# THE STATE OF METALS IN HIGH-SILICA ZEOLITES AND THEIR CATALYTIC ACTIVITY IN ETHANE AROMATIZATION

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ABSTRACT

The catalytic properties of metal-containing high-silica zeolites in ethane aromatization and XPS spectra of these catalysts have been investigated. Both electronic states of metals (Pt,Rh) and catalytic activity strongly depended upon pretreatment conditions and changed in the course of the reaction. The development of the catalytic activity observed during successive catalytic runs in pulse mode was accompanied by an increasing of positive charge on highly dispersed metallic clusters located in the vicinity of acidic OH-groups of zeolite. The $Me^{\bar{\delta}+}$ centers in combination with acidic sites are likely to be responsible for ethane transformations into aromatics over metal-containing high-silica zeolites.

INTRODUCTION

As shown earlier by the XPS studies /1-3/ , the interaction of highly dispersed metal particles (Pt,Pd,Ru,and Re) and electron acceptor sites of $\gamma$-Al$_2$O$_3$ or zeolite Y yields electron deficient metal clusters which display high activity in various reactions. The state of metals can be modified additionally under catalytic reaction conditions /4,5/.

Investigations of ethane and ethylene aromatization in the presence of a number of metal-zeolite catalysts revealed /6/ that in the course of these reactions the Me/H-ZVM (Me=Pt or Pd) catalytic system experiences the so-called activity development effect accompanied by increased yields of aromatics. The causes of the observed phenomenon have so far remained obscure, although an assumption has been put forward as regards the feasibility of metal valent state alternation during the reaction as a result of metal-support and

metal-reagents interactions.

The present study was undertaken with a view to examining by the XPS method how the pretreatment conditions ( air,hydrogen or air and then hydrogen) and the reaction medium affect the electronic state of Me(Pt,Rh)-containing pentasil-type high-silica zeolites (H-ZVM). Accordingly,the dependence of Me/H-ZVM catalytic activity in ethane aromatization process on the state of Pt or Rh in corresponding bifunctional system was investigated. In contrast to faujasites,in which the physico-chemical properties of Pt and Rh have been examined in detail /7,8/,practically no data are available in the literature on the valent state of these metals and their migration ability in high-silica zeolites of the ZSM-5 structure. It is further noteworthy that in the majority of investigations /3,5,9-11/ the structure of catalysts was determined prior to the reaction (after carrying out a particular pretreatment procedure) and upon reaction completion. Of greater information value are the data characterizing the catalyst at different reaction steps,which are obtained by the present authors /4/ and refined in the work reported here.

EXPERIMENTAL

Catalysts. In this study use was made of two specimens of Pt catalysts prepared from $NH_4$-ZVM,viz., 0.48% Pt/H-ZVM (Cat-I) and 1.78% Pt/H-ZVM (Cat-II) as well as of sample ca.2% Rh/H-ZVM (Cat-III) The starting material comprised Na-ZVM obtained by the crystallization of alumosilicagels under hydrothermal conditions in the absence of organic cation /19/,molar ratio of $SiO_2/Al_2O_3$ =35,content of $Na_2O$ =3%,and of $Fe_2O_3$=0.12% ; 100% phase purity. The Me-containing zeolites were prepared by treating $NH_4$-ZVM (after decationation,the residual content of $Na_2O$ was 0.1%) with $[Pt(NH_3)_4]Cl_2$ or $[Rh(NH_3)_5 Cl]Cl_2$ aqueous solution under ion-exchange conditions,the degree of exchange being controlled by the residual content of Me in the mother liquor. The resultant powdered specimens were dried and pressed into pellets (without binders). In experiments,0.5-1.0 mm fractions were employed.

For spectral investigations,catalyst samples were subjected to different pretreatment procedures,viz.,1) calcination in a flow of air for 5h (Cat-II at 550°C,Cat-III at 450°C); 2) calcination in air flow at the same temperatures and then in $H_2$ for 2h(Cat-II at 520°C,Cat-III at 400°C). After above treatments the samples were co-

oled in dry argon to room temperature and transferred into spect-
rometer (see below).

Catalytic experiments  involving ethane were carried out in a
pulse microcatalytic unit /20/. The samples of Cat-II or Cat-III
were placed in an U-shaped reactor and pretreated according above
procedure,followed by replacing $H_2$ with He (20 ml/min),and in ~20
min starting to feed ethane (0.082 ml). Upon reaction termination
and analysis completion (about 30 min),the catalyst was cooled in
a stream of He. The XPS spectrum of first sample was recorded after
one ethane pulse,of second sample-after two ethane pulses,etc. (see
table 2). Each sample consisted of a fresh weighed portion of cata-
lyst.

