SPECTROSCOPY APPLIED TO ZEOLITE CATALYSIS

By

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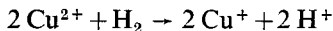
Introduction

The remarkably broad and rapid development of works dealing with zeolite is obviously due to the diversity of the discipline. Because of the diversity of the problems existing in the zeolite science it appeared important to have effective and fruitful communication among the different branches. During the past years several workers from various origins have joined their efforts for a better understanding of the phenomena occuring in zeolites. It is not necessary to recall the important part taken in this field by the catalytic reaction. However it must be noticed that a better correlation between the catalytic activity and/or selectivity and the structure and the nature of active sites was obtained when the parameters interferring in the hydrocarbon transformation have been defined precisely. The numerous papers already published have shown that spectroscopic techniques are potentially of great value for the investigation of exchanged zeolites and almost indispensable for the unambiguous identification of the active sites of the localization, oxidation state and electronic structure of the exchanged cations and of the chemical changes occuring during the activation of the zeolites. Indeed much of the rapid progress in zeolite chemistry can be attributed partially to the increased works dealing with characterization of the material and also to the wide-spread availability of equipments. The usual chemical and spectroscopic techniques employed up to now were elemental analysis, infrared spectroscopy, X-ray crystallography, electron spin resonance, nuclear magnetic resonance, optical spectroscopy and more recently ESCA technique. Several well referenced reviews have already been published [1—6]. In the recent ACS monograph "Zeolite chemistry and catalysis" edited by RABO [7] the reader will find most of the spectroscopic data concerning zeolites. In view of the variety of outstanding reviews published we have the feeling that our contribution at this meeting will be more fruitful if we develop few examples where unusual chemical processes were found in the study of zeolites and where new applications for zeolites have been developed. The emphasis here will be on the way in which informations of chemical interest can be extracted from various spectroscopic techniques. No attempt will be made to give exhaustive data. Two major topics will be reviewed in the present report: redox behaviour of transition metal ions in zeolites along with the interaction of the metallic component with the carrier in zeolite-supported metal catalysts and solid solvent effect of the zeolite matrix for synthesizing or/and immobilizing metal complexes within the zeolite framework.

Redox behaviour of metal ions

Chemical reduction of transition metal ions

More than a decade ago RABO and COWORKERS [8] have shown that univalent nickel ions can be formed and stabilized within the zeolite framework by heating exchanged $Ni^{2+}Y$ zeolite with sodium metal vapor. The presence of Ni^+ ions, which have a $3d^9$ electronic configuration was demonstrated by esr and optical spectroscopy. Since the esr parameters of Ni^+ ions depend strongly on the local crystal field, the analysis of the esr parameters of Ni^+ ions within the zeolite has led these authors to conclude that for a low nickel content Ni^+ ions were essentially localized in S_I sites while for a high nickel loading Ni^+ ions were present both in S_I and S_{II} sites. The interesting finding was that univalent nickel ions were chemically and thermally more stable toward further reduction or disproportionation into nickel metal when they are located at S_I sites. This stabilization effect was ascribed to lower mobility of both nickel ions or atoms in S_I than in S_{II}. Hence one should expect that, in general, hidden ions or atoms in S_I will be more stable toward reduction and/or aggregation than surface species in S_{II}. As it will be shown later, the influence of cation localization or their reducibility and aggregation, conclusively established for nickel, gave reasonable explanation for the various metal dispersions obtained when the metal ions exchanged zeolites were thermally treated at different temperatures before hydrogen reduction.

Further investigations on the formation of univalent nickel ions within Y zeolite have been performed. Generally esr, optical spectroscopy and infrared techniques were used to identify Ni^+ ions. It has been shown that $Ni^{2+}Y$ zeolite contacted with NO at room temperature gave esr signals assigned to Ni^+ ions [9—10]. The formation of such species results from the transfer of the odd electron from NO to a d orbital of Ni^{2+} ion. The formation of Ni^+ NO^+ species was further proved by the presence of an ir band at 1892 cm^{-1} form the nitrosyl group [10]. It is known that the stretching frequency of the N—O bond reflects sensitively the change of electron density along the N—O bond. Since Ni^+ was formed by the removal of the odd electron of the antibonding π^* orbital of NO molecule followed by a π back-donation from the nickel to the π^* orbitals of NO one should expect a shift of v_{NO} with respect to the free NO. Similarly NO_2, known for its high oxidizing properties, is able to reduce Ni^{2+} within the zeolite framework, into Ni^+ as shown by esr and ir studies [10]. Furthermore NO or NO_2 adsorption has been used to reveal the presence of Cr^{2+} ions in H_2-reduced $Cr^{3+}Y$ zeolites. Indeed upon NO or NO_2 adsorption on these samples a strong esr signal, attributed to Cr^+ having a low spin d^5 electronic configuration, was observed. The ir spectra of Cr^+ NO^+ and Cr^+ NO_2^+ complexes presented bands at respectively 1895—1780 cm^{-1} and 1580, 1410, 1370 cm^{-1} due to the NO^+ and NO_2^+ groups [10]. The most interesting feature of these studies is that they reinforce the generally accepted fact that zeolites possess high polarizing and ionizing properties which could radically affect the electron affinity of the transition metal ions within the zeolite toward a substrate and/or the ionisation potential of the substrate. Thus the zeolite framework would facilitate electron transfer reactions. With respect to these properties the zeolites have been viewed as a "solid electrolytic solvent" [8—9]. This property is responsible for the ionization of water molecule into OH^- and H^+ by the zeolites as well for the occlusion of salts such as NaCl

