Plenary Paper— Catalysis

RECENT DEVELOPMENTS IN CATALYSIS BY ZEOLITES

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INTRODUCTION

The catalysis of hydrocarbon cracking, isomerisation, alkylation, hydrogen transfer and related reactions, by zeolites has been extensively studied during the last two decades. Much of the work in this area has been carried out on faujasite and mordenite-type zeolites in their acidic forms. As a result of the enormous number of studies devoted to this subject a fair understanding of acid-catalysis by zeolites has resulted. Recently several excellent reports have reviewed the subject |1-7| . A characteristic feature of zeolites is their promoting effect in bimolecular reactions and their selectivity due to the shape of the channels. The shape-selectivity has also been reviewed recently |8-10|.

More recently among the many branches of zeolite chemistry three topics have attracted the attention i.e.

i) Since the discovery of a new class of zeolites called ZSM-5 or "pentasil" at Mobil Laboratories interest has been refocussed on shape selectivity catalysis by small pore zeolites of the mordenite or pentasil-type.

ii) "Heterogeneized" homogeneous catalysts have received increasing study. The use of zeolite to attach soluble catalysts appears very promising and has resulted in a new class of catalysis by zeolites.

iii) Well dispersed metal catalysts have been obtained on zeolite carriers. Some unexpected catalytic properties have been unveiled. Furthermore H-form zeolite supported metal showed interesting bi-functional catalytic properties.

In this report we will consider these three topics. Much of the discussion which follows will be related to the more recent available data.

SHAPE-SELECTIVE ZEOLITES.   Factor influencing the activity and
selectivity.

     Since the pioneer work of Weisz and Frilette |11| , shape-
selective zeolites have been studied intensively and the great interest
of this aspect of catalysis by zeolites recognised. Recently Csicery
has reviewed the most important features of shape selectivity |10| .
In heterogeneous catalysis the reaction proceeds through several steps:
diffusion and adsorption of the reactant, formation of the activated
intermediate, reaction and finally desorption and diffusion of the
product. The shape-selectivity principle is based on these different
steps and results in three major types of shape-selectivity.
     i) Since the active centres are located within the zeolite cavi-
ties or channels, the reactant should diffuse within the channels
through the zeolite pores. Therefore only molecules which size is small
enough will penetrate the cavities and thus will interact with the
active site. This type of selectivity is due to the sieving properties
of zeolites. For sample as a result n-paraffins are selectively cracked
in the presence of branched paraffins.
     ii) When the catalytic reaction within the pores or channels pro-
duces large or bulky molecules the slow diffusion of the product out of
the small zeolite pores might hinder the reaction. Indeed this low
diffusion will increase the contact time which either will allow a fur-
ther transformation of the product into a less bulky one or will degra-
de it totally and the residue acts then as a poison for the active
centre. This type of shape-selectivity has been called "Reverse mole-
cular size selectivity" |10| .
     iii) The intermediate species might not be formed due to a lack
of space within the channel or cavity. This also gives rise to shape-
selectivity. At low conversion, the isomerisation of methylethylben-
zene to trialkylbenzene in H-mordenite is inhibited because the forma-
tion of the diphenylmethane intermediate will require more space than
available in the mordenite channel |12| .
     The above outline suggests that the selectivity can be controlled
by selecting the zeolite having adequate pore size.
     The faujasite-type zeolite framework is composed by a system of
cavities. The largest cavity "supercage" has a free diameter of about
1.2 nm and a 12-oxygen window of 0.72 nm. In general these relatively
large pore zeolites do not show shape-selective properties.
     The most interesting shape-selective behaviour were found with
small pore zeolites such as mordenite and recent Mobil ZSM-5 zeolites.
These zeolites have channels which are interconnected. The channels,
in the mordenite framework, are parallel to the |001| and |010| axes.
These channels are straight and the dimensions of their 12- and 8- oxy-
gen windows are respectively 0.67 x 0.7 nm and 0.29 x 0.57 nm. The
structure of the ZSM-5 zeolite has been described recently|13|. Typical
chemical composition is $Na_x Al_x Si_{96-x} O_{192}$ |14| , where x varies in
the range 3-27. The crystal structure consists of an arrangement of
tetrahedra forming five-membered rings (pentasil). One unit consists
of eight pentasil rings. These units are linked through edges forming
chains, and the chains connected to form sheets and finally the three
dimensional structure is obtained by linking sheets. This arrangement
results in a system of channels straight and parallel to the |010|
direction, these 10-oxygen channels having dimensions of 0.54 x 0.56 nm
They are interconnected by channels of 0.51 x 0.55 nm sinusoidal in

the |001|direction.

Therefore the molecular sieve properties of the mordenite and
ZSM-5 zeolites should be attributed to the system of interconnected
channels. The important difference existing between these two materials
is certainly the fact that in mordenite the molecules will diffuse only
in one direction, that corresponding to the 0.67 x 0.7 nm while, in
ZSM-5 they will diffuse along two directions. Thus for molecules whose
critical diameters are in the range of the channel dimensions, mordenite
would act as one dimensional molecular sieve, while ZSM-5 would act as
a two-dimensional molecular sieve.

