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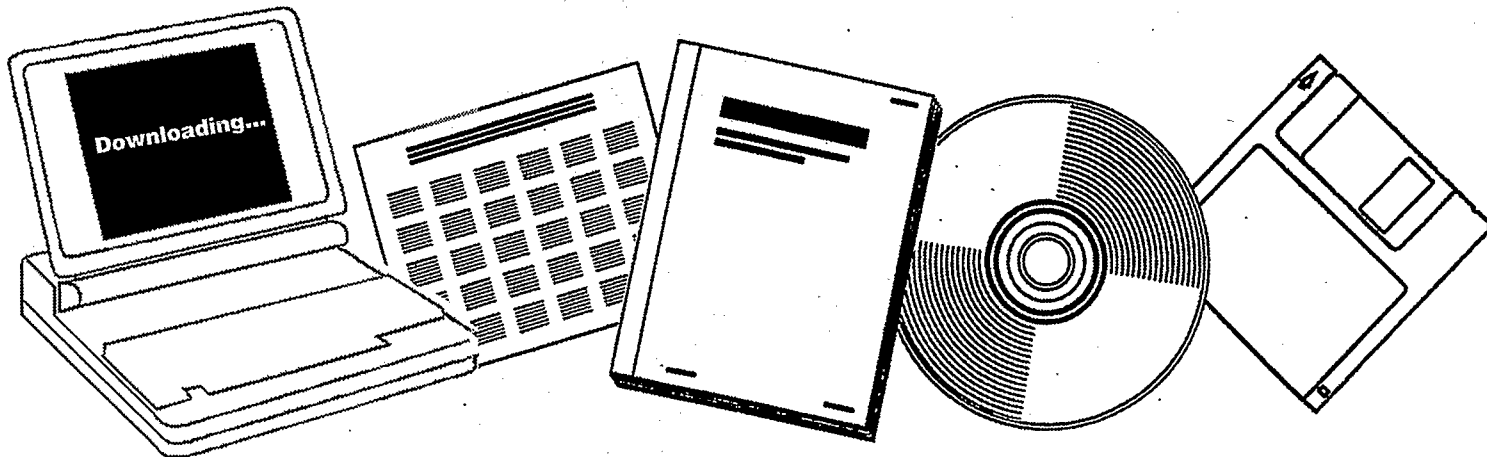
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**CHEMICAL INTERACTIONS IN  
MULTIMETAL/ZEOLITE CATALYSTS. PROGRESS  
REPORT, JANUARY 7, 1987--JANUARY 6, 1990**

**NORTHWESTERN UNIV.  
EVANSTON, IL**

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# CHEMICAL INTERACTIONS IN MULTIMETAL/ZEOLITE CATALYSTS

## PROGRESS REPORT

FOR PERIOD JANUARY 7, 1987 - JANUARY 6, 1990

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## PERFORMANCE REPORT ON BUDGET PERIOD 1987 -1989

### ABSTRACT

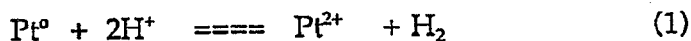
The results of our research under this DOE grant on mono- and multimetal systems in zeolite Y confirm the validity of the principal hypotheses contained in the original proposals: (1) metal sintering in zeolites can be controlled to some extent by "chemical anchoring"<sup>1,2,3,4</sup> and (2) the reducibility of zeolite supported transition metal ions can be markedly increased by blocking their escape from large to small zeolite cages<sup>5,6,7</sup>.

In addition, new concepts have emerged and pertinent literature results confirmed. Mechanistic explanations have been found for the migration of atoms and ions through the zeolite channels, leading to the specific distribution of ions and the metal clusters, that was observed previously by electron microscopy and X-ray diffraction. In this performance report, we summarize the state of understanding attained on a number of topics in the area of mono- and multimetal/zeolite systems, to which our recent research has made significant contributions. The following topics are discussed:

1. Formation of isolated metal atoms in sodalite cages.
2. Differences of metal/zeolite systems prepared by ion reduction in channels or via isolated atoms.
3. Rejuvenation of Pd/NaY and Pd/HY catalysts by oxidative redispersion of the metal,
4. Formation of mono- or bimetal particles in zeolites by programmed reductive decomposition of volatile metal complexes,
5. Cation-cation interaction as a cause of enhanced reducibility,
6. Formation of palladium carbonyl clusters in supercages,
7. Enhanced catalytic activity of metal particle-proton complexes for hydrocarbon conversion reactions,
8. Stereoselectivity of catalytic reactions due to geometric constraints of particles in cages.

