \text{ kJ} \cdot \text{mol}^{-1}$) which could mean that the process is diffusion controlled. A full characterisation of a CuY sample partially reduced under specific conditions is a difficult task which request the combination of several techniques. Table II pre-

Table II
Characterisation of a $\text{Cu}_{18}\text{Na}_{19}\text{Y}$ zeolite after reduction and reoxidation

Treatment	Cu^{++} a	Cu^+ a	Cu^0 b	CuO c
(1) Reduction H_2 400 °C (1.25 hr)	0.00	17.38	1.22	—
(2) Reduction H_2 400 °C (10 hr)	0.00	13.07	5.53	—
(3) Reduction H_2 400 °C (20 hr)	0.00	11.09	7.51	—
(4) = 1 + oxidation (1 hr)	18.08	—	—	0.52
(5) = 2 + oxidation (1 hr)	16.01	—	—	2.59
(6) = 1 + oxidation (1 hr)	14.16	—	—	4.44

Figures are in numbers per unit cell.

a. In lattice positions.

b. Inside + outside the zeolite.

c. Measures Cu^0 outside zeolite.

sents an example taken from the work of HERMAN ET AL. [51]. These data were obtained by a combination of methods first applied by HALL ET AL. [59] on Cu^{++} containing hydroxyapatite.

The formation of Ni(I) during the reduction of a NiY zeolite with hydrogen has been reported by GARBOWSKI ET AL. [60]. The evidence presented is based on EPR and electronic spectroscopy but a quantitative estimate of the amount present in that oxidation state is not given. Since the TPR experiments [50] do not reveal a distinct two-step mechanism, it can be assumed that the eventual concentration of Ni(I) must be small and that further reduction to Ni^0 goes fast.

The detailed mechanisms proposed by BEYER, JACOBS ET AL. [31, 50, 57] cannot necessarily be applied to other zeolites than the zeolite Y. Ag mordenite was investigated by BEYER AND JACOBS [53]. The kinetic data showed again a low and high temperature mechanism from which the authors inferred that a similar mechanism as in AgY operated. In the low temperature phenomenon the formation of a Ag_5^+ cluster was postulated.

The reduction of NiX cannot be explained by the mechanism which was found for NiY. GUILLEUX ET AL. [55] advanced a mechanism in which a variable diffusion coefficient ($D = D_0(1 - R)$) is applied. This equation is suitable for low levels of reduction. To interpret data on zeolite NiX over a broad range of reduction levels, VER-

DONCK [57] adopted a mixed type mechanism (SETT AND ROSS) controlled by an interface reaction and by diffusion. When only diffusion is rate determining, the equation

$$\left(\frac{1}{2} - \frac{R}{3} - \frac{(1-R)^{2/3}}{2} \right) = t \quad (\text{time})$$

fits the data. Two straight lines are obtained which intersect at $R=0.4$. VERDONCK concludes from this that two different diffusion mechanisms each with a constant diffusion coefficient must exist. Since the NiX contained 27.6 Ni ions per u.c., of which 16 are located in site SI, VERDONCK assumes that the distinction between two diffusion processes can be made on the basis of the location of the cations. The two processes have a different activation energy (100 kJ and 120 kJ). In NiX degrees of reduction approaching 90% could be realised at 550 °C in less than 4 hours. GUILLEUX ET AL. [55] reported the beneficial effect of metallic Pd on the rate of reduction of Ni^{2+} in a zeolite X. The Pd^0 was formed in a (PdNiX) zeolite by reduction with H_2 at 100 °C. To reduce the Ni the temperature was increased to 230°–300 °C. At this temperature the rate of reduction of Ni was increased with increasing concentration of Pd. Heating at 400 °C resulted in a sintering of the Pd and destroyed the activating effect. Similar observations were reported by RABO ET AL. [72].

Reversibility of the reductions and participation of the zeolite lattice in redox phenomena

In most of the papers the possible participation of the lattice in redox phenomena is not considered. TSUTSUMI [49] reported the formation of metallic silver in AgNaY and in Ag mordenite heated in a stream of helium at 600 °C and 750 °C. SEFF [61] recently reported the formation of a Ag_6 cluster in a zeolite AgA. The samples, (single crystals) were dehydrated at 400 °C during two days *in vacuo*, and during two more days in the presence of 100 torr of oxygen, or *in vacuo* at 425 °C during 10 days. The colour of these samples was between brick red and golden yellow. The results of the X-ray diffraction analysis indicated the existence of a Ag_6 octahedral cluster located in the center of the cubooctahedron with their threefold axis oriented towards eight Ag^+ ions in the centre of the 6-rings.