This family of materials exhibits interesting catalytic properties
for hydrocarbon conversion. Disproportionation of alkylbenzene over
H-form mordenite has shown that 1-methyl-2 ethylbenzene is dispropor-
tionated without the formation of the symmetrical trialkylbenzene |15|
while one should expect that at equilibrium the symmetrical trialkyl-
benzene will be the main component. The 12-membered ring of H-mordenite
is larger than the value given for Na-form. The cross sections of
various alkyl aromatics have been determined |15| and it appears from
these values that the symmetrical trialkylbenzenes have a minimum cross
section of about 0.86 nm. Hence these molecules when formed inside the
channels cannot diffuse out of the 12-membered window. The other trial-
kylbenzene isomers with a minimum cross section of less than 0.82 nm
are able to diffuse out of the pores, the selectivity for the formation
of unsymmetrical trialkylbenzene isomers thus increases. This concept of
shape-selectivity was further completed by the so-called "shape-selec-
tive non-intermediate formation" which is mainly due to the small space
available in the mordenite channels |16|. The absence of 1,3,5-trialkyl-
benzene in the products of dialkylbenzene disproportionation would
result from the impossible formation of the large 1,1-diphenylalkane-
type intermediate in the small space available in the mordenite channels
|16|. These shape-selectivity concepts were further illustrated by the
study of the xylene-disproportionation over H-form mordenite exchanged
by various cations |17|. The catalytic disproportionation of xylenes
is expected to give an equilibrium mixture of the three trimethylben-
zene. It was found that over H-mordenite the selectivity for 1,2,4 tri-
methylbenzene is low. The selectivity was increased by a further exchan-
ge of H-from with Mg, Ni, Co, Zn, Cu ions. Simultaneously the fraction
of 1,3,5 trimethylbenzene decreases. It was concluded that the cations
affect the selectivity by reducing the pore size, which lowers the dif-
fusion of the symmetrical isomer out of the channels, and by decreasing
the space available in the channels so that the formation of the tran-
sition state 1,1 diphenylalkane intermediate is partially inhibited.
Shape selective adsorption has also provided an elegant means for sepa-
ration of hydrocarbon mixtures. Normal paraffins are separated from the
other paraffins by a selective adsorption on Ca-A zeolite |18|. Recently
complete separation of 2-methylpentane and 2,2 dimethylbutane mixture
was achieved by means of shape-selective adsorption on modified morde-
nite |19|. H-mordenite partially exchanged with Sr^{2+} or Ca^{2+} allowed
complete separation of 2-methylpentane and 2,2 dimethylbutane. Accor-
ding to the authors |19| H-ZSM-5 exhibited the same shape-selective
adsorptive properties for 2-methylpentane and 2,2 dimethylbutane.

In the above discussion no discrimination between large and narrow
channel zeolites has been considered. Next we will refocus the discus-
sion on the new zeolites ZSM-5, 11, 21 that Mobil has developed . The
catalytic properties which have been studied much more extensively and

which are of the utmost practical importance, are concerned with methanol conversion to aliphatic and aromatic compounds| 20-26|, selective production of paraxylene |27-28| , olefin aromatisation|29|and hydrodewaxing |30|. The ZSM-5 new type synthetic zeolites have been the subject of several characterization during the last few years, and their properties compared to those of more conventional zeolites. The hydrophobic character of ZSM-5 has been well established and this hydrophobic character is parallel to the hydrophobic property of dealuminated mordenite |31|and silicalite |32|. All Mobil patents concerning these materials point out the high steam stability of ZSM-5. It is also known that mordenites have a relatively good steam stability. The acid strength of the H-form ZSM-5 was investigated by several techniques |33-34| . The infrared results have shown a very close similarity between the acidic OH groups present on H-ZSM-5 and H-mordenite. Furthermore the heats of NH_3 adsorption on H-ZSM-5 and H-mordenite are very close for both samples which indicates that almost similar acid strength characterizes the two catalysts. Cracking of n-hexane has been used as a test reaction for acid catalysts. Quantitative comparison between various acidic cracking catalysts was attained by evaluating the relative first order rate constants for disappearance of n-hexane   . This so called " α test" applied to various H-ZSM-5 zeolites differentiated by various SiO_2/Al_2O_3 ratios showed that the n-hexane cracking rate constant increases as SiO_2/Al_2O_3 decreases |35|. Furthermore it was shown that both H-ZSM-5 and H-mordenite have a high value in comparison with H-Y zeolite. One can conclude that the acidity of H-mordenite and H-ZSM-5 does not differ considerably. The major difference between these two materials is reflected by the rapid aging of H-mordenite in contrast with the high catalytic stability of H-ZSM-5 |35|. This point will be further discussed.

The shape selectivity of the zeolite is directly related to the size of the channels. Further insights into the relationship existing between shape-selectivity and pore dimension are obtained by examining the relative adsorptive properties of zeolites for various hydrocarbons having different critical dimensions. The relative adsorptive capacity showed by various "Pentasil" like-structure materials is found to depend on the SiO_2/Al_2O_3 ratio. Indeed K (n-hexane adsorbed/cyclohexane adsorbed) is found equal to 4.5 for silicalite |32| (trace of aluminium ions), 5.93 and 5.55 for Na ZSM-5 |35| (SiO_2/Al_2O_3 respectively 122 and 60), 2.25 |26|and 3.35|35|for Na ZSM-5 (SiO_2/Al_2O_3 between 30 and 40 ¦. The constraint index (C.I. = log k n-hexane conversion/log k 3 methyl pentane conversion) is also an interesting parameter to differentiate the various catalysts. Constraint index has been determined for several zeolites |26 |. The results are given in the following table.