Spectral investigations. From the catalytic reactor,the samp-
les were transferred into a spectrometer in an inert atmosphere. To
do so , the reactor was discharged in a box filled with pure argon,
and a sample was pressed into a Pb plate  and mounted on a holder
followed by connecting the box to the sample insertion lock of the
spectrometer and thereafter transferring the sample holder,in an Ar
countercurrent,into the spectrometer vacuum system. XPS spectra we-
re recorded with an ES 200B spectrometer using the technique descri-
bed in /12/. Spectral measurements were carried out at $5 \times 10^{-8}$ Torr
using the C 1s ($E_b$=285.0 eV) and Si 2p ($E_b$=103.8 eV) lines as refe-
rence standards. After the catalytic process,no pronounced distor-
tion of the C 1s line shape was observed. The Me/Al and Si/Al ato-
mic ratios were evaluated using respective integral intensities cor-
related for, the photoionization cross-sections /12/. Since the Pt
4f spin-doublet and the Al 2p line are partially overlapping,deter-
mination of spectrum parameters comprised spectrum analysis by the
program of deconvolution for the unresolved Gaussian lines using
PDP 11/03L minicomputer. The accuracy of $E_b$ determination was 0.2 eV,
and that of estimating atomic ratios,20-30%.


RESULTS AND DISCUSSION

Ethane catalytic conversion in the presence of Cat-I was studied
in the 300-600°C temperature range in a pulse microreactor (fig.1).
Under these conditions ethane undergoes the following principal tran-
sformations: hydrogenolysis,formation of $C_6$-$C_8$ aromatics,and also
the formation of condensation products. Using the same catalyst under
flow conditions yields closely allied results.

Next,with Cat-II at 550°C a series  of runs (A) was carried
out,in which the effect of catalyst activity development became ma-

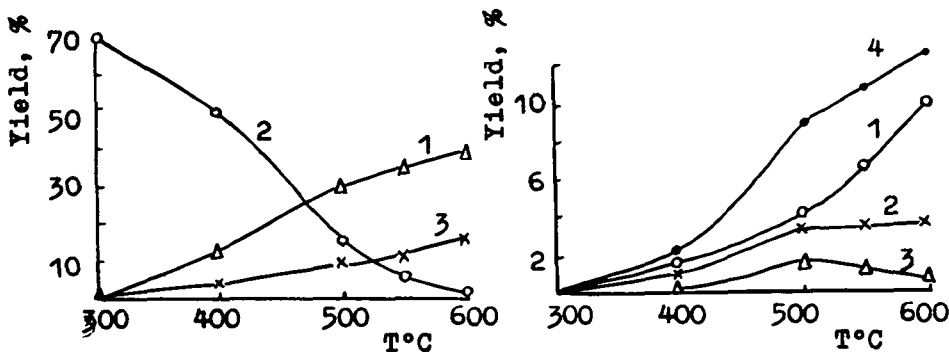nifest, activity maximum being attained after 3-5 pulses (fig.2).



Fig.1. Dependence of the yield of ethane conversion products
over 0.5% Pt/H-ZVM on temperature: a) 1-$CH_4$; 2-un-
converted $C_2H_6$; 3-sum of $C_6$-$C_8$ aromatics; b) 1-benzene;
2-toluene; 3-xylene; 4-sum of $C_6$-$C_8$ aromatics

With Rh/H-ZVM rather high yields of $C_6$-$C_7$ aromatics were succeded
at temperature as low as 450°C, similar development of the activity
being observed, as in the case of Cat-II (fig.3). In both of cases
increasing aromatics yield with pulse number is accompanied by sub-
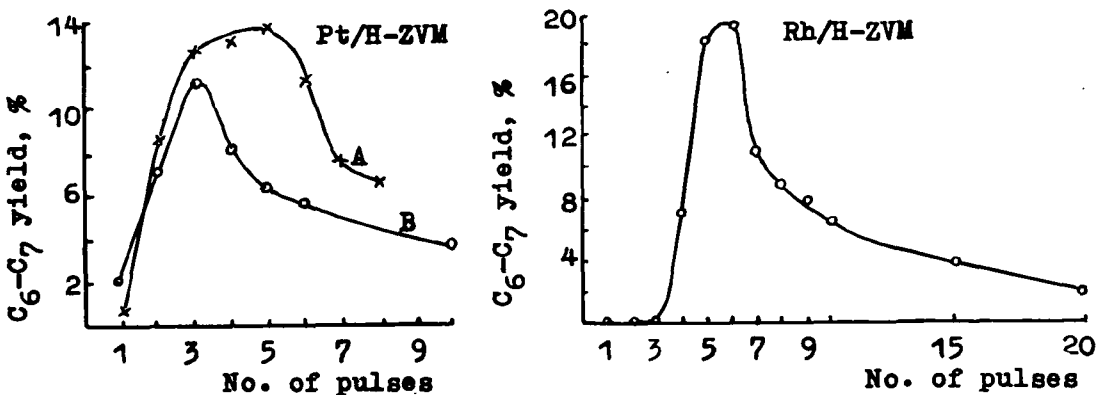stantial decreasing $CH_4$ amount which is maximum at the first pulses.