1. Formation of isolated metal atoms in sodalite cages

When studying temperature programmed desorption of hydrogen from platinum which was encapsulated in NaY or HY, we found<sup>6</sup> that a TPD peak near 500°C was the most prominent feature of the TPD spectrum. This high temperature production of H<sub>2</sub> occurred after low temperature reduction of an ion exchanged catalyst which was previously calcined at high temperature, i.e. under conditions where our EXAFS data and the X-ray diffraction data of Gallezot et al<sup>8</sup>. show that Pt ions migrate from the supercages into the smaller sodalite cages. We wondered whether this TPD peak was really due to "desorption" or to the reoxidation of isolated Pt atoms by protons:



i.e. the reversal of the original reduction of the Pt ions. To test this hypothesis, we studied the IR signal due to the zeolite O-H groups. We found that this IR band was undetectable after calcination of the ion exchanged catalyst at 500°C; after reducing the Pt<sup>2+</sup> ions with H<sub>2</sub> the band appeared with considerable intensity. During subsequent TPD operation, i.e. with pure Ar flowing over the sample while raising the temperature, this band disappeared at the temperature where the release of H<sub>2</sub> was observed. We then repeated the same experiment using HY rather than NaY as the zeolite and obtained an even larger TPD peak at the same temperature. Additionally, the peak was absent when the sample had originally been calcined at a temperature not exceeding 360°C. Under these conditions the Pt ions lose their original NH<sub>3</sub> ligands, but remain in the supercages. We believe that these results prove that isolated Pt atoms in sodalite cages can be oxidized by protons.

Similar results were observed for Ni/NaY, where a H<sub>2</sub> release due to reoxidation by protons was also identified<sup>7</sup>. However, it is not

known at present, whether the phenomenon of reoxidation by protons is confined to isolated Ni atoms in the sodalite cages or that Ni clusters in the supercages can also be reoxidized in this way. In the case of Pd/NaY, the formation of isolated Pd atoms in sodalite cages was derived from the combined TPR/TPD data<sup>9,10</sup> which are discussed in the next section.

In summary, the following evidence from literature and our own work indicates the existence of isolated Pt<sup>8,11,12,13</sup> or Pd<sup>12,14,15,16</sup> atoms in the small zeolite cages: (1) consumption of H<sub>2</sub> during reduction of Pd<sup>2+</sup> ions in sodalite cages; (2) reaction of zeolite protons and Pt atoms forming Pt<sup>2+</sup> ions and gaseous H<sub>2</sub>, and the absence of this phenomenon when Pt atoms are located in the supercages<sup>6</sup>; (3) decrease of the IR band characteristic for zeolite OH groups during this reoxidation process<sup>6</sup>; (4) inability of the isolated metal atoms to dissociatively chemisorb H<sub>2</sub> also when the passage of H<sub>2</sub> through the cage window is possible; (5) inaccessibility of these atoms for catalytic processes, such as hydrogenation of benzene<sup>17</sup>.

## 2. Different characteristics of Metal/zeolite systems prepared by direct reduction of ions or via isolated atoms.

The thermodynamic driving force for ion reduction depends significantly on the atomic environment: isolated metal ions in the small zeolite cages are reduced to isolated atoms, but when ions are reduced which are already in contact with a metal nucleus, they immediately form part of the metal particle. The former type of reduction can be highly endothermic; ions such as Co<sup>2+</sup> are, therefore, virtually non-reducible in small cages. The latter type of reduction is

fairly exothermic for Group VIII metals under the conditions considered here; reduction of the ion immediately results in growth of a metal particle. Unreduced ions which have lost their original ligands but are still inside the supercages, can easily migrate to nuclei. Ions that are entrapped in sodalite cages or hexagonal prisms are reduced to isolated atoms, which have to migrate through a narrow cage window before they can be attached to a metal particle.