Zeolites	Erionite	ZSM-5	Offretite	H-mordenite	ReY
Membered oxygen-ring	8	10	12	12	12
dimension of the ring in nm	0.52x0.38	0.54x0.56	0.64	0.67x0.7	0.7
C.I.	38	8.3	3.7	0.5	0.4

These results show that n-hexane is selectivity cracked over Erionite and ZSM-5 while the other zeolites exhibited no shape-selective properties for a mixture of n-hexane and 3.methylpentane. Cracking experiments were extended to other hydrocarbons. For example the conversion of a ternary mixture of n-hexane, 3 methylpentane and 2,3 dimethylbutane was studied |36|. The results were expressed in terms of log $k_{n-hexane}$/log k_{3MP} and log k_{3MP}/log $k_{2,3DMB}$. The data confirmed that amorphous silica-alumina cracking catalyst as well as exchanged Y zeolite exhibit no shape-selectivity for the conversion of n-hexane isomers while erionite and to a lesser extent ZSM-5 are highly shape-selective. The interesting feature of this work is the decrease of the shape selectivity as the temperature of the reaction increases. Over ZSM-5, and below 370°C, n-hexane is cracked about 10 times faster than 3 methylpentane and 100 times faster than 2,3 dimethylbutane while at 500°C the three hexane isomers are cracked at approximately the same rate. The cracking of heptane isomers was also studied |36|. It appears that, "cage effect" was not found in ZSM-5 since the relative rate constants are respectively n-C_7 > n-C_6 > n-C_5 as expected ; furthermore it is possible to differentiate hydrocarbons having a straight chain, a methyl or a dimethyl substitution and finaly branched hydrocarbons which diffusion is activated |36|. The sieving effect of H-ZSM-5 was also illustrated by the rates of benzene and toluene alkylation|36|. While intrinsically toluene is alkylated more easily than benzene over H-ZSM-5 cata lysts the inverse was found. Since both benzene and toluene are readily adsorbed on ZSM-5 zeolite, the authors concluded that alkylbenzene should diffuse much more slowly than benzene, although both molecules have a critical diameter of about 0.63 nm, hence the rate of toluene alkylation being lower than that of benzene alkylation. It was also found that this new class of zeolites promoted the production of para-xylenes with respect to the o - and m-isomers in the catalytic alkylation of toluene. Alkylation of toluene by methanol produced a mixture of the three xylene isomers containing 92 % of paraxylene |27|.

Recently ZSM-5 zeolites were used to convert methanol into gasoline. Since the work performed at Mobil Laboratories, several reports were published, attempting to approach the mechanism of the methanol conversion into aliphatics and aromatics |20-26|. It is generally agreed that the high performance of H-ZSM-5 in the methanol conversion is attributed to its high acidity and to the very peculiar shape, arrangement and dimension of the channels. In this section we do not intend to discuss the various mechanisms already proposed but rather to report the major features which distinguish ZSM-5 from other zeolites in the catalytic conversion of hydrocarbons. We have already pointed out the great similarity existing between the acidity of H-ZSM-5 and that of H-morde-nite for example, thus these two materials should act similarly in the methanol conversion. Indeed it has been shown |37|that methanol was readily converted over acidic mordenite. Similarly H Nu-1 converted methanol into products having the same composition as those obtained over H-ZSM-5 |38|. The major difference between these materials was reflected by the rapid aging of all zeolites used except the series of ZSM-5 which exhibited an exceptionally high stability |20|. The very low aging of ZSM-5 was also observed during the alkylation of aromatics and the cracking of paraffins |36|. It has been suggested previously that one of the major causes of zeolite deactivation which occured during the alkylation of benzene over ReY was the formation of polyalkyl aromatics within the cavities |39|. These bulky aromatic

compounds are too large to diffuse out of the 12-oxygen-rings and
lead to carbonaceous deposits. Radio-tracer studies with faujasite
and mordenite have confirmed the direct role played by aromatics in
the coke formation. These studies were further extended to other zeoli-
tes. The coke yield on several zeolites such as Y, L,mordenite,
ferrierite and erionite was measured and compared to their selectivi-
ties in the conversion of n-hexane and 3-methylpentane |40|. Zeolites,
showing a high $k_{n-hexane}/k_{3MP}$ ratio, such as ferrierite, erionite,
produced less coke than large-pore zeolites (Y, L. mordenite) charac-
terized by a low $k_{n-hexane}/k_{3MP}$ ratio. It is therefore suggested that
there is a direct correlation between the tendency of coke formation
and the structure and/or pore dimension of the channels. Coke yield,
using the radio tracer technique, was found two orders of magnitude
higher on mordenite than on ZSM-5 |41|. We have seen that the composi-
tions of the products from methanol conversion over mordenite, Nu-1 and
H-ZSM-5 in the first minutes of the reaction are very similar, but that
mordenite and Nu-1 deactivate rapidly for the selective formation of
aliphatics and aromatics. This deactivation may be regarded as the
result of coke formation from poly-alkyl aromatics produced during the
methanol conversion. In contrast the low aging rate of H-ZSM-5 is due
to the fact that in the restricted space available within the channels,
polyalkyl aromatics cannot be formed which limits the coke yield. The
great interest of these studies is to have shown distinctly the close
relationship existing between shape selectivity and coke formation.
Such information   is especially valuable because it has allowed a
better understanding of the function of small pore zeolites in shape-
selective catalysis. Further effort should be devoted to this area.
Keeping in mind the fact that restricted space in the channels should
limit the formation of coke, further advances in shape-selective cata-
lysis may perhaps be attained by selectively modifying the pore dimen-
sions of zeolites.