Fig.2. Dependence of $C_6$-$C_7$ aromatics yield over 1.8% Pt/H-ZVM
pretreated subsequently in air and in $H_2$ on the number of
ethane pulses at 550°C. Series A-sample weight 100 mg; series
B-sample weight 70 mg

Fig.3. Dependence of $C_6$-$C_7$ aromatics yield over Rh/H-ZVM pre-
treated subsequently in air and $H_2$ on the number of ethane
pulses at 450°C

It is noteworthy that in the absence of metal (H-ZVM catalyst)

no such effect was observed in the cases of ethane or ethylene,although ethylene aromatization proceeded at an adequately high level /6/. The effect observed is,therefore, due to the presence of a metal in the catalyst and appears to be associated with the variation of metal-support interaction during the reaction. A similar effect was observed by us earlier when comparing the catalytic properties and XPS spectra of alumina supported rhodium catalysts in ethylene cyclotrimerization /4/. During the reaction,the catalyst activity and the electronic state of Rh undergo significant changes with a positive charge (maximum $E_b$ shift for Rh $3d_{5/2}$~0.7 eV) appearing on Rh clusters in the Rh/Al$_2$O$_3$·F catalyst.

Taking this into account, in series of catalytic runs B (fig.2, table 1) investigations of catalytic activity were parallelled by determination of the Pt electronic state during ethane aromatization on seven Cat-II samples. As can be seen from fig.2, in series B the maximum activity falls,as in the case of series A, at third and fourth pulses. Table 2 presents the data on the state of Pt in the Cat-II specimens.

Table 1

Ethane conversions over 1.8% Pt/H-ZVM catalyst at 550°C
in pulse mode (Series B)

| Pulse No. | Total product yield,% | Gas and liquid products composition, wt.% | | | | |
|---|---|---|---|---|---|---|
| | | $CH_4$ | $C_2H_4$ | $C_2H_6$ | benzene | toluene |
| 1 | 76 | 35.6 | 5.4 | 27.0 | 1.6 | 0.4 |
| 2 | 73 | 57.9 | 1.6 | 6.5 | 6.0 | 1.0 |
| 3 | 80 | 56.6 | 3.2 | 8.7 | 9.0 | 2.3 |
| 4 | 76 | 32.9 | 7.1 | 27.7 | 6.0 | 2.2 |
| 5 | 70 | 24.4 | 9.2 | 28.9 | 4.5 | 2.0 |
| 6 | 74 | 10.7 | 10.3 | 47.2 | 3.9 | 1.8 |
| 10 | 74 | 26.4 | 13.6 | 50.1 | 2.5 | 1.4 |

In the spectra of the starting specimen only the Pt $4d_{5/2}$ line was observed,the Pt 4f doublet being completely masked by the Al 2p line. The value of $E_b$ for Pt $4f_{7/2}$ found by the deconvolution of these spectra is close to that of the starting complex. After air calcination in the spectrum there appears a new line with $E_b$=72.2 eV. Its position is nearly that observed in the spectra of reduced specimens and can be attributed to the finely dispersed Pt$^o$ particles /3,12/. The decomposition of Pt complex cations in air appears to

be accompanied by partial reduction of Pt. Pt$^O$ formation was obser-
ved earlier in the oxidative treatment of $\left[Pt(NH_3)_4\right]$ -NaY /7,8/.

Although the positions of Pt 4f main peaks for two reduced
specimens are close to each other,a significant increase ( six-
fold) of the Pt/Al atomic ratio was observed for the specimen re-
duced in H$_2$ without preliminary treatment in air. This phenomenon
results from Pt$^O$ migration to the external surface of zeolite
/8,12/. The data obtained are consistent with the electron micro-
scopy measurements,according to which in the zeolite reduced in H$_2$
at 500$^O$C there are large metal crystallites from 30 to 150 Å in si-
ze along with finely dispersed Pt particles ( $\sim$10 Å ).