X-ray diffraction and electron microscopic data of Bergeret et al<sup>18</sup>. and Kleine et al<sup>19</sup> indicate that metal particles inside faujasite zeolites tend to become roughly spherical and of dimensions comparable to those of the supercages. Radial electron distribution data are in good agreement with these electron microscopic findings, for Pt they correspond to spherical polyhedra containing 25-45 atoms, the best fit was obtained for the model of a truncated fcc tetrahedron containing 40 atoms. However, if the metal/faujasite system was calcined at a rather low temperature before reduction, a different morphology is apparent, as "grape-shaped" particles are observed i.e. contiguous metal particles, larger than supercages, filling several adjacent supercages without destroying the zeolite matrix<sup>18</sup>.

We have been able to clarify the cause of this phenomenon: Calcination at low temperature implies that the metal ions remain in the channel system of the supercages. In the case of Pd, they even retain part of their ammine ligands for calcination temperatures lower than 250°C. Upon reduction some metal nuclei are formed which grow by trapping migrating metal ions as described above. Primary particles may also migrate and coalesce with each other. The growing particles ultimately bulge through cage windows into neighboring supercages, i.e. grape-shaped particles are formed, filling several adjacent supercages. The situation is entirely different if isolated atoms have first been formed in smaller cages. When these atoms

migrate into supercages, they become not only trapped by Pd particles, but formation of new nuclei is frequent and a high metal dispersion results. The number of metal particles inside supercages will, therefore, increase with the reduction temperature.

Convincing experimental evidence for this model has been obtained by using the fact that dissociative adsorption of dihydrogen requires at least two adjacent metal atoms, but is impossible on isolated metal atoms. Since  $H_2$  is able to pass through the  $O_6$  window and reduce metal ions which are located in sodalite cages, adsorption of  $H_2$  is a sensitive probe for metal particles containing more than one atom. Indeed we observed that hydrogen adsorption changes with reduction temperature and this pattern of  $H/Pd = f(T_R)$  depends markedly on the preceding calcination.

For samples which had been calcined at  $500^\circ C$ , most Pd atoms are isolated in the sodalite cages after reduction at low temperature and thus unable to adsorb  $H_2$ . With increasing reduction temperature an increasing number of Pd atoms escape to supercages where they form small particles capable of chemisorbing  $H_2$ . This is illustrated in Fig. 1a: where the amount of chemisorbed hydrogen, per reduced Pd atom, (the latter number was measured independently by TPR) is plotted versus the reduction temperature for two metal loadings. It is obvious that in this case hydrogen adsorption initially increases with the temperature of reduction. At very high temperature hydrogen adsorption passes through a maximum and further decreases due to particle growth, as is usually observed (vide infra).

An entirely different pattern is observed for samples that had been calcined at a much lower temperature, viz.  $250^\circ C$ , where the majority of the Pd ions are retained in the supercages. Results are shown in Figure 1b, where the same type of measured data is plotted as in Fig 1a. As reduction leads directly to growing particles,

dispersion decreases with increasing temperature of reduction. Primary particles that are able to pass through 7.5+ windows coalesce and trap more ions, and "grape-shaped" particles<sup>18</sup> result. A semi-stable situation is attained when all ions and primary particles, able to migrate through cage windows, are used up. At still higher temperature secondary particle growth sets in, presumably by Ostwald ripening or by partial lattice collapse of the zeolite matrix. The break



between these stages depends on the metal loading in a predictable manner. The differences between Figures 1a and 1b illustrate the potential of controlling catalyst behavior by locating ions in predetermined positions.

An independent confirmation of the above statement that the dissociative nature of hydrogen adsorption is responsible for the distinction between mono and multiatomic Pd particles is found in the adsorption of CO, which is non-dissociative on Pd and therefore also possible on isolated metal atoms even inside sodalite cages. Accordingly, we found that the amount of CO adsorption decreases with reduction temperature both for samples which had been calcined at 500°C, or at 250°C.