CATALYSIS BY TRANSITION METAL IONS EXCHANGED ZEOLITES

It is well established that zeolites are capable of effecting a
broad range of catalytic reactions. Although the major applications of
zeolites in hydrocarbon transformations are based on acid-form zeoli-
tes, a fairly important body of studies on non carbonium ion type
reactions catalyzed by cation exchanged zeolites have been carried out,
the exchangeable cations themselves being involved in the reaction
pathways. The unique and attractive feature of zeolites is that their
structures offer the possibility of introducing in the lattice exchan-
geable cations, isolated from one another, strongly associated with the
lattice and still possessing available coordination sites potentially
active. In recent years there has been renewed interest in transition
metal ions exchanged zeolites for catalytic applications. This appears
to be the consequence of : i) the large amount of studies which demons-
trate that the chemistry of the exchanged transition metal ions is
generally similar to that of the analogous cations in solution, ii)
the recent developments in the catalysis by "immobilized" transition
metal catalysts, the use of zeolites to anchor metal complexes appea-
ring very promising. However in many cases the critical dimension of
the organometallic complex which has to be immobilized within the zeo-
lite cavity is too large to diffuse through the 10-or 12-membered-rings.
This restriction was overcome by synthesizing the metal complexes

directly within the cavities. In this section we will treat several
recent aspects of these reactions.

The homogeneous catalytic formation of imines by addition of pri-
mary aliphatic amines to acetylenes in the presence of zinc acetate
is feasible only at high pressure |42|. Recently Zn(II) exchanged Y
zeolite was found active for the addition of methylamine to methyla-
cetylene at atmospheric pressure. N-isopropylidene methylamine resulted
following $CH_3NH_2 + CH_3C\equiv CH \rightarrow (CH_3)_2 C = NCH_3$ |43| Y zeolite exchanged
by Ni, Pd, Pt, Hg and Cu (I) which is isoelectronic with Zn(II)
failed to catalyze the amine-acetylene condensation ; it was suggested
that the rapid reduction of the cation is responsible for the lack of
activity |43|. Acetylene trimerisation to form benzene |44| was cata-
lyzed by Ni (II) exchanged Y zeolite. Similarly X-type zeolites con-
taining zinc, cadmium, copper or silver catalyze the hydration of
acetylene to acetaldehyde |45|. The dependence of the reaction conver-
sion on the sodium exchange level indicates that the exchangeable
cation was directly involved in the reaction.

Transition metal ions exchanged Y zeolites were found active for
selective oxidation of hydrocarbons. The close similarity between
exchanged zeolites and homogeneous catalysts is illustrated by the
selective oxidation of ethylene to acetaldehyde catalyzed by Pd^{2+}/Cu^{2+}
complexes. It is widely accepted that the reaction pathway involves
the reduction of Pd(II) to Pd(0) by the olefin, the role of Cu(II) is
to oxidize Pd(0) to Pd(II). Heterogeneous catalysts for the vapor
phase oxidation of ethylene to acetaldehyde were obtained by introdu-
cing in NaY zeolite both Cu(II) and Pd(II) cations |46|. Pd(II) Y and
Cu(II) Y zeolites are poor catalysts for the oxidation of ethylene.
Furthermore these two catalysts deactivate rapidly. By contrast, Pd-Cu
Y zeolite shows an activity for acetaldehyde formation two orders of
magnitude higher than that of PdY or CuY. Furthermore the Pd-Cu Y
zeolite activity remains constant over a long period of time. Thus the
reaction is promoted by the copper ions as in solution. In the absence
of Cu(II), Pd(0) is slowly reoxidized to Pd(II) by oxygen, while Cu(II)
present in Pd Cu Y would reoxidize Pd(0) according to an electron
transfer mechanism $Pd(0) + Cu(II) \rightarrow Pd(II) + Cu(0)$ and then would be
oxidized readily by O_2 in the presence of H_2O. The efficiency of the
catalyst obviously increases with the number of Pd(II) present but
also with the amount of Cu(II) ions. From the published data |46| it
appears that the highest efficiency is attained for a Cu(II)/Pd(II)
ratio equal to about 6.

It should be noted that the yield of acetaldehyde decreased at
reaction temperatures higher than 115°C, probably as the result of the
reduction of Pd(II) ions into palladium metal crystallites. Over Pd-Cu
Y zeolites propene and butenes are selectively oxidized into ketones
|46|. Benzyl alcohol was selectively oxidized into benzaldehyde over
Cu(II) exchanged Y zeolites |47|. Although several experimental eviden-
ces on the participation of Cu(II) do exist, the role of the acidity
of the zeolite and the effect of CO reduction, on the activity and
selectivity are not well established. In yet unpublished investigation
|48| it was shown contrary to earlier reports |49| that Cu(II) Y zeolite
is active in the oxidation of propylene to acroleine selectively. This
is more in agreement with the well known selectivity towards acroleine
of copper oxide. It is also shown |48| that Cu(II) is partly reduced
to Cu(I) indicating that the oxidation process involves a Redox beha-
viour of copper ions. Also the Cu(I)/Cu(II) appeared to be drastically