in the form of Na^+ Cl^- [9]. Other workers [11—12] have reported the formation of Ni^+ ions resulting from the reduction by hydrogen of NiCaY zeolite. Univalent nickel ions were identified mainly by means of uv, optical spectroscopy esr and infrared. It was shown that after dehydration of the zeolite both Ni^{2+} and Ca^{2+} compete for S_I sites, thus for a high nickel loading Ni^{2+} ions occupy S_I and S_{II} sites. CO could adsorb on Ni^{2+} in S_{II} sites to give a ν_{CO} infrared band at 2215 cm^{-1}. Upon hydrogen reduction at about 200 °C Ni^+ ions were formed as revealed by the appearance in the uv spectrum of bands at 13 500 and 29 500 cm^{-1} assigned to d—s transitions from the ground state d^9 to the excited state $d^8 s^1$ and one band at 4500 cm^{-1} attributed to d—d transition of Ni^+ ions. With the use of esr it was confirmed that Ni^+ was formed. This ion forms readily a $Ni^+(CO)_x$ adduct. The structure of the Ni (I)-carbonyl adduct was determined by ir and esr. The ir spectrum of this species showed two bands at 2140 and 1930 cm^{-1} which have been attributed respectively to the symmetric and antisymmetric ν_{CO} stretching vibrations for $Ni^+(CO)_2$ species. Furthermore the esr signal of this species enriched with ^{13}C was interpreted as resulting from the interaction of the unpaired electron with two ^{13}C nuclei which confirms the structure $Ni^+(CO)_2$ for the nickel carbonyl species. MINACHEV et al. [13] have also shown using ESCA technique the formation of Ni^+ ions in Ni^{2+}Y zeolite reduced by hydrogen. Transition ions exchanged zeolites have been used as catalysts for reactions such as oxidation, isomerization, oligomerization of olefins etc. Satisfactory correlations between the catalyst and the catalytic activity may be obtained if the structure of the active site is well understood. Thus it is necessary to investigate the properties of the material subjected to treatment with CO or hydrogen. Copper exchanged Y zeolites have been extensively investigated with regard to the reduction of Cu^{2+} ions. NACCACHE and BEN TAARIT [14] have shown that the esr signal intensity of Cu^{2+} in Cu^{2+}Y zeolite decreased upon treatment of the sample with hydrogen at 500 °C. The kinetic data concerning the disappearance of Cu^{2+} follow a second order rate law with respect to Cu^{2+} concentration. Furthermore upon H_2-reduction ir bands at 3650 and 3540 cm^{-1} appeared and they were removed by a subsequent adsorption of pyridine to give the characteristic pyridinium bands at 1630, 1540 and 1488 cm^{-1}. Reoxidation of the reduced sample produced only CuO. It has been concluded that Cu^{2+} ions are easily reduced by hydrogen at high temperature with the subsequent formation of large copper crystallites which migrate outside the cavities. Simultaneously Brönsted acid sites were formed. The following scheme for reduction was suggested [14]
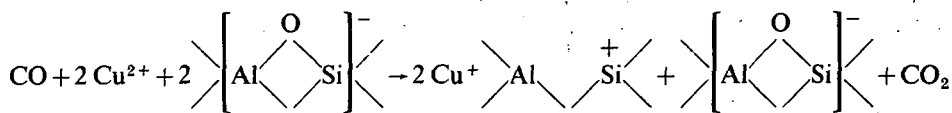
$$2\,Cu^{2+} + H_2 \rightarrow 2\,Cu^+ + 2\,H^+$$

or

$$(Cu^{2+}\!-\!\!O^{2-}\!\!-\!Cu^{2+}) + H_2 \rightarrow 2\,Cu^+ + H_2O$$
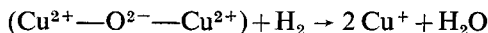
followed by $2\,Cu^+ + H_2 \rightarrow Cu$ metal $+ 2\,H^+$.

In contrast reduction by carbon monoxide generated cuprous ions Cu^+ as evidenced by the disappearance of Cu^{2+} esr signal and by chemical analysis. Furthermore in contrast with H_2-reduction, CO-reduction produced Lewis acid sites evidenced by ir bands at 1620, 1488 and 1451 cm^{-1} upon pyridine adsorption, attributed to pyridine coordinatively bonded to tricoordinated aluminium atoms, and by the formation

of positive radicals when anthracene is adsorbed on the CO-reduced sample. The reduction process may be [14]

$$CO + 2\,Cu^{2+} + 2\,\Big\rangle\!\!\Big[Al\diagdown\diagup_{O}^{}\diagdown\diagup Si\Big\langle\Big]^{-} \rightarrow 2\,Cu^{+}\,\Big\rangle Al\diagdown\diagup\overset{+}{\diagup} Si\Big\langle\ +\ \Big\rangle\!\!\Big[Al\diagdown\diagup_{O}^{}\diagdown\diagup Si\Big\langle\Big]^{-} + CO_2$$

A similar approach has been employed by MAXWELL and DRENT [15] to study the reduction of Cu^{2+} exchanged faujasite with butadiene and ammonia. It was shown that on reduction by butadiene at 100 °C the color of the sample initially green-blue turned white. Simultaneously the esr Cu^{2+} signal decreased. Phosphorescence spectra in the excitation mode showed a band at 390 nm assigned to Cu^{+} ions. Thus a direct proof of the formation of Cu^{+} was obtained. Kinetic studies of Cu^{2+} disappearance again indicated a second order rate law for Cu^{2+} reduction. Furthermore it was shown that the second-order rate constant decreased when the copper exchanged zeolite was dehydrated at increasing temperature. Since it is known that Cu^{2+} ions migrate toward hidden S_I sites [16] as the dehydration temperature increases it was concluded that Cu^{2+} located in the supercages are the more reactive toward reduction. Same conclusions have been reached by JACOBS, UYTTER-HOEVEN et al. [17]. Their kinetic results strongly support the general trend: the reducibility of metal ions within the zeolite framework is mainly determined by their location. Cations localized in hidden sites, S_I, $S_{I'}$ are less reducible than those in S_{II} sites.

Zeolites have been used as carriers to prepare highly dispersed supported metal catalysts. Again it was observed that the location of the cations before the reduction plays an important role. For example it was shown [18] that in Pt^{2+} exchanged Y zeolites thermally treated at 350 °C, almost all the Pt^{2+} ions were localized in the supercages, H_2-reduction leads to the formation of metal particles of about 10 Å diameter. In contrast, if the sample was heated up to 650 °C prior to reduction, X-ray analysis indicated that Pt^{2+} ions have migrated to the sodalite cages, and after H_2-reduction about 75% of the platinum atomically dispersed within the sodalite cages, and only a relatively small amount of the platinum was found in the form of metal particles and available for reactions. The implication of all the results described herewithin is that both the mobility and the reducibility of cations in the sodalite cages or in the hexagonal prisms are low. Thus one should avoid to have the active precursor cations in these sites when high dispersion and accessible particles are desirable. A useful way to achieve this goal would be to exchange first the Na^{+} by unreducible cations such as Ca^{2+}, Ba^{2+}, Mg^{2+}, La^{3+} etc. showing a strong preference for S_I and $S_{I'}$ sites and then to introduce the active component such that it will remain in the supercage.