Catalytic activity of three types of samples was also diffe-
rent. Maximum activity was displayed by sample calcined in air with-
out subsequent reduction (the highest yield of aromatics was 19.4%)
whereas the spicemen reduced directly in H$_2$ possessed the lowest
activity (aromatics yield, 0.4%). To investigate Pt state modifica-
tion under the action of reaction medium,use was made of the speci-
men reduced by H$_2$ after precalcination in the air (maximum aroma-
tics yield, 11.3%),the most pronounced effect of activity develop-
ment being observed for this catalyst in the pulse reactor (fig.2).

Activity variation was accompanied by definite changes in Pt
4f parameters (table 2). For instance,after the second pulse of
C$_2$H$_6$ the Pt 4f lines exhibited broadening from 2 to 3 eV and remai-
ned so after the third and forth pulses. Subsequently the lines be-
come somewhat narrower but their HWFM exceeds that of the starting
sample. An increase in HWFM is likely to be caused by the appearan-
ce of several non-equivalent Pt states. Indeed,an analysis of the
Pt 4f + Al 2p spectra after the second and third pulses disclosed
that they are better approximated by Al 2p singlet and two Pt 4f
spin-doublets having the Pt 4f$_{7/2}$ E$_b$ of 71.3-71.7 eV and 72.7 eV,
respectively. After 10 pulses, Pt 4f spectrum was likewise broade-
ned and resolved into two doublets,but the high-energy doublet pa-
rameters being close to thouse observed in initial spectrum (table
2). The spectra of specimens after 4 to 6 pulses could be adequate-
ly approximated by one Pt 4f spin-doublet and the Al 2p line.

It is,therefore,evident that Pt state changes occur in the
course of catalyst activity development. According to the XPS data,
two types of Pt centers could be discriminated which differ in the-
ir spectral characteristics: 1) Pt species with the spectra signi-
ficantly shifted (+1.3 eV) with reference to bulk metal spectrum;

Table 2

XPS spectra parameters of 1.8% Pt/H-ZVM catalysts [a]

| Sample No. | Pretreatment conditions | Number of $C_2H_6$ pulses at 550°C | Binding energy for Pt $4f_{7/2}$, eV | HWFM for Pt $4f_{7/2}$, eV | $\dfrac{I (Pt\ 4f)}{I (Al\ 2p)}$ | $\dfrac{Pt}{Al}$ | $\dfrac{Si}{Al}$ |
|---|---|---|---|---|---|---|---|
| 1 | starting | – | 73.4 | 2.1 | 0.9 | 0.027 | |
| 2 | air,550°C | – | 73.6(55%) [b] 72.2(45%) | 2.4;1.8 | 0.6 | 0.015 | 22 |
| 3 | $H_2$,520°C | – | 72.0 | 2.4 | 3.2 | 0.1 | 28 |
| 4 | air,550°C+ $H_2$,520°C | – | 72.0 | 2.0 | 0.5 | 0.015 | 18 |
| 5 | –"– | 1 | 72.2 | 2.1 | 0.5 | 0.015 | 20 |
| 6 | –"– | 2 | 72.7(67%); 71.4(33%) | 2.4;1.6 | 0.8 | 0.024 | 18 |
| 7 | –"– | 3 | 72.7(67%); 71.7(33%) | 2.4;1.6 | 0.7 | 0.021 | 20 |
| 8 | –"– | 4 | 72.0 | 2.8 | 0.8 | 0.024 | 19 |
| 9 | –"– | 5 | 72.2 | 2.4 | 0.6 | 0.018 | 18 |
| 10 | –"– | 6 | 72.0 | 2.6 | 0.9 | 0.027 | 20 |
| 11 | –"– | 10 | 72.3(67%); 70.7(33%) | 1.8;2.1 | 0.8 | 0.024 | 25 |

[a] $E_b$ for $[Pt(NH_3)_4]Cl_2$ and Pt (metal) are equal to 73.6 and 71.5 eV, respectively

[b] The percentage of a given Pt state is shown in parenthesis

2) Pt species characterized by the absence of a positive shift or
by a small negative shift (e.g. after ten $C_2H_6$ pulses). Positive
shifts in the spectra of finely dispersed metal can be attributed to
a number of factors /1,3,12/,such as a decrease in the extra-atomic
relaxation energy,the metal-support interaction, and the inherent
electronic structure of fine particles. In compliance with tentative
estimates /13/, the relaxation shift for Pt particles from 10 Å to
15 Å in size does not exceed 0.5 eV. Hence,the observed shifts stem,
at least in part, from electron density transfer to the acceptor si-
tes of the support. In the course of catalyst activity development,
the positive charge on Pt increses and , subsequent to maximum acti-
vity passage, undergoes slight diminution, although both in the star-
ting and deactiviated samples a part of Pt centers appear to carry
a small positive charge.