The formation of Ag^0 under these conditions can only be explained by the reduction of Ag^+ by oxide ions of the zeolite lattice. The resulting zeolite lattice must be oxygen deficient.

JACOBS ET AL. [62] observed a similar chemistry with a CuY zeolite. They made a quantitative study of the phenomenon, which they called auto-reduction, by measuring the amount of oxygen evolved. They characterized the oxygen deficient sites in the lattice as Lewis acid centers by adsorption of pyridine and infrared spectroscopy. In the case of CuY the auto-reduction of the Cu^{++} ions proceeded to the Cu^+ state and did not produce metallic copper.

In the case of CuY [62] the auto-reduction was reported to be reversible, the oxygen evolved was reabsorbed and the Cu^+ reoxidised when the zeolite was cooled in the presence of oxygen. The existence of an equilibrium pressure of oxygen over a CuY zeolite heated to higher temperatures showed that the reaction was indeed an equilibrium reaction. The reactions can be idealised as in Fig. 5.

Auto-reduction of Pd^{++} in PdX has been reported by MINACHEV ET AL. at temperatures above 140 °C. At that temperature they consider the possible formation of Pd^0 , while at lower temperatures Pd^+ could be stabilized [46].

It was known that the zeolite lattice participated in the reduction of transition metals with hydrogen by accepting the protons to make hydroxyl groups. The experiments described in previous paragraphs show that the oxygen framework of the zeolite can in some cases actively participate in redox reactions also.

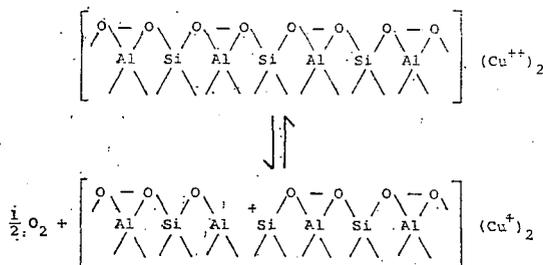


Fig. 5. Participation of zeolite lattice in the reduction of Cu^{++}

We can now consider the question of reversibility of the reduction. Reduced metals can be reoxidized with oxygen. It is generally accepted that reduction-reoxidation of transition metal zeolites using H_2 and O_2 is reversible only when moderate reduction has taken place.

BEYER, JACOBS ET AL. [31, 50—53, 57, 62] have investigated the stoichiometry of hydrogen and oxygen consumption in AgY , CuY , NiY and NiX and in a few other zeolites. They have shown that, in terms of the stoichiometry of the H_2 and O_2 consumption the reduction and reoxidation reaction are virtually reversible, but reversibility is not always realised in terms of the physicochemical properties of the system. Their results can be summarised as follows:

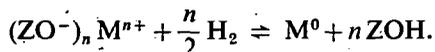
(i) The processes which occur inside the zeolite cavity are reversible in any case. This can be expressed in the following equation in which the subscript (in) indicates that the metal is inside the zeolite cavities.



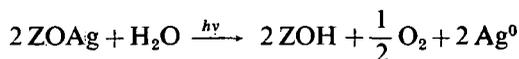
(ii) Irreversibility in the reduction-oxidation cycle is observed when the reduction step was performed at high temperatures so that considerable dehydroxylation had taken place [57] as was the case for NiY .

(iii) If sintering has occurred resulting in a metal phase outside the zeolite, reoxidation of that metal phase produces an oxide species, provided the oxide phase is thermodynamically stable. When the oxide phase is unstable, as is the case with Ag_2O , reoxidation at 350°C will regenerate the initial zeolite. This is important for regeneration of practical catalysts. Reactivation of Pt containing catalysts is done in processes which include an oxidation step to burn off the coke. Since Pt oxides are unstable (decomposition between 400 — 500°C) this reoxidation step might favour a redispersion of the Pt under ionic form, especially when the reoxidation is combined with a controlled rehydration [63].