Selfreduction of transition metal ions

It is now well accepted that the very strong electric fields present in zeolites are responsible for the ionization of water by multivalent exchanged cations. There are enough experimental evidences to state that the exchanged zeolites activated at moderate temperatures contain $Me^{n+}(OH)_x$ groups and acidic OH. The thermal decomposition *in vacuo* of transition metal ion exchanged zeolites very often led to the

reduction of the cations. MINACHEV et al. [13] using X-ray photoelectron spectroscopy have unambiguously shown that cobalt, iron, nickel, silver and palladium cations in zeolites were partially reduced during the thermal treatment in vacuo at high temperature. In general the reduction has been attributed to the presence of undesirable hydrocarbons adsorbed on the zeolite surface. Although adsorbed hydrocarbons may effectively act as reducing agents it appears now that H_2O molecules were involved in the reduction process. In the present section we have selected a few studies because of their relevant contribution to the role of water in the reduction process.
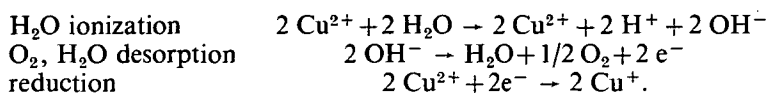
MORICE and REES [19] have many years ago shown that dehydration of $Fe^{3+}Y$ zeolite produced ferrous ions. Later GARTEN et al. [20] used Mössbauer spectroscopy to investigate the reversible oxido-reduction of iron zeolite and the effect of water on the chemical states of iron. Starting from $Fe^{2+}Y$ zeolites they showed that the Mössbauer spectrum of the Fe^{2+} ions present in the dehydrated sample changed drastically when the zeolite was calcined at 673 K in dry oxygen. The new spectrum was ascribed to $Fe^{3+}-O^{2-}-Fe^{3+}$ groups resulting from the oxidative insertion of one oxygen atom between two Fe^{2+} ions. This suggestion was further proved by quantitative measurements of adsorbed oxygen which gave O:Fe ratio 1:2. Water adsorption resulted in the hydrolysis of $Fe^{3+}-O^{2-}-Fe^{3+}$ into $2\ Fe^{3+}(OH)^-$. Upon dehydroxylation at high temperature oxygen gas was produced. Mössbauer results indicated that ferric ions were reduced to ferrous ions according to the following equations

$$2\ Fe^{3+}(OH)^- \rightarrow 2\ Fe^{2+} + H_2O + 1/2\ O_2$$

$$2\ Fe^{3+}(OH)_2^- \rightarrow Fe^{2+}-O-Fe^{2-} + 2\ H_2O + 1/2\ O_2.$$
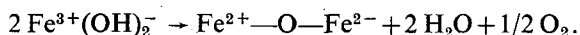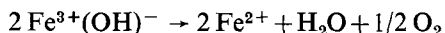
The formation of bridged species in Y zeolite has been suggested by several authors. This type of auto-reduction prevails for Cu^{2+} exchanged Y zeolite. JACOBS et al. [21] have demonstrated that reduction occured during the calcination of $Cu^{2+}Y$ in vacuo. Several spectroscopic techniques have been used. Infrared spectra of CO and CO_2 adsorbed on copper ions are indicative of the oxidation state of the ions since CO adsorbed on cuprous ions gives a stretching vibration at $2180\ cm^{-1}$ while CO_2 adsorbed by ion-dipole interaction on cupric ions gives an ir band at $1370\ cm^{-1}$. Thus the fact that upon dehydration at increasing temperature there is a decrease of the intensity of the $1370\ cm^{-1}$ band and an increase of the $2180\ cm^{-1}$ band one could conclude that Cu^{2+} ions were reduced to Cu^+ ions. Furthermore the ir spectra of pyridine and dimethylpyridine adsorbed on dehydrated samples were indicative of the formation of true Lewis acid sites. The formation of Cu^+ ions was proven by the appearance of a band near 400 nm in the phosphorescence spectra characteristic for Cu^+ ions, this band disappearing by reoxidation at 823 K. Finally these authors detected by mass-spectrometry analyses the presence of oxygen in the products evolved during the calcination at high temperature. All these results again indicate in agreement with the above statement that transition metal ions within the zeolite framework can be reduced during the dehydration in vacuo, oxygen is removed from the lattice with the subsequent formation of true Lewis sites.

Following the same experimental trend as those described above, KASAI and BISHOP reported that zeolites possess the remarkable property to decompose water into oxygen and hydrogen, when they are exchanged by suitable cations, in a two-way thermochemical cycle. Their studies started from the observation, by esr

technique, that the esr signal intensity of Cu^{2+} in copper exchanged mordenite-type zeolite decreased by about one half when the sample was outgassed above 573 K. Mass spectroscopy analyses of the uncondensable gas desorbed during the thermal treatment revealed the presence of oxygen. On the basis of these results they suggested that Cu^{2+} ions were reduced to Cu^+ ions by water molecules as follows: [22]

H_2O ionization $2\,Cu^{2+} + 2\,H_2O \rightarrow 2\,Cu^{2+} + 2\,H^+ + 2\,OH^-$
O_2, H_2O desorption $2\,OH^- \rightarrow H_2O + 1/2\,O_2 + 2\,e^-$
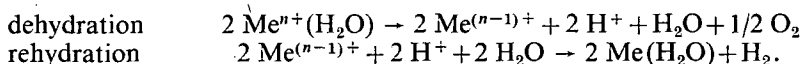reduction $2\,Cu^{2+} + 2e^- \rightarrow 2\,Cu^+.$

Since cuprous ions were reoxidized to cupric ions at room temperature only if oxygen and water are both contacted with the sample one could conclude that following the equation:

$$H_2O + 1/2\,O_2 + 2\,Cu^+ \rightarrow 2\,Cu^{2+}\,OH^-$$
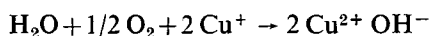
the reduction and oxidation by water form only oxygen. However, since the reduction potential for

$$H^+ + e \rightarrow 1/2\,H_2$$
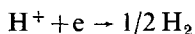
is $E^\circ = -0.414$ V, they concluded that multivalent cations in zeolites for which the reduction potential of the halfcell reaction $Me^{n+} + e \rightarrow Me^{(n-1)+}$ is more negative than -0.414 V will be reoxidized by water, hydrogen being generated. Indeed, they found that oxygen evolved during dehydration *in vacuo* of Cr^{3+} exchanged mordenite and hydrogen by rehydration of the dehydrated sample. Similar results were obtained on In^{3+} exchanged mordenite, the reduction potential for In^{3+}/In^{2+} cell being -0.49 V. The following equations summarize the water decomposition

dehydration $2\,Me^{n+}(H_2O) \rightarrow 2\,Me^{(n-1)+} + 2\,H^+ + H_2O + 1/2\,O_2$
rehydration $2\,Me^{(n-1)+} + 2\,H^+ + 2\,H_2O \rightarrow 2\,Me(H_2O) + H_2.$