The smallest platinum particle which would be just too large to pass through the 7.5 Å window of a faujasite supercage would be an icosahedron or a cubooctahedron consisting of 13 Pt atoms, one in the center and 12 equivalent "surface" atoms. The icosahedron has been proposed by Burton<sup>20</sup> and Gordon et al.<sup>21</sup> as a stable configuration of a Pt<sub>13</sub> particle, but experimental evidence for its existence inside supercages is lacking, all SAXS and XRD data show that the symmetry of small zeolite entrapped metal particles is of the fcc type<sup>22,23</sup>. The nearest neighbor metal-metal distances of these zeolite entrapped Pt particles are slightly shortened with respect to the macroscopic fcc lattice, this shortening is relaxed when hydrogen is adsorbed.

### 3. Rejuvenation of Pd/NaY and Pd/HY catalysts by oxidative redispersion of the metal

During use as a catalyst, agglomeration of small metal particles takes place. Rejuvenation of such catalysts requires, among other things, that the large particles are redispersed to smaller ones. This should, preferentially be performed while the catalyst remains in the

reactor. Following Bergeret et al.<sup>12,17,18</sup> we have tackled this problem for zeolite supported palladium by making use of the preference of multivalent metal ions for sodalite cages. The high negative charge density of the hexagonal prisms is usually quoted as one of the driving forces for multivalent metal ions to migrate into the smallest cages that are commensurate with the size of the ions; this migration implies retention of electroneutrality at atomic scale, i.e. monovalent alkali ions change position with multivalent transition ions.

Two types of oxidation can occur for metal particles in zeolite when exposed to oxygen:

1. Formation of metal oxides
2. Formation of metal ions plus water.

We found that in the case of Pd/NaY the processes take place sequentially; at low temperature oxide formation prevails, at elevated temperatures the oxide particles react with zeolite protons to form water and metal ions. The identity of the oxidized product was characterized by subsequent TPR: PdO has a large reduction peak near 0°C, Pd<sup>2+</sup> ions in sodalite cages show a TPR peak at 190°C. Integrating the TPR spectrum thus provides reliable information on the fraction of Pd in each of these two oxidation states<sup>24</sup>. The results have been summarized in a paper submitted to Applied Catalysis. Oxidative redispersion requires protons in order to create metal ions. In NaY the extent of redispersion is, therefore, limited by the low concentration of protons that were formed during metal reduction. Once the protons in the vicinity of an oxidized metal particle have been exhausted, redispersion becomes very slow. A much higher redispersion is, however, achieved in acidic zeolites such as HY with a high concentration of protons. In unpublished work we achieved redispersions from H/Pd = 0.37 to H/Pd = 0.99; or from H/Pd = 0.23 to H/Pd = 0.87. The H/Pd ratios after redispersion and reduction

correlate well with the fraction of  $\text{Pd}_2^+$  ions in the oxidized sample before the second reduction.

4. Formation of mono- or bimetal particles in zeolites by programmed reductive decomposition of volatile metal complexes

In our tests of transition metal/zeolite combinations as catalysts for model reactions involving conversion of hydrocarbon molecules at temperatures between 250°C and 500°C and pressures between 1 bar and 15 bar, it appeared that the protons, formed when metal ions in zeolites are reduced with  $\text{H}_2$ , initiate carbenium ion reactions with hydrocarbons when the metal function catalyzes dehydrogenation of paraffins to olefins. Some of these carbenium ions are notorious coke precursors; their presence thus leads to catalyst deactivation. With methylcyclopentane as the feed, catalyst deactivation of Pt/NaY and Pd/NaY was found to be particularly rapid; subsequent oxidation confirmed that considerable quantities of coke are deposited on the catalyst even after brief reaction times.

The formation of Brønsted sites during catalyst preparation is avoided by using organometallic clusters with zerovalent metal atoms as metal precursors. This technique has been frequently applied, e.g. by Psaro and Ugo<sup>25</sup>, Bein<sup>26</sup>, Mc Laine<sup>27</sup>, and Gallezot et al<sup>28</sup>. Bimetallic supported catalysts were obtained by the group of Basset<sup>29</sup> by hydrogen reduction of bimetallic clusters, deposited on MgO, e.g.  $\text{H}_2\text{FeOs}_3(\text{CO})_{13}$ ,  $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$  and  $\text{H}_2\text{FeCo}_3(\text{CO})_{12}$  resulting in the formation of FeOs, FeRu and FeCo particles.