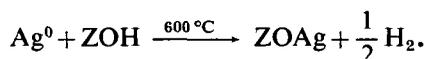
RIEKERT [35], has formally represented the reduction of transition ions in zeolites as an equilibrium reaction



The first experimental proof that this is really so (in some cases) was recently given by JACOBS ET AL. [64]. They reported the release of hydrogen gas from AgY and Ag mordenite previously reduced with hydrogen. The process was not due to the desorption of chemisorbed hydrogen since a concomitant transformation of Ag^0 into Ag^+ was evidenced by CO adsorption and i. r. spectroscopy. The maximum rate of hydrogen desorption in a temperature programmed desorption process was at 600 °C. Only the Ag^0 inside the zeolite pores took part in this process. The reversibility was further proved by applying repeated cycles of reduction with hydrogen and thermal desorption on the same sample of AgY, but dehydroxylation resulted in a progressive decrease of crystallinity of the zeolite. The reversibility of the reduction reaction was used by the same authors for the dissociation of water using a sunlight-activated reduction with water as the reduction step



and a thermal desorption of hydrogen as the oxidation step



Due to the high temperatures and to degradation of the zeolite by dehydroxylation this process has little chance to be of practical application.

Electronic properties of the metal particles in zeolites

As reviewed above, JACOBS, BEYER ET AL. have postulated to existence of charged clusters in zeolites loaded with different types of transition metals. Proof was derived from kinetic experiments.

Even without postulating the existence of such charged clusters, the metallic particles in zeolites were shown to be electron deficient. This conclusion was obtained on the basis of different methods. NACCACHE ET AL. [33] derived this electron deficiency in PdY zeolites from the shift towards higher frequencies of the CO vibration observed in i. r. spectroscopy. CHUCIN ET AL. [70] utilized the same technique on a series of PdY zeolites chemically treated (by Al extraction) in such a way that an increasing number of Lewis sites was created. The electron deficiency of the metal was explained on the basis of electron donation to these Lewis centers. Increased sulphur resistance in catalytic experiments was attributed to this electron deficiency.

Electron deficiency of Pt particles in Y zeolites was also observed by VEDRINE ET AL. [71] in X-ray photoelectron spectroscopy. They also arrive at the conclusion that Pt aggregates associate with Lewis acid sites, and that electron deficiency arises from electron donation from the metal to the zeolite lattice. The particle size ($\cong 20 \text{ \AA}$) did not influence this property.

Alloy formation

Several attempts have been reported to produce alloys by reducing zeolites which contain different types of reducible cations. Ni—Cu, Ni—Cd, Ni—Ag Y zeolites were treated at 500 °C with hydrogen [73]. In the case of Ni—CuY alloy formation was demonstrated using magnetic methods, while no direct evidences for the formation of alloys was given for the other systems.

MINACHEV ET AL. [74] investigated the reduction of Ag—CuY, Cu—NiY and Co—NiY zeolites using XPS. From the changes in the valence band spectra they concluded that the most mobile metal migrates towards the external surface before the other. They also concluded that there is an interaction between Ag and Cu but this is not further characterized. For the Cu—Ni and Co—Ni zeolites it was difficult to obtain unambiguous evidence suggesting the formation of alloys.

JACOBS (unpublished) investigated a few mixed zeolite systems (CuZnY, CuAgY) by the TPR method. He found that the behaviour of these elements in mixture was not different from that in the homo-ionic zeolites. Therefore, alloy formation, as reported by REMAN [73] is probably occurring at the external surface. Indeed, the evidence from magnetic measurements can only be obtained with particles too large to be inside the zeolite.

ROMANOVSKI [75] performed a more detailed magnetic study of the Cu—Ni/Y system. He followed the changes in magnetization during sintering at 450 °C as a function of time for several Cu contents. The systems were previously dried at 350—380 °C. The changes in magnetization were due to two processes going on during sintering: diffusion from the highly dispersed state into crystals at the external surface and homogeneization of the metal phase at the outside of the zeolite crystal. This work also leads to the conclusion that alloy formation occurs as a secondary phenomenon outside the zeolite. A proof of the formation of mixed metal particles inside the zeolite pores has not been produced till now.

Conclusion

The preparation of metallic clusters in zeolites has, in a very short time, stimulated a large amount of research and this is likely to increase. Insufficient data are available for a systematic understanding of the redox behaviour of transition metals and of their complexes in different types of zeolites.

Sintering of the metal phase and agglomeration of large particles outside the zeolite was reported as the general rule, even at low and moderate temperatures. Satisfactory methods to improve the stability of metal particles inside the zeolites must still be found.

Characterization of metal particles inside the zeolites is not an easy task and more work is needed. Gas adsorption experiments fail if bidisperse systems are available, and physical techniques to measure properties of ultra small particles inside the zeolite cavities are still insufficiently understood.

The electronic properties of ultra small metal particles inside the zeolites are probably different from those of larger clusters on the classical amorphous supports. It seems worthwhile to look for special catalytic properties of zeolites loaded with ultra small metal particles.

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