It is interesting to note that the two-step decomposition of water is associated with the polarization of adsorbed water molecules by the electric field. Since, in general, it is suggested that the unshielded cations in the zeolite are responsible for the intense electrical fields, one should except a more pronounced effect with mordenite than with faujasite type zeolites. This general trend has been observed for palladium exchanged zeolites [23—24]. Unfortunately the products evolved during the dehydration process were not analyzed. $[Pd^{2+}(NH_3)_4]$ exchanged zeolite containing about 12.5 Pd^{2+} ions was deammoniated and subsequently dehydrated *in vacuo* at 773 K. Both *esr* measurements [23] and ESCA analysis [25] indicated that almost all the palladium ions were in the 2+ oxidation state. By *esr* a small signal attributed to Pd(III) ions was found. In contrast mordenite type zeolite exchanged with $[Pd^{2+}(NH_3)_4]$ showed after dehydration *in vacuo* at 773 K a very strong esr signal with 2-g-values at $g_{\parallel} = 2.97$, $g_{\perp} = 2.146$ unambiguously assigned to Pd(I) ions [24]. These findings imply that, as stated above, mordenite type zeolites are intrinsic favorable materials for auto-reduction of the exchanged cations. The mechanism suggested for copper exchanged zeolites should also prevail for Pd^{2+}-zeolites.

Metal zeolite interaction in metal supported zeolite catalysts

RABO *et al.* [25] have reported that atomically dispersed platinum catalysts may be obtained by hydrogen-reduction of Pt^{2+} exchanged Y zeolites. Since this work, several papers concerning the method of preparation, the metal dispersion and the catalytic properties of these materials appeared in the literature. These materials showed unusual catalytic behaviour [25—28] which was ascribed to the metal-zeolite interaction. One type of interaction which was frequently invoked was "electron transfer interaction" between the metal and the zeolite carrier [26, 29]. Recently it has been tempted to obtain, using spectroscopic techniques, direct proofs on the possible interaction between the metal and the zeolite. In the next paragraph the various phenomena occuring during the reduction process will be discussed.

The mechanism of reduction of palladium exchanged Y zeolite was investigated by ir spectroscopy [23]. $Pd^{2+}(NH_3)_4Y$ zeolite thermally treated at 773 K showed weak ir bands in the OH stretching region. At room temperature about 60% of the palladium was reduced into Pd(0) and Pd(I) by hydrogen. Monovalent palladium ions were revealed by *esr* since Pd(I) has a $4d^9$ electronic configuration and hence is paramagnetic. Infrared spectra of the H_2-reduced samples showed two intense bands at 3635—40 and 3540—45 cm^{-1}, the intensity of which increased with the reduction temperature up to 473 K. Above 473 K and in a wide temperature range these bands remained unchanged [30]. It was concluded that Pd(II) ions were almost completely reduced by hydrogen at 200 °C with the subsequent formation of Brönsted acid sites following the reaction

$$(Zeol)_2Pd^{2+} + H_2 \rightarrow Pd(0) + 2\,Zeol\,OH.$$
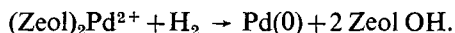
Using infrared spectra of pyridine adsorbed on reduced samples PRIMET and BEN TAARIT [30] have determined the state of the zeolite surface. They stated that the 8a vibration mode of adsorbed pyridine would appear at 1620—30 cm^{-1} for pyridine adsorbed on Lewis sites and at 1595—1610 cm^{-1} for pyridine coordinated to palladium atoms. The presence of a band at 1605 cm^{-1} (8a) and 1452 (19b) upon pyridine adsorption on Pd Y samples reduced under mild conditions (298—473 K) led these authors to suggest that atomically dispersed palladium atoms were formed and may give a Pd(0)-pyridine complex. Since the band at 1605 cm^{-1} strongly decreased as the reduction temperature increased up to 773 K provides strong evidence that isolated palladium atoms aggregate to form palladium metal particles. MINACHEV *et al.* [31] have shown that heating $Pt^{2+}(NH_3)_4$—NaY zeolite *in vacuo* at high temperature removed NH_3 ligands and simultaneously produced Brönsted acid sites as evidenced by the appearance of an infrared band at 3657 cm^{-1}. Furthermore a band at 2120 cm^{-1} assigned to Pt—H$^-$ hydrido complex was formed. The hydrido platinum complex was destroyed *in vacuo* at about 523 K. They concluded that Pt^{2+} cations were reduced during the thermal treatment *in vacuo*. Complete reduction of the platinum was obtained in the presence of hydrogen at 673 K. DALLA BETTA and BOUDART [26], FIGUERAS *et al.* [29] have concluded that the enhancement of the catalytic activity of zeolite-supported platinum or palladium was probably due to electron transfer between the metal and the zeolite. RABO *et al.* [25] have observed an increased sulphur resistance in Pt—CaY catalyst which was related to the atomic dispersion of the metal in the zeolite. There is little doubt that zeolite-supported metal catalysts behave differently from conventional metal catalysts. The question is what is the nature of

the metal-zeolite interaction. Several spectroscopic techniques were recently used to try to answer this question.

In a previous publication [32] we have suggested that Pd(1) ions formed by hydrogen reduction at 297 K of $Pd^{2+}NH_4Y$ exchanged zeolite resulted from the formation of atomically dispersed Pd(0) which interact with Lewis acid sites, one electron being transferred to the carrier following $Pd(0)+$ Lewis site $\rightarrow Pd^{+}+e^{-}$ Lewis site. However further experiments carried out on these systems have shown [33] that:

i) Pd^{+} esr signal disappears when the sample which has been reduced by hydrogen at 270 K is outgassed at 573 K and reappears by a subsequent adsorption of hydrogen. The cycle may be repeated several times.

ii) The type of zeolite used as carrier (NaX or NaY) and the number of Lewis sites present had no effect on the number of Pd^{+} formed on samples with the same palladium loading.