A second incentive for the usage of metalorganic complexes as metal precursors for zeolite supported metal catalysts is that some metals of Group VIb and Group VIIB, e.g. Mo, W. or Re tend to form anions in aqueous solution and the pH range compatible with zeolite

stability. We have examined the temperature programmed decomposition of  $\text{Re}_2(\text{CO})_{10}$  on NaY and NaHY zeolites, and we studied the effect of prereduced Pt in the supercages on this decomposition.<sup>30,31</sup> It was found that the metal-free zeolite decomposition in flowing  $\text{H}_2$  results in the formation of metal particles via a Re hydride-carbonyl intermediate. The presence of Pt in supercages of NaY has a profound effect on the decomposition process: in this case no hydride-carbonyl is formed, but subcarbonyls are trapped by Pt particles and mixed PtRe particles, covered with CO, are formed. The kinetics of CO release and  $\text{CH}_4$  formation suggest formation of PtRe alloy particles with Re-rich surface. Decomposition of  $\text{Re}_2(\text{CO})_{10}$  on NaHY occurs in two steps: formation of  $\text{Re}(\text{CO})_x$  subcarbonyls ( $x \approx 3$ ), which strongly interact with Brønsted protons, is followed by aggregation. Mixed PtRe particles are indicated by (1) a low temperature TPR peak of Re after sample oxidation, (2) a high selectivity for hydrogenolysis of methylcyclopentane to methane.

We also studied PtRe/NaY and PtRe/NaHY as catalysts for the conversion of n-heptane<sup>32</sup> and compared them with samples of similar composition, that were prepared from a mixed carbonyl, viz.  $\text{Re}_2\text{Pt}(\text{CO})_{12}$ . It appeared that the catalytic signature of the bimetallic PtRe clusters that were preferentially formed from  $\text{Re}_2(\text{CO})_{10}$  and zeolites containing prereduced Pt particles, is typical for mixed PtRe<sub>x</sub> clusters: high selectivity for deep hydrogenolysis of n-heptane to methane. This is in agreement with earlier findings on  $\text{Al}_2\text{O}_3$  supported PtRe catalysts, for which high selectivity for deep hydrogenolysis paralleled with high extent of alloy formation.<sup>33,34</sup> Formation of PtRe clusters in zeolites is, however, much lower when a THF solution of the bimetallic carbonyl cluster  $\text{PtRe}_2(\text{CO})_{12}$  is used as the metal precursor or when a perrhenate is used as the precursor. In this case, the product pattern obtained with the reduced catalyst differs little

from that of Pt supported on non-acidic  $\text{Al}_2\text{O}_3$ . From these results we conclude that in future work along these lines we should concentrate on volatile organometallics as precursors, which can be incorporated in the zeolite by deposition from the vapor, thus avoiding all complications due to solvents.

5. Cation-cation interaction as a cause of enhanced reducibility.

During calcination, ions of Ni or Co in faujasites tend to migrate into hexagonal prisms where they are virtually irreducible. For Co/NaY we found no detectable reduction in TPR below 750°C. Suzuki et al.<sup>35,36</sup> report that reduction of these elements can be enhanced by applying a high pH during or after ion exchange, forcing the metal ions to hydrolyse inside supercages. In a subsequent calcination step small oxide particles are formed. In our ongoing research we are applying this method to bimetallic catalysts.