        As it is shown by XPS a modification of Rh electronic state
in Rh-containing zeolite is also observed under reaction conditions.
But before reaction (calcination in air at 450$^{o}$C and then reduction
with hydrogen at 400$^{o}$C) substantial part of Rh is still remained in
icnic state ( 40%). This makes more complicated to follow the chan-
ges of Rh state during reaction since some part of ions is additio-
nally reduced to Rh$^{o}$ at 450$^{o}$C. Nevertheless, tha data obtained reve-
al that, as in the Pt case, some fraction of Rh has a positive char-
ge when maximum activity is reached.

        The second type of centers observed for Pt/H-ZVM (~30% after
the second and third pulses) is characterized, according to XPS da-
ta, either by charge absence or by a small negative charge. Large Pt
crystallites disposed, as shown by electron mocroscopy, on the zeoli-
te external surface may be regarded as belonging to such centers. In
the case of this size particles the relaxation effects are non-essen-
tial and the parameters of spectra should not be different from tho-
use of bulk metal. For this assignment, a more clearly defined mani-
festation of the second-type centers after the initial ethane pulses
should denote that the reaction is accompanied by an additional si-
ntering of Pt. Although Pt/Al ratio growth observed in the course of
the reaction may be due to additional Pt$^{o}$ migration to the external
surface, this increase is insignificant and remains so during the
reaction. The above assumption is further inconsistent with the fact
that the catalysts containing a larger fraction of crystallites on
the external surface exhibit much lower activity.

        The appeerence of second-type Pt centers is more likely to be
due to the so-called strong metal-support interaction (SMSI) /14/

resulting in the inhibition of the adsorptive capacity of metals towards $H_2$ and in decreasing their activity in the processes of hydrocarbon hydrogenolysis and hydrogenation /15/. Although the SMSI effect is most typical of metals supported on readily reducible oxides ($TiO_2$, $Nb_2O_5$, ZnO), recent data show this effect to be also valid in the case of $Pt/Al_2O_3$ /16/. It is believed that under severe reaction conditions ($550^\circ$C, hydrocarbons, and $H_2$) there occur the formation of oxygen vacancies in the zeolite lattice and the reduction of $Al^{3+}$ ions located in the vicinity of Pt. The interaction of Pt with such electron-donor centers is expected to result in the appearence of electron density excess on Pt, this being indeed the case as demonstrated by XPS data.

In the same manner as with faujasites, the reduction of Pt in high-silica zeolites gives rise the localization of Pt atoms or clusters in the zeolite structure and their partial migration to the external surface. In view of geometric limitations, the localization of large clusters is impossible in the structure of ZSM-5, although formation such clusters in large cavities of zeolite Y has been postulated /6/. In the case of Pt/H-ZVM zeolite a more substantial migration of Pt atoms to the external surface was also observed during direct $H_2$ reduction. At the same time, preliminary zeolite dehydration (in air) provides for retaining a significant fraction of Pt inside the structure. A positive charge arises on a part of Pt atoms as a result of interaction with the acceptor sites of the zeolite framework (possibly, with Brönsted centers). As with $Rh/Al_2O_3$ /4/, the charge grows with increase in the degree of ethane or ethylene conversion into aromatics. In addition, a part of Pt centers is in the zerovalent state or has a negative charge due to a strong interaction with the reduced Al atoms. These Pt species may be responsible for a variation in reaction selectivity, in particular for the inhibition of feedstock ethane hydrogenolysis.

Summarizing the data on the state of Pt in Pt/H-ZVM and taking into account catalytic activity variation, it is reasonable to suggest the existence of the Pt form ($Pt^{\delta+}$ with shift of 1.3 eV) that appears to govern the aromatization activity of Cat-II in ethane conversions. Similar conclusion seems to be valid for Rh/H-ZVM. Since the pore sizes of ZSM type zeolites are equal to 5.5-6 $\overset{\circ}{A}$ /17/, the most likely reaction site would apparently be the channel mouths of a zeolite catalyst. It is believed that catalysis takes place on the fraction of Me dispersed to a crystallite size of about 10 $\overset{\circ}{A}$ and lo-

cated in the pore mouths. These are probably the active centers for
ethane dehydrogenation to ethylene. The latter,having penetrated into
channels,undergoes further conversions into aliphatic oligomers and
aromatics,the formation of which involves the participation of bridge
acidic OH-groups identified by diffuse reflectance IR /18/.

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