iii) Reduction at high temperature removes completely the Pd^{+} esr signal this phenomena was attributed to the aggregation of atomically dispersed palladium atoms. From these results we are now tempted to conclude that a better explanation for the formation of Pd^{+} is that hydrogen reacts with Pd^{2+} ions to give atomically dispersed Pd(0) which in turn could interact with hydrogen to form palladium hydrido complex Pd H^{+} similarly to Pt—H^{+} [31]. However another explanation might be suggested from the results of CHUKIN *et al.* [34]. These authors used HY and dealuminated Y zeolite forms. These samples dehydrated at 673 K showed infrared bands in the OH stretching region respectively at 3650—3550 and 3640—3550 cm^{-1}. The small v_{OH} shift ($10 cm^{-1}$) to lower frequencies observed, in the case of dealuminated zeolite was ascribed to a stronger proton donor or electron acceptor properties of the OH groups in deal-HY zeolite. When these samples were exchanged with $Pd^{2+}(NH_3)_4$ complex and then activated at 573 K, a strong decrease of the 3640 cm^{-1} band in deal-HY zeolite was observed while no change occured with the original HY sample. They concluded that upon thermal treatment of the palladium exchanged zeolites $Pd^{2+}(NH_3)_4$ complexes were decomposed and that the evolved NH_3 acted as a reducing agent leading to the formation of palladium metal. Pd metal would interact with the strongest Brönsted sites present in dealuminated HY zeolite. It resulted a decrease in the number of these OH groups as evidenced by the decrease of the 3640 cm^{-1} *ir* band. It was suggested that an electron transfer from the metal to the more acidic OH groups has occured with the formation of a charge transfer complex $Pd^{+\delta}...^{-\delta}HO$-zeolite. These palladium atoms interacting with strong acidic OH groups would be electron deficient and thus less sensitive to sulphur poisoning [34]. Electron transfer between metal aggregates and the zeolite carrier has been evidenced by infrared spectroscopy and ESCA using CO as a probe and by esr of adsorbed hydrocarbons. It is well known that the v_{CO} frequency of CO adsorbed on an atom is very sensitive to the charge density around the atom. CO adsorbed on zeolite supported palladium aggregates gave v_{CO} infrared band around 2100 cm^{-1}, while this band appeared around 2085—2070 cm^{-1} for CO adsorbed on unsupported or supported conventional palladium catalysts. The shift of v_{CO} to higher frequency in the case of zeolite carrier is due to a lower π-back-donation of *d*-electrons into the CO π-antibonding orbitals. This one could conclude that palladium supported on zeolite is electron deficient compared with Pd supported on conventional carrier. Similar conclusions were drawn by VEDRINE *et al.* [35] from their ESCA and *esr*

results. These authors found an XPS chemical shift of $+1.3$ eV and $+1.4$ eV respectively for Pt 4f and Pd 3f lines in the case of platinum or palladium aggregates supported on zeolite, with respect to bulk metals. Furthermore they studied the electron-donor and electron-acceptor properties of these materials with and without metal by following the formation of positive or negative radical ions upon adsorption of perylene or tetracyanoethylene. It was found that in general the introduction of a metal such as Pt produced a decrease of the number of electron acceptor sites and simultaneously an increase of the electron donor sites. They concluded that Pt aggregates act as electron donors thus poisoning the electron acceptor sites for perylene. This electron transfer form Pt atoms to the carrier would increase the electron density around the electron donor sites of the zeolite thus increasing its reducing properties.

Immobilized metal complexes on zeolite. Zeolites as "solid solvents"
for synthetizing metal complexes

Homogeneous catalysts are in many cases more efficient and more selective than heterogeneous catalysts. In general the reactions take place at much lower temperature but need higher pressure in homogeneous catalysis. One major disadvantage of soluble catalysts is the difficult separation of the products from the catalyst, and the self-aggregation of the active sites which decreases the efficiency of the catalyst. These disadvantages may be overcome by linking the active metal complex on a solid carrier through covalent bonds. The catalyst attached to a non-soluble phase thus would conserve the high activity and selectivity of its soluble counterpart and still maintain the advantage of heterogeneous catalysts. As stated above, generally the metal complex is anchored to a functionalized organic support, the metal complex being coordinatively bonded to the functionalized surface groups. An alternative means for converting homogeneous metal catalysts into heterogeneous catalysts is to introduce the active complex in the intercrystal space of a swelling layer lattice silicate. These materials are made up of silicate layers, the void space between two layers is occupied by exchangeable cations such as Na^+ and water. Thus if one exchanges Na^+ cations with cationic transition metal ion complexes it would be possible to anchor the homogeneous catalysts to the mica-like structure carrier by electrostatic binding. PINNAVAIA and WELTY [36] have introduced by ion exchange Rh_2^{4+} cations in the intercrystal space of the mineral hectorite. Triphenylphosphine reduced Rh_2^{4+} cations into a rhodium (I) triphenylphosphine complex are bound to the silicate lattice by electrostatic forces. As expected the silicate-anchored rhodium catalyst exhibits high catalytic activity for hydrogenation of 1-hexene and no activity for benzene hydrogenation. These findings demonstrate that the rhodium complex immobilized within the layer silicate by electrostatic forces is stable toward aggregation into rhodium metal, known for its high activity for reduction of aromatic hydrocarbons, and that it has preserved its molecular properties. Thus the use of zeolites for immobilizing metal complexes appears very promising since cationic species may be uniformly dispersed within the zeolite framework by ion exchange and furthermore strongly held to the solid by ionic forces. However one of the major disadvantages of zeolites is that in many cases the organometallic complexes are too large to enter the zeolite cavities through the small windows of the material but small enough to fit the di-

mensions of the cavities. Thus it appeared that this difficulty may be overcome if one synthesizes the metal complex directly within the zeolite cavities. In this section we will describe how spectroscopic techniques have been used to characterize such complexes. Examples showing the similitude of the chemistry of the zeolite entrapped species with their soluble analogues will be given. This chapter is intended to provide general and representative cases of the formation of transition metal complexes in zeolites.

Transition metal ion-oxygen adducts in zeolites

The ability of solutions of transition metal salts to adsorb molecular oxygen has been known for many years. It has been shown that a variety of oxygen adducts may form, with or without electron transfer from the metal atom to the dioxygen ligand.
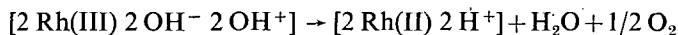
Cobalt-O_2 adducts have been extensively studied. It has been shown that tetra-phenylporphyrin cobalt(II) adsorbs molecular oxygen. The electron configuration of the oxygen complex TPP Co(II)—O_2 approaches Co(III)—O_2^- [37]. Pentaammine Co(II) in ammonia solution was shown to react with molecular oxygen to form a μ-peroxodicobalt ammine complex $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ the oxygen molecule bridging two cobalt ions. HOWE and LUNSFORD [38] have demonstrated that such oxygen adducts were formed when cobalt(II)ammine exchanged Y zeolite were contacted with molecular oxygen. esr spectra of $L_xCo(II)$—O_2 adducts, where L was ammonia, methylamine or propylamine, were interpreted as resulting from the formation of monomeric $[Co^{III}(CH_3—CH_2—CH_2—NH_2)_xO_2^-]^{2+}$ or dimeric $[Co(III)(NH_3)_xO_2Co(NH_3)_x]^{4+}$ oxygen adducts similar to those of analogous adducts in solution. Cobalt exchanged zeolites thus may serve as model systems for reversible oxygen carriers.