A different strategy for reduction enhancement is adding a noble metal such as Pt, which is reduced at low temperature and then provides sites for dissociative adsorption of  $\text{H}_2$ . We have applied this method in work on PtCu/NaY<sup>37</sup> and PtNi/NaY<sup>7</sup> and on several non-zeolite systems, in particular PtRe/ $\text{Al}_2\text{O}_3$ <sup>38,39</sup>. It appeared that for the latter system a geometric proximity between rhenium precursor and platinum is necessary for reduction enhancement to become observable. The same conclusion also emerged from our recent study of (Pd+Co)/NaY.<sup>40</sup> When the Pd ions were retained in the supercages, while the Co ions were positioned in smaller zeolite cages, reduction enhancement was very low; only 15% of the Co was reduced below 750°C. However, when Pd ions were forced to migrate to the

sodalite cages by applying a calcination temperature of 500°C, 75% of the Co was reduced alongside with 100% of the Pd. The results show an additional unexpected phenomenon: reduction sets in at lower temperature for (PdCo)/NaY than for Pd/NaY. The results suggest to us that a cation-cation bond is formed between Pd and Co, when both ions are in each other's proximity; dissociative chemisorption of hydrogen might be easier on this ion pair than on an isolated ion; moreover, the formation of atom pairs will be favored thermodynamically over the formation of isolated atoms.

#### 6. Formation of metal carbonyl clusters in supercages

The size of metal particles in Pd/NaY, prepared by the sequence of ion exchange/ calcination/ reduction, is controlled by the calcination and reduction conditions. With Pd/NaY samples which had been reduced at low temperature, e.g. 200°C, we observed that admission of CO gave rise to highly structured FTIR spectra. These show very sharp bands and are markedly different from the familiar spectra of CO on supported Pd, which consist of two broad bands, conventionally attributed to linear and bridging CO respectively.<sup>41</sup> However, broad IR bands reminiscent of these familiar spectra can also be observed for CO on Pd/NaY, if the sample has been extensively reduced at higher temperature. The former spectra, exhibiting very narrow and symmetrical bands, have been attributed to a palladium carbonyl cluster. An analysis of the spectra has been published<sup>42</sup>. The position of the major bands agrees with those reported by Bradshaw and Hoffmann<sup>43</sup> for CO adsorption on Pd single crystal faces. However, additional bands indicate CO adsorbed on Pd<sup>+</sup> and Pd<sup>2+</sup>; four bands are observed, which are attributed to triply bonded CO, doubly bonded CO and a butterfly configuration of a pair of doubly bonded CO. A Pd cluster having a core of 13 Pd atoms,

surrounded by a shell of CO ligands, would perfectly fit in the supercage of NaY. So far, no Pd carbonyl clusters having exclusively CO ligands have been reported in the literature, apparently the environment of a faujasite supercage is very favorable for their formation. Mixed tetranuclear and decanuclear Pd clusters, containing carbonyl and phosphine ligands have been reported by Mednikov et al.<sup>44</sup> A rhodium carbonyl complex with 13 Rh atoms is known.<sup>45,46</sup>

The FTIR spectra attributed to the zeolite entrapped Pd carbonyl cluster change markedly with changing CO pressure: the intensity of most bands decreases upon purging with Ar at room temperature, but new bands emerge, and sharp isosbestic points are observed. The spectra are completely reversible upon admitting CO at room temperature. The kinetics of CO release and readsorption are intriguing: the activation energy of CO release is much lower than that reported for CO release from Pd single crystal planes, although the stretching frequencies of the adsorbed CO ligands are equal for clusters and macroscopic crystal planes.<sup>47</sup> Our data indicate that CO release from the cluster is not a simple thermal desorption process, but the carbonyl clusters react with zeolite protons, resulting in a positively charged  $[Pd_x-(CO)_y-H_2]^{2+}$  complex. This is confirmed by the IR data of the zeolite O-H bond: the intensity of this band decreases, when CO is released from the cluster, it increases when gaseous CO is redosed. A paper with details of this kinetic analysis has been submitted to the J. Am. Chem. Soc.<sup>48</sup>

## 7. Enhanced catalytic activity of metal particle-proton

### complexes for hydrocarbon conversion reactions

The existence of electron-deficient metal particles in supercages has been proposed by several researchers. Gallezot et al.<sup>49</sup> showed that the low sensitivity to sulphur of Pt/NaY is due to their electron deficiency. Foger and Anderson<sup>50</sup> found the presence of electron deficient platinum in Pt/(La)Y and Pt/(Na)Y by XPS. In both cases, the Pt catalysts were calcined at 300°C, which should leave Pt ions inside the supercages. Gallezot applies a number of physical techniques for the characterization of electron deficient particles and concludes that electron deficiency increases with increasing acidity of the zeolite. No model is presented by these researchers for the electron accepting centers.