affected by a number of parameters including the flow composition and
the acidity of the zeolite and that this ratio predominantly deter-
mines the product distribution. In particular increased acidity of the
matrix favoured an oxidative attack on the double bond rather than
the allylic protons thus producing more acetaldehyde and CH_2O and
eventually CO_2 at the expense of acroleine. Also it was confirmed that
Cu(II) Pd(II) zeolite effectively catalyzes the oxidation of ethylene
to acetaldehyde and eventually acetic acid, however EPR measurements
showed that reduction of Pd(II) into Pd(I) rather than Pd(0) occurred
and reoxidation was indeed favoured by the presence of Cu(II) ions.
Again the influence of the matrix appeared clearly as reoxidation was
made even easier in the H Cu Pd zeolite system as compared to the Na
Cu Pd zeolite, concommitally the former showed a remarkable stability
in its activity and a higher selectivity compared to the latter |48|.

Group VIII transition metal ions are usually active for a large
variety of olefin reactions such as hydrogenation isomerisation, dime-
risation, hydroformylation ; carbonylation of methanol to acetic acid,
which is of considerable industrial importance was found to be cata-
lyzed by cobalt, rhodium, iridium complexes in both homogeneous and
heterogeneous media. Since it is now well established that transition
metal ions in zeolites behave similarly to their   solution analogues,
interesting heterogeneous catalysts active for a series of olefin
reactions have been designed by exchanging sodium ions to transition
metal ions. In this section our discussion will be limited to some
recent results obtained on rhodium and iridium exchanged NaY zeolites.

Dimerisation of ethylene is known to be catalyzed by rhodium
complexes in solution |50| .A detailed   study of this reaction has
suggested that monovalent rhodium is the active species. Because the
activity was enhanced by HCl it was suggested that the reaction pro-
ceeds via an oxidative addition reaction. Later it was found that
ethylene is selectively dimerized over nickel or rhodium exchanged
Y zeolites |51|. The products formed were 1- and 2-butenes, trans-2
butene being favoured with respect to cis-2-butene. Since the highest
activity was achieved by heat treatment in vacuo at 400°C of the
catalyst while H_2-reduction at 500°C lowered drastically the activity
it was concluded that atomic rhodium is the active site for the ethy-
lene dimerization. However the authors |51| have not considered that
following the thermal treatments Rh(I) may form and might be the active
center. Indeed it is well known, that in solution, Rh(III) chloride is
rapidly reduced to Rh(I) by ethylene |52| . Similarly using ESCA and
infrared spectroscopy it has been shown that Rh(III) within the zeolite
cavity is also easily reduced to Rh(I) by CO |53|. Very recently
dimerization of ethylene on rhodium (III) exchanged Y zeolite was
reinvestigated |54|. The authors have used X-ray photoelectron spectros-
copy to follow the oxidation state of rhodium. It was shown that the
thermal activation of Rh(III) Y is accompanied by a substantial reduc-
tion of Rh(III) to Rh(I). Further reduction resulted in the formation
of Rh(0) followed by aggregation mechanism to form rhodium metal.
Both Rh(I) and metallic rhodium were found active for ethylene hydro-
genation while only Rh(I) was active in the dimerization of ethylene.
In addition, similarly to what was observed with soluble rhodium (I)
catalysts, HCl enhanced the rate of ethylene dimerization on rhodium
zeolite. These results clearly show the very similar behaviour of the

homogeneous and heterogeneous catalysts.

Recent studies in the field of supported transition metal complexes suggest that the activity and/or selectivity of the soluble catalysts was retained when bonded to a solid carrier. Several recent investigations were devoted to immobilize soluble transition metal complexes within the zeolite cavities. This may be accomplished in two different ways : a direct synthesis of the desired complex within the zeolite cavities or insertion of the transition metal complex within the pores. Thus starting from NaY exchanged with $|Rh(NH_3)_5Cl|^{2+}$ $|53|$ or with $|Ir(NH_3)_5Cl|^{2+}$ $|55|$ metal carbonyl complexes have been prepared. The decomposition of the rhodium and iridium pentammine complexes was followed by monitoring the infrared band around 1350 cm^{-1} assigned to NH$_3$ ligands. The removal of these molecules according to the reaction scheme :

$$|M(III)(NH_3)_5Cl|^{2+} + {}^-O - zeol \xrightarrow[H_2O]{\Delta, \ O_2^-} |M(III)(OH)_2 Cl|^{2-x^+}$$
$$+ HO - zeol + 5 NH_3$$
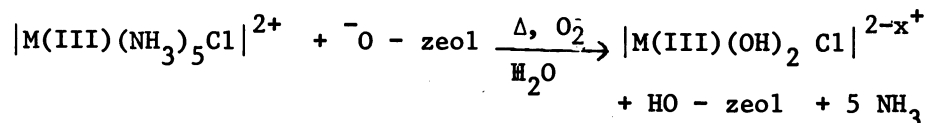
produced chlorohydroxo complexes entrapped within the zeolite cavities. The dehydration of the hydroxo complex might result in the formation of oxide clusters and/or isolated ions. In the presence of carbon monoxide metal carbonyl species were formed and identified using X PS and IR spectroscopy. From these studies it was concluded that, as in solution, Rh(III) ions in Y zeolite are converted by CO into a Rh(I) dicarbonyl complex (ν_{CO} at 2100 and 2040 cm^{-1}) following $|54|$