Rhodium(II)porphyrin in dimethylformamide was found to adsorb hydrogen at 293 K in a molecular H_2:Rh ratio of 0.5:1 [39]. Rh(II) was thus converted into Rh(I) following the reaction: $2 \, Rh(II) + H_2 \rightarrow 2 \, Rh(I) + 2 \, H^+$. Rh(I) species was found very sensitive to oxygen and was reoxidized with the subsequent formation of water and Rh(II) following the reaction:

$$2 \, Rh(I) + 2 \, H^+ + 1/2 \, O_2 \rightarrow 2 \, Rh(II) + H_2O.$$
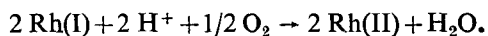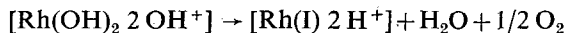
NACCACHE *et al.* [40] have investigated by esr technique the oxygen adsorption on rhodium exchanged zeolites. The sample was prepared by exchanging Na^+ ions with an aqueous solution of $[Rh(III)NH_3)_5Cl]^{2+}$. The rhodium complex is completely decomposed *in vacuo* at 573 K as indicated by the absence of *ir* stretching vibration around 1300 cm^{-1} of NH_3 molecules. *esr* technique revealed the presence of a small number of Rh(II) cations. Furthermore, oxygen was adsorbed reversibly at 77 K with the formation of a paramagnetic species with $g_{||} = 2.015$, $g_\perp = 1.913$. The line broadening of the *esr* spectrum when ^{17}O enriched molecular oxygen was used and the g-values led these authors to conclude to the formation of an Rh(II)—O_2 adduct. Furthermore, simultaneous adsorption of H_2O and O_2 developed an *esr* signal at $g_1 = 2.11$, $g_2 = 2.016$, $g_3 = 1.98$, similar to that of Rh(II)-porphyrin compound [39]. Thus it has been suggested that μ-peroxodirhodium(II) species were formed within the large cavities of the zeolite. From these results it can be suggested that upon thermal treatment *in vacuo* part of the Rh(III) cations undergoes the following
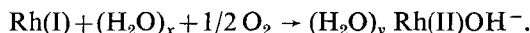
reactions:

$$[2\,Rh(III)\,2\,OH^- \, 2\,OH^+] \rightarrow [2\,Rh(II)\,2\,H^+] + H_2O + 1/2\,O_2$$

and

$$[Rh(OH)_2 \, 2\,OH^+] \rightarrow [Rh(I)\,2\,H^+] + H_2O + 1/2\,O_2$$

O_2 molecule reacts with two close Rh(I), one electron from each Rh(I) ion is transferred to the antibonding π^* orbitals of O_2 to form the μ-peroxo rhodium(II) complex Rh(II)—O—O—Rh(II). Rh(I) is irreversibly reoxidized by H_2O and O_2 to form mononuclear Rh(II) species

$$Rh(I) + (H_2O)_x + 1/2\,O_2 \rightarrow (H_2O)_y\,Rh(II)OH^-.$$

The conversion of rhodium(I) to Rh(II) and the reverse reaction observed in zeolites appeared similar and this emphasizes the "solid solvent" properties of these materials. The great interest of these materials is also based on the fact that the new type of oxygen-adduct, which has not been isolated in solution may be stabilized in zeolite framework. An example is given by palladium exchanged mordenite type zeolite. We have shown in the first paragraph that Pd(I) species were formed when a mordenite type zeolite exchanged with $[Pd(NH_3)_4]^{2+}$ is dehydrated at 773 K *in vacuo*. The *esr* spectrum of this species is characterized by two g-values at $g_{\parallel} = 2.97$ and $g_{\perp} = 2.146$. The adsorption of oxygen at room temperature on this sample [24] resulted in the disappearance of the *esr* signal attributed to Pd(I) and a new signal at $g_{\perp} = 2.05$, $g_{\parallel} = 1.99$ developed. The adsorption of oxygen enriched with ^{17}O ($I = 5/2$) led to a spectrum with two sets of 6 and 11 hyperfine lines attributed to the interaction of the unpaired electron with one ^{17}O nucleus (^{17}O—^{16}O) and two ^{17}O nuclei ($^{17}O_2$) respectively. From the hyperfine splitting $A_{\parallel} = 77$ gauss it was shown that the unpaired electron is almost completely localized in the π^* antibonding orbitals of O_2. It has been suggested that Pd(II)—O_2^- adduct was formed. This interpretation was not unique since the authors proposed an alternative interpretation of the esr spectrum and the possible formation of $[Pd(II)]_3$—O_2^{3-} oxygen adduct. In this work the zeolite appeared again very suitable material for stabilizing unusual complexes which might have interesting catalytic properties.

Chemistry of transition metal ions in zeolites

A particular point of interest of transition metal ions exchanged zeolites is their catalytic property for reactions such as oligomerization of olefins, carbonylation of methanol, hydroformylation of olefins, *etc.*, generally catalyzed by soluble complexes. During the past years several spectroscopic techniques have been used to investigate the structure of various transition metal ion complexes stabilized within the zeolite framework. We intend to present here some of the recent results obtained in this field. Although extensive works on zeolites exchanged with transition metal ions have been reported in the literature less attention has been paid to zeolites exchanged with group VIII metal ions. Group VIII metal complexes are known for their catalytic properties for oxidation, oligomerization isomerization, hydrogenation, hydroformylation, carbonylation, *etc.* We are of the opinion that interesting materials might be obtained by exchanging zeolites with group VIII salts. Indeed, during the recent past years, works have been published which indicated that zeolites loaded with group VIII metal ions can be used as catalysts for the above reactions.

Although the amount of information so far published in this area is limited the results of these studies should stimulate new investigation on the properties and the specificities of group VIII exchanged zeolites. Our purpose is to describe several results showing the great similitude existing between ruthenium or rhodium exchanged zeolites and their homologous complexes in solution.
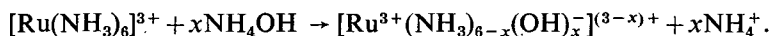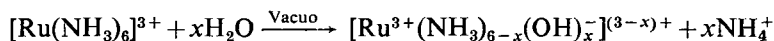
LUNSFORD et al. [41] studied by infrared spectroscopy the formation of dinitrogen ruthenium complexes in Y zeolites. $[Ru(NH_3)_5NO]^{3+}$ exchanged zeolite showed ir bands at 1927 cm^{-1} assigned to ν_{NO} and at 1365 cm^{-1} due to NH_3 bonded to ruthenium cations. Hydrazine treatment resulted in the formation of characteristic dinitrogen stretching band at 2132 cm^{-1}. Simultaneously ir bands at 1885 cm^{-1} due to nitric oxide and at 1460 cm^{-1} attributed to NH_4^+ appeared. These latter two bands were easily removed at 298 K in vacuo. It has been suggested the formation of $[Ru(NH_3)_5N_2]^{2+}$ complexes in a similar way to that proposed in solution [42]. $[Ru(NH_3)_5N_2]^{2+}$ exchanged zeolites showed the same ir feature as those of $[Ru(NH_3)_5NO]^{3-}$ reduced by hydrazine. However this complex was highly unstable since it decomposed in the infrared beam into $[Ru^{3+}(NH_3)_5OH]^{2+}$ following the reaction