We are proposing that "electron-deficient" Pt or Pd particles in zeolites are metal clusters that react with zeolite protons (or just retain some of the protons formed during metal reduction). In this model "electron deficient Pd clusters are particles of the composition  $[Pd_n - H_x]^{*+}$ . This model is in line with our IR data mentioned above; in particular the observed decrease of the IR band characteristic of zeolite O-H groups in situations where zeolite protons become supposedly attached to metal particles, supports this model.

Dalla Betta and Boudart<sup>51</sup> found that the rate of neopentane hydrogenolysis on 1 nm Pt aggregates in Y zeolites is 40 times larger than on Pt supported on conventional supports. Foger and Anderson<sup>50</sup> showed by means of XPS that Pt in Y catalysts is electron deficient. When we tested Pd/NaY samples, which had been prepared by ion exchange, calcination and reduction with hydrogen, as catalysts for this reaction, we found that the catalytic activity per exposed and accessible Pd atom was by almost two orders of magnitude higher than that of Pd/SiO<sub>2</sub> catalysts, tested in the same apparatus under the same conditions. Neopentane conversion, in contrast to most other



hydrocarbon conversions, does not cause catalyst deactivation by "coke" formation, because the neopentane molecule is not able of forming olefins or carbenium ions which are notorious coke precursors. This reaction is thus exceptionally appropriate for determining the intrinsic activity of catalysts. We verified by mass spectrometry in subsequent catalyst oxidation runs that no carbonaceous deposit had been produced during catalysis. The surface exposed Pd atoms were determined by hydrogen adsorption and the accessible Pd atoms by CO adsorption. The catalytic activity per accessible Pd atom showed little dependence on particle morphology<sup>52</sup>; The decisive cause for the enhanced activity of zeolite supported vis-à-vis SiO<sub>2</sub> supported Pd or Pt appears to be the electron-deficiency. Markedly enhanced catalytic activity of positively charged palladium particles in neopentane conversion<sup>53</sup> and hydrogenation of carbon monoxide to methanol<sup>54</sup> has been reported also for other oxide supported catalysts. However, on amorphous supports the incompletely reduced and therefore "electron deficient" metal particle is thermodynamically unstable under reducing conditions, whereas in zeolite cages complexes of the type [Pd<sub>n</sub>-H<sub>x</sub>]<sup>x+</sup> are likely to be stable, though subject to equilibrium with other ligands.<sup>48</sup> The potential of such complexes as superior catalysts merits further study.

8. Stereoselectivity of catalytic reactions due to geometric constraints of particles in cages.

High stereoselectivity of zeolite catalyzed reactions has been established for the acid form of several zeolites. We refer to the well known Mobil process with ZSM-5 catalysts and to work of Csicsery<sup>55</sup>. The potential of zeolite entrapped metals as stereoselective catalysts has been explored. The hydrogenolytic ring opening of methylcyclopentane to the three

isomeric hexanes: n-C<sub>6</sub>, 2-methyl-C<sub>5</sub> and 3-methyl-C<sub>5</sub>, has been used as a probe for testing Pt/NaY catalysts. We found product distributions which differed markedly from those obtained with Pt/SiO<sub>2</sub> of the same dispersion<sup>56</sup>. In particular, the formation of n-hexane was lower for Pt/NaY; this result was rationalized in terms of inhibited roll-over of the adsorbed methylcyclopentane molecule in the narrow slit between Pt particle and cage wall.<sup>57</sup> For bimetallic PtCu/NaY with supposedly cage filling particles a preferential formation of 3-methyl-C<sub>5</sub> was observed<sup>37</sup>, as might be expected on the basis of the geometric orientation of a methylcyclopentane molecule, hitting a PtCu particle through the cage window. This tentative conclusion was supported with monometallic Pt/NaY that was prepared in a way favoring formation of cage filling Pt particles.<sup>58</sup>

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