$$Rh(III) + CO \xrightarrow{H_2O} Rh(I) (CO)_2 + 2H^+ + CO_2$$
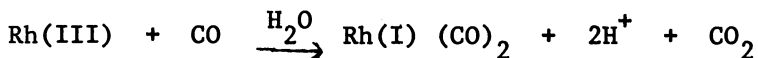
Ir(III) ions in Y zeolite are also reduced by CO to Ir(I) but only around 170°C $|55|$. Quantitative volumetric measurements, as well as infrared studies indicated the formation of CO$_2$ and suggested the reduction of iridium (III) to iridium (I) along with the subsequent carbonylation of iridium (I) as indicated by the appearance of two ν_{CO} bands at 2089 and 2001 cm^{-1}. Analysis of the IR spectrum observed following the use of an equimolecular mixture of $^{13}CO - {}^{12}CO$ led to the conclusion that an Ir(I) (CO)$_3$ complex was formed within the zeolite cavities $|55|$.

Rhodium and iridium carbonyl clusters such as Rh$_6$(CO)$_{16}$, Rh$_4$(CO)$_{12}$, Ir$_6$(CO)$_{16}$, Ir$_4$(CO)$_{12}$ are potentially active catalysts for reactions such as hydrogenation of olefins and aromatics, CO reduction by H$_2$, hydroformylation of olefins etc... Immobilization of these clusters on a carrier is expected to increase their stability toward aggregation. The procedure used in $|56|$ was to exchange NaY zeolite with Rh^{3+} (NH$_3$)$_6$ and then to carry out the reduction of Rh(III) in the presence of CO. Infrared studies showed the existence of two strong carbonyl bands at 2095 and 1765 cm^{-1} when the rhodium exchanged zeolite was reacted with CO : H$_2$ equimolecular mixture at 130°C under a pressure of 80 atmosphere. It was suggested that Rh$_6$(CO)$_{16}$ cluster was formed and entrapped within the zeolite cavity. By contrast treatment of Rh(III)Y with an equimolecular mixture of CO : H$_2$ at 130°C but only at atmospheric pressure led almost exclusively to the formation of Rh(I) (CO)$_2$ complex $|57|$.

Supported or entrapped Rh$_6$(CO)$_{16}$ could be easily decarbonylated and recarbonylated without significant loss of its molecular structure $|57|$. Thus when sublimed onto the zeolite, Rh$_6$(CO)$_{16}$, due to its large size, sits on the zeolite external surface. Upon decarbonylation by oxygen, the rhodium cluster might migrate into the zeolite cavity. At this stage the decarbonylated rhodium species

are easily recarbonylated by CO at atmospheric pressure. The rhodium
cluster entrapped within the zeolite identified by two infrared bands at
2095 and 1764 cm^{-1} |57| is identical to that formed by high pressure
carbonylation of Rh(III) exchanged zeolite |56|. $Ir_4(CO)_{12}$ $Ir_6(CO)_{16}$
have also been synthesized within Y zeolite by reducing
Ir(III) exchanged Y zeolite with a H_2 : CO mixture at 170°C at atmos-
pheric pressure |58| . These   known   rhodium and iridium carbonyl
compounds entrapped within the zeolites exhibited interesting catalytic
properties. $Rh_6(CO)_{16}$-Y zeolite was tested for the hydroformylation
of 1-hexene |56|.   When 1-hexene was reacted with CO and H_2 over
rhodium exchanged Y zeolite at 80°C and a pressure of carbon monoxide
and hydrogen higher than 50 atmospheres, a high conversion to aldehydes
is obtained. Similarly to homogeneous catalysts, RhY catalyst yields a
normal/iso aldehyde ratio of about 1. The isomer distribution of alde-
hydes was 51 % 1-heptanal, 41 % 2- methylhexanal and 8 % 2-ethyl penta-
nal.