$$[Ru^{2+}(NH_3)_5N_2]^{2+}-Y+H_2O \rightarrow [Ru^{3+}(NH_3)_5OH]^{2+}-Y+NH_4^+.$$
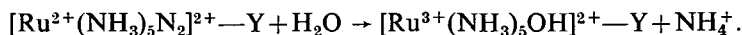
The N_2 ligand may be removed by outgassing and was restored by adding N_2 to the sample, futhermore the formation of NH_3 has been observed. However, experiments performed with $^{15}NO_2$ ruled out that these ruthenium exchanged zeolites may achieve ammonia synthesis.
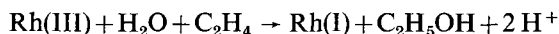
NACCACHE et al. [43] have investigated ruthenium(III) ammine exchanged zeolites by esr and infrared spectroscopy. An aqueous solution of hexaammine ruthenium(III) chloride was used for ion exchange. A white exchanged zeolite was thus obtained wich turned wine-red or purple over a period which depended on the experimental conditions. The sample turned also rapidly wine-red in the infrared beam. The infrared spectrum of the sample degassed at room temperature was characterized by a strong band at 1335 cm^{-1} due to NH_3 ligands and bands at 1460 cm^{-1} and 1930 cm^{-1} attributed to NH_4^+ and NO respectively. These results indicated that $[Ru(NH_3)_6]^{3+}$ underwent significant change in the infrared beam. The esr spectrum of $[Ru(NH_3)_6]^{3+}$—Y zeolite showed an anisotropic line shape with $g_\perp = 2.20$ and an undetectable $g_\parallel$ component. The esr spectrum was considerably broadened at 293 K. Ru(III) has a low spin configuration and in an octahedral field such as in $[Ru(NH_3)_6]^{3+}$ the ground state is $(t_{2g})^5$. The triply degenerate (t_{2g}) orbitals split into a non-degenerate d_{xy} and a doubly degenerate (d_{xz}, d_{yz}) orbital when the spin-orbit coupling is superimposed to the octahedral crystal field. This spectrum was assigned to $[Ru(NH_3)_6]^{3+}$. It was found that $[Ru(NH_3)_5Cl]^{3+}$ in zeolite did not show an esr spectrum even at 77 K as expected since it is known that the π interaction with chlorine ion is stronger than with ammonia and the d_{xz}, d_{yz} molecular orbitals become less stable than the xz orbital which leaves the unpaired electron in a degenerate d orbital. There was a drastic change in the esr spectrum when the sample was outgassed at about 353 K. The sample turned wine-red and it exhibited an esr spectrum with 3g-values at $g_1 = 2.70$, $g_2 = 2.24$, $g_3 = 1.60$. The same esr change occurred when Ru(NH$_3$)$_6$—Y sample was contacted at 298 K with NH$_4$OH. The fact that the esr spectrum has 3 g-components indicates that Ru(III) experienced an orthorhombic crystal field thus it was suggested that the former octahedral crystal field in Ru(NH$_3$)$_6^{3+}$ was

lowered by ligand change. Since the appearance of the 3 g-value *esr* spectrum was always accompanied by the formation of NH_4^+ ions as shown by the appearance of an *ir* band at 1460 cm^{-1} and that basic medium such as NH_4OH accelerated these modifications, it was suggested that NH_3 ligands may be easily replaced by OH^- groups following the reactions:

$$[Ru(NH_3)_6]^{3+} + xH_2O \xrightarrow{\text{Vacuo}} [Ru^{3+}(NH_3)_{6-x}(OH)_x^-]^{(3-x)+} + xNH_4^+$$

$$[Ru(NH_3)_6]^{3+} + xNH_4OH \rightarrow [Ru^{3+}(NH_3)_{6-x}(OH)_x^-]^{(3-x)+} + xNH_4^+.$$

YASHIMA *et al.* [44] recently studied the dimerization of ethylene over nickel or rhodium exchanged Y zeolites. The products formed were mainly 1 and 2-butenes which distribution changes with the reaction time. *Trans*-2-butene formation was favoured with respect to *cis*-2-butene. The catalytic properties of rhodium and nickel exchanged zeolites were modified by changing the activation procedure. The highest activity was achieved when the samples were outgassed at about 673 K. Furthermore H_2-reduction at moderate temperature ($\sim$ 573 K) changes little the activity of the samples while more severe reduction ($\sim$ 773 K) lowered the catalytic activities. The nature of active sites was studied by poisoning experiments and by *esr* and *ir* spectroscopy. It was found that CO poisoned drastically the active sites for ethylene dimerization. Carbon monoxide interacts with NiY and RhY to give *ir* bands at 2070, 2030, 1995 cm^{-1} (Ni) and 2110, 2045 cm^{-1} (Rh) respectively. From these results they concluded that the active sites were highly dispersed zerovalent nickel and rhodium. Although the present results appear consistent, it is not clear how atomically dispersed rhodium or nickel were formed during thermal treatments *in vacuo* of the samples, and homogeneous analogues are not obvious since in general Rh(I) and Ni(I) are generally cited in the literature. Recent studies on rhodium exchanged zeolites may serve for a better understanding of the nature of active sites formed following various treatments of the samples.

Rh(III) salts are active catalysts for the oxidation of ethylene into acetaldehyde. The first step of this reaction involves the reduction of Rh(III) to Rh(I) following

$$Rh(III) + H_2O + C_2H_4 \rightarrow Rh(I) + C_2H_5OH + 2H^+$$

and C_2H_4 coordinates rapidly with Rh(I) to form $Rh(I)(C_2H_4)_2$ complex [45]. NACCACHE *et al.* [46] have investigated the formation of rhodium carbonyl complexes in zeolites. NaY type zeolite was exchanged with an aqueous solution of $[Rh(III)(NH_3)_5Cl]^{2+}$. The sample was examined by XPS. Samples degassed at room temperature showed the $3d3/2$ and $3d5/2$ peaks at 315.7 and 310.8 eV respectively. The binding energy of various Rh(III) salts are close to those found for Rh Y zeolite. Furthermore the Si/Rh atomic ratio derived from ESCA and chemical analysis are about the same. Then one can conclude that the surface composition is identical to the bulk composition. Thus the rhodium complex is homogeneously distributed within the zeolite as one should expect for samples prepared by ion exchange. Thermal treatment at increasing temperature produced a decrease of the Cl/Rh and N/Rh ratios and at about 773 K almost all the NH_3 and chlorine ligands were removed. The interesting feature was that the $3d$ binding energy of Rh in RhY degassed at 773 K was found also at 315.7 and 310.8 eV which suggests that almost all the loaded rhodium remains at 3 + oxidation state. It was noticed that the Rh $3d5/2$ peak was