The carbonylation of methanol to acetic acid is a reaction of
considerable industrial importance. The patent developed by Monsonto
for the liquid phase methanol carbonylation used rhodium based catalysts
in the presence of an iodide based promoter .   It is now recognized
that the reaction pathways starting from Rh(III) halides include CO
reduction of Rh(III) to Rh(I) forming a $Rh(CO)_2$ complex   which subse-
quently, with excess halide, gives the $|Rh(CO)_2X_2|^-$ species. The
reaction of the promoter CH_3I with the active species gives
$|CH_3Rh(CO)_2 X_2|$ complex which then undergoes a rapid methyl migration
to form the acyl moiety : $|(CH_3CO)Rh(CO)I X_2|^-$. Methanolysis or hydro-
lysis of the complex generates methylacetate or acetic acid |59|. In
homogeneous liquid phase the reaction was found first order in CH_3I
and zero order in methanol and carbon monoxide |60|. Rhodium or iridium
exchanged zeolites exhibited interesting catalytic properties for low
pressure vapor phase carbonylation of methanol. Sodium X zeolites exchan-
ged with an aqueous solution of rhodium chloride exhibited a high acti-
vity and selectivity for the carbonylation of methanol |61-62|. As in
homogeneous systems the reaction started only in the presence of a
halide promotor such as CH_3I. The kinetics of the carbonylation reaction
on Rh X have shown a first order in CH_3I for low CH_3I partial pressure,
and zero order in CH_3OH and CO |62|. The observed activation energy
of methanol carbonylation on Rh X was identical to that previously
measured in homogeneous systems (14 kcal/mole). Infrared and ESCA were
used to characterize the active species and the intermediates in the
carbonylation of methanol on Rh X |63|. Dicarbonyl rhodium (I) species
were identified when CO reacted with Rh X at 100-160°C. However it
appeared that only a very small fraction of the total rhodium was
involved. It is obvious that the method of ion exchange employed by
the authors is not appropriate to obtain the highest rhodium ion dis-
persion within the zeolite. The reaction of Rh X with a mixture of
CO: CH_3I resulted in the formation of an acetyl rhodium species which
after an extended period of time is converted to acetic acid by a
hydrolysis reaction. Carbonylation of methanol over Rh Y zeolites was
also investigated |64-66 |. In these studies it is also recognized that
the formation of a Rh(I) carbonyl complex capable of oxidative addition
of methyl iodide is the rate determining step. Rhodium Y zeolites
appeared much more active than rhodium supported on other conventional
supports. It seems that in Y zeolite each rhodium cation is accessible
to the reactants. However this is only true for low rhodium content.
Indeed as the rhodium loading increased a drastic

decrease of the activity was observed. Kinetic studies again indicated
that the rate of the methanol carbonylation was first order in CH_3I and
zero order in CH_3OH and Co [65-66]. Furthermore infrared studies showed
that $Rh(I)(CO)_2$ readily absorbed CH_3I to give the rhodium carbonyl acetyl
species $|Rh(CO)(CH_3CO)|^+$. Comparison of these results with the well
established homogeneous process indicated similar behaviour of the solu-
ble and zeolite supported rhodium based catalysts. Similarly iridium
exchanged zeolite and iridium based homogeneous catalysts exhibited
identical catalytic properties in the methanol carbonylation. The liquid
phase carbonylation of methanol catalyzed by a soluble iridium complex
in the presence of methyl iodide was found first order in methanol and
zero order in both methyl iodide and carbon monoxide |67| . Similar
kinetics were obtained for the vapor phase reaction on Ir Y |66|. Infra-
red studies |66| suggest that the active species are the tricarbonyl
iridium(I) species formed by the reaction of CO on Ir(III); CH_3I under-
goes on this carbonyl species a dissociative addition to form the
$|CH_3 \, Ir \, I_2(CO)_3|$ or $|CH_3 \, Ir \, I \, (CO)_3|^+$ species ; in these complexes no
methyl migration was observed. To account for the observed first order
with respect to methanol the authors suggested that one possible pathway
for the reaction is the attack of the methyl iridium carbonyl species
by a CH_3OH molecule to form the methoxy group $|(CH_3) \, Ir \, I_2 \, (CO)_2$
$(COOCH_3)|$. Another route may be that in the presence of methanol
the methyl group in the $|(CH_3) \, Ir \, I_2(CO)_3|^-$ species undergoes a rapid
migration to form the iridium acetyl species. Methyl acetate was then
formed by hydrolysis of either the methoxy or the acetyl moiety |66|.

The work reported in this part is sufficient to show that a large
number of reactions catalyzed by soluble metal complexes can be carried
out, in the vapor phase, by zeolites exchanged with the analogous
metal ions. In general the zeolite matrix affords the highest metal ion
dispersion in comparison with other supports. In addition, in several
cases,on zeolites,the reaction can be carried out at much lower pressu-
res than those required by other homogeneous or heterogeneous catalysts.
The applicability of the zeolites containing transition metal ions is
still far from being exhausted.

ZEOLITE-SUPPORTED METAL CATALYSTS.

Hydrocracking conversion of heavy feed stock into low boiling
hydrocarbons is an important process in petroleum industry. For many
years hydrocracking catalysts preparation involved the dispersion of a
metal possessing   dehydrogenating properties on an acidic support
which was HF-treated montmorillonite, acid-treated clays or amorphous
silica-alumina. However these conventional hydrocracking catalysts were
very sensitive to nitrogen and sulfur compounds. More recently hydro-
cracking catalysts based on acidic zeolites have been developed. The
great advantage of these new catalysts is their high resistance against
nitrogen and sulfur poisoning and also the very high dispersion of the
incorporated metallic component. The specific feature of zeolite-
supported metal is certainly that very small metal particles can be
stabilized within the framework which affords interesting materials to
study metal-support interaction, particle size effects. Well documented
reviews have been published recently |68|. In this section we will be
concerned with some relevant aspects of zeolite-supported metals.