broadened, this broadening being attributed to the presence of Rh(I). Nevertheless, these results indicate that evacuation at high temperature leaves almost all the rhodium ions at the 3+ oxidation state in contrast with the proposal of YASHIMA *et al.* [44]. The action of carbon monoxide on RhY was also examined [46]. It was found that partially hydrated RhY reacts at 298 K with CO and gives two sharp infrared bands at 2100 and 2030 cm^{-1}, each *ir* band is further splitted. Dicarbonyl rhodium(I) complexes have two infrared bands in the same region which are attributed to the antisymmetric and symmetric vibration modes of CO. Thus it was suggested that Rh(III) in zeolite is reduced to Rh(I) with the concomitant formation of Rh(I)(CO)$_2$ complex. This was further proved by ESCA measurements which showed that the new rhodium carbonyl complex formed within the zeolite presented the 3*d*5/2 binding energy at 308.1 eV which is very close to 308.3 eV found for zeolite supported [Rh(I)(CO)$_2$Cl]$_2$. RhY dehydrated *in vacuo* at 773 K showed the same feature, however it was found that water adsorption accelerated the reduction of Rh(III) by CO. Furthermore CO adsorption and *ir* measurements when performed at 77 K gave *ir* bands at 2172 and 2138 cm^{-1} which slowly decreased as the temperature increased and simultaneously the *ir* bands at 2100 and 2030 cm^{-1} developed. Thus it was concluded that the reduction of Rh(III) by CO is an activated process and at 77 K only Rh(III)—CO complex was formed. The mechanism suggested for the reduction of Rh(III) by CO is
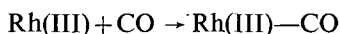
$$Rh(III) + CO \rightarrow Rh(III)—CO$$

Rh(III)—CO complex decomposed by water or hydroxyl groups following

$$Rh(III) + 2\,CO + 2\,OH \rightarrow Rh(I) + 2\,H^+ + 2\,CO_2$$
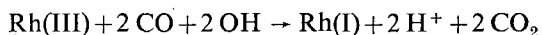
and Rh(I) forms readily in the presence of an excess of CO the dicarbonyl Rh(I) complex entrapped in the zeolite. The evolved CO$_2$ was detected by an *ir* band near 2350 cm^{-1}. The action of carbon monoxide on hydrated Rh(III)Y zeolite appears similar to the reactions occurring in solution [47]. The reductive carbonylation reaction to give Rh(I)(CO)$_2$ may be an interesting precursor in several reactions. Indeed it has been shown by CHRISTENSEN and SCURRELL [48] that Rh(III) exchanged X zeolite is active and selective for the carbonylation of methanol, methyl iodide was used as promoter. The selectivity in acetic acid and methyl acetate was 90%. Ethanol carbonylation was also performed however the selectivity decreased at high temperature, this was associated with the conversion of ethanol into ethylene and diethylether. It appeared that rhodium exchanged 13 X zeolites are more active than other heterogenized rhodium catalysts. This work confirms the feasibility of using group VII metal ion exchanged zeolites as heterogenized homogeneous catalysts. However in the case of RhY, the structure of the embedded rhodium complex efficient for methanol carbonylation is not yet well defined. In general the methanol carbonylation is catalyzed by anionic rhodium complexes such as Rh(CO)$_2$I$_2^-$ while in zeolite cationic complexes were found.

Rhodium carbonyl clusters entrapped in zeolites have also been studied recently. Infrared spectroscopy [49] has shown that when Rh(III) exchanged Y zeolite is treated at 403 K under a pressure of 80 atm of CO:H$_2$ mixture the sample turned red and showed CO stretching vibrations at 2095 (vs) 2080 (sh) 2060 (w) and 1765 (s) cm^{-1}. It was suggested the formation of Rh$_4$(CO)$_{12}$ or Rh$_6$(CO)$_{16}$ clusters within the zeolite

cavities. Similar conclusions were reached by GELIN *et al.* [50]. Zeolite supported $Rh_6(CO)_{16}$ was prepared by sublimation *in vacuo* of $Rh_6(CO)_{16}$ on dehydrated NaY zeolite. The sample has *ir* bands near 2090 (s) 2074 (sh) 2021 (w) and 1830 (w) which are slightly shifted to higher frequencies in comparison with those found for unsupported $Rh_6(CO)_{16}$. CO ligand was removed by outgassing the sample at about 473 K or by reaction with oxygen at 373 K with the concomitant formation of CO_2. The decarbonylated sample heated at 373 K under 100 torr of CO showed two strong *ir* bands at 2098 and 1761 cm^{-1} which were attributed to linear and bridged CO. It was suggested that $Rh_6(CO)_{16}$ first was supported on the external surface of the zeolite since the cluster is too large to enter the cavities through the 8 Å pores. Upon decarbonylation fragmentation of the cluster occurred, and the Rh fragments migrate in the zeolite framework and are stabilized toward aggregation. These Rh fragments reacted with CO at 373 K to form $Rh_x(CO)_y$ clusters containing a limited amount of rhodium atoms. In contrast rhodium metal supported on zeolite prepared by H_2-reduction of Rh(III) exchanged Y zeolite behaves differently. Electron microscopy has shown that the particle size was in the 5—10 Å range [51]. CO adsorbed at 298 K on this sample gave two *ir* bands near 2100 and 2035 cm^{-1} which were assigned to dicarbonyl rhodium species $Rh^{+\delta}(CO)_2$, a band near 2060 cm^{-1} attributed to linear by bonded CO on rhodium metal and bands at frequencies lower than 2000 cm^{-1} due to multibonded CO. The need of higher CO pressures in the case of rhodium exchanged zeolite to form rhodium cluster as shown in [49] as compared with $Rh_6(CO)_{16}$ supported on zeolite [50] is probably due to the formation, by H_2-reduction, of larger rhodium particles, which increases the cohesion of Rh—Rh bonds. The zeolite entrapped rhodium carbonyl clusters were found active and selective for hydroformylation of olefins [49]. 1-hexene was converted into 1-heptanol, 2-methylhexanal and 1-ethylpentanal.

In conclusion these few examples have shown clearly the possibility of conducting with transition metal ions exchanged zeolites, reactions which are generally performed with homogeneous catalysts.

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