Zeolite-supported group VIII transition metals were generally pre-
pared by ion exchange technique with a solution of ammine complex such

as $|Pd(NH_3)_4|^{2+}$, $|Pt(NH_3)_4|^{+}$, $|Ru(NH_3)_6|^{3+}$, $|Rh(NH_3)_5 Cl|^{2+}$,
$|Ir(NH_3)_5Cl|^{2+}$. These cationic ammine complexes are generally stable
in solution over a wide pH range and thus suitable for cation exchange
technique. In some cases aqueous solutions of the metal chloride have
been used. In our opinion this method should be avoided since it is
well known that a rapid hydrolysis of the chloride occurs with the
subsequent formation of hydroanionic metal complexes. Thus this method
would lead to heterogeneous samples containing the active metal precur-
sor both on the external and internal zeolite surface. The exchanged
zeolite is then thermally treated in various atmospheres and subsequen-
tly reduced in hydrogen at elevated temperatures. From the published
results it appears that the metal dispersion depends on the pretreat-
ment of the exchanged zeolite before the hydrogen reduction. Extensive
work in this area has been performed. It was found that $Pt^{2+}(NH_3)_4$ - Y
reduced in H_2 at 350°C without a pretreatment gave very large metal
particles while samples thermally treated in oxygen before H_2-reduction
led to metal particles of less than 1 nm in diameter $|69|$. The authors
suggested that direct reduction of $Pt^{2+}(NH_3)_4$ by H_2 forms a neutral
highly mobile platinium hydride such as $H_2Pt(NH_3)_2$, which results in a
very rapid particle growth. By contrast in the oxidized samples Pt^{2+}
cations are strongly held on the zeolite surface thus the particle
growth is hindered. The effect of the oxygen treatment on the platinum
dispersion was reinvestigated $|70|$. The location of the Pt^{2+} ions before
H_2-reduction was determined by the X-ray method and correlated to the
metal dispersion determined by electron microscopy, X-ray line broade-
ning and hydrogen adsorption. It has been shown that the platinum
dispersion depended strongly on the location of the Pt^{2+} ions before
the hydrogen reduction $|70|$. Pt^{2+} located in the supercage as determi-
ned by X-ray led to particles of about 1 nm in diameter entrapped within
the large cavities, while Pt^{2+} ions located in the sodalite cages give
upon H_2-reduction atomically dispersed platinum atoms and 2 nm diameter
crystallites embedded within the zeolite. It was suggested that during
the metal aggregation which occured in the large cavities, part of the
zeolite framework around the crystallite was destroyed which would
enlarge the supercage in order to accommodate easily these large
size particles. Thus platinum particles up to 2 nm diameter might
grow $|70-71|$ within the zeolite framework. The use of zeolites as
carriers has been proposed for several other noble metals such as palla-
dium$|70|$rhodium $|72|$, iridium$|73|$, ruthenium $|74-75-76-77|$. The wide
spread use of supported ruthenium catalysts for CO + H_2 reaction and
the suggested effect of the support and the particle size have led
several authors to develop the study of zeolite-supported ruthenium
catalysts. In general the ruthenium metal precursor was introduced in
NaY zeolite by ionic exchange with $Ru^{3+}(NH_3)_6$. Most of the authors
agreed that during the thermal decomposition of $Ru^{3+}(NH_3)_6$ in vacuo,
the reduction of Ru^{3+} to ruthenium metal occured $|75-77|$. According
to these studies $|75-77|$ the reduction should be connected with the
presence of NH_3 or H_2O during the thermal decomposition. Furthermore it
was concluded from ESCA, X-ray diffraction electron microscopy and
selective adsorption of H_2, O_2, CO that the ruthenium metal particles
resulting from the vacuum thermal decomposition are located in the
supercages and their size estimated to about 1 nm. Calcination in
oxygen following reduction was accompanied by the sintering of the metal
particle. In a recent publication it was shown that water affected
considerably the size and the distribution of the ruthenium particles $|77|$

Thus bi-dispersed Ru particles were obtained when the reduction was carried out in the presence of water, the binodal distribution being controlled by the amount of water present during the reduction process. It was suggested that water destroyed, by hydrolysis, part of the zeolite lattice, thus creating holes. Ruthenium particles previously located in the supercages might migrate in these holes and grow to a diameter limited by the size of the holes. These interesting results suggest that it would be possible to control the size and the accessibility of the particles by monitoring the temperature and the water vapor pressure.

The use of zeolites as carriers for metal catalysts is of interest since these supports offer, in catalysis by metals, several approaches to the study of i) particle size effect, ii) metal support interaction iii) bifunctional catalysis.

Small platinum particles in Y zeolites have shown a high resistance toward sulfur poisoning |78|. This important properties was attributed to the fact that,in zeolite,platinum was almost atomically dispersed, Pt atoms in this state would bind less strongly to sulfur |78|. Another suggestion was that small Pt metal particles in zeolites would be electron deficient which would lead to weakly adsorbed sulfur |69|. There is wide agreement that the hydrogenating properties of zeolite-supported platinum were enhanced with respect to silica-supported platinum|69-71-79|. It was suggested that electron deficient platinum particles in zeolite behave like iridium|69|. However a different interpretation was put forward|79|:the direct effect of the acidity and electro-static field of the zeolite was considered to affect the reactants rather than the platinum|71|. Recently the conversion of neopentane and neohexane on zeolite-supported platinum has been investigated|8|. The results were interpreted in terms of electron deficient platinum, the extent of electron transfer between the metal and the zeolite support being greater for La Y than for Na Y support. However contrary to what has been reported for Pt-zeolite systems, it is claimed that the zeolitic support plays no role in the hydrogenation of benzene over ruthenium zeolite |74|. Hence the nature of the metal-support interaction is not clear yet as well as the parameters which determine the nature and the extent of this interaction. Certainly further effort is needed to achieve a better understanding of the support effects on supported metals in order to predict the modifications of the catalytic behaviour of metals determined by the carrier.

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