

Metal Clusters in Zeolites: An Intriguing Class of Catalysts

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Introduction

In 1756 the Swedish scientist Axel Frederik Cronstedt examined a new mineral, using the blowpipe. When the material was heated, it apparently came to life; gas bubbles were released. Combining the Greek words for *boiling* and *stone*, the surprised observer called the material *zeolite*.¹ He could not anticipate that what he had discovered and named would later be used on a vast scale for separating gases, for softening hard water, and as catalysts in the petroleum and chemical industries. The first use of zeolite catalysts in petroleum processing, in the 1960s, was followed by an avalanche of publications and patents. It has been estimated that by 1981 5000 zeolite-related U.S. patents had been issued and 25 000 articles had appeared in the scientific and technical literature. The present paper tries to describe one particular area within this vast territory: zeolites which contain small particles of a few atoms of a transition element. As their main application is in heterogeneous catalysis, we will focus on the catalytic potential of these materials.

Zeolites are crystalline microporous solids, in particular aluminosilicates, with characteristic pore and cage structures. The basic building block is a tetrahedron consisting of a central cation surrounded by four O²⁻ ions. Each tetrahedron is linked to four others; two adjacent tetrahedra share one O²⁻ corner. On the basis of this simple blueprint, a large variety of structures is realized; 64 topologically distinct networks had been identified by X-ray diffraction in 1986.² An example is the *Yzeolite*, of which the structure is shown in Figure 1; each corner point symbolizes a central cation; the O²⁻ ions are located roughly halfway between them. Some preferred positions for guest ions are indicated. In this particular zeolite three types of cages are immediately recognized; in the order of decreasing size, they are called supercages, sodalite cages, and hexagonal prisms. Other zeolites have different cages or only straight channels or tortuous channels which intersect with each other. Regarding the dimensions, it will be obvious that some molecules will easily enter the labyrinth of zeolite channels and cages, while others have to stay outside. Zeolites thus are molecular sieves and as such are widely applied for gas separations.

If in every tetrahedron of a zeolite the central ion was a Si⁴⁺ ion, the charges of the O²⁻ ions would be precisely compensated. Most zeolites are, however, *aluminosilicates*, i.e., some tetrahedra contain Al³⁺ ions; the

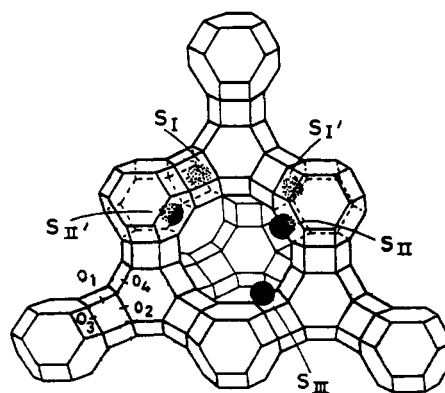
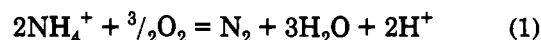


Figure 1. Structure of Y zeolite.

resulting positive charge deficit is compensated by "guest ions", e.g., Na⁺ ions which are located in the zeolite cages or channels. As these ions are fairly mobile and can easily be exchanged, zeolites are also useful as ion exchange agents. Use of this propensity is made on a large scale, e.g., in detergents for softening hard water.

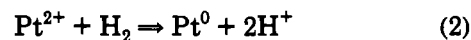
To understand the role of zeolites in heterogeneous catalysis, two additional features are relevant:

(1) *Acid zeolite catalysts* can be produced by first exchanging guest ions against NH₄⁺ ions and subsequently heating the material to high temperature in air or O₂; in this process the ammonium ions are converted into protons, i.e., Brønsted acid sites:



Due to the high acidity of these protons, carbocations are formed when such zeolites are exposed to hydrocarbons. They are intermediates in important industrial processes such as isomerization, cracking, and alkylation. Acid zeolite catalysts are, therefore, used at very large scale in the petroleum industry.

(2) *Zeolite-supported metal catalysts* are the main focus of the present paper. They are often prepared by first exchanging part of the original guest ions in the zeolite against ions of the desired metal, for instance platinum. Usually, these metal ions are introduced in their complexed form; e.g., a Pt tetraammine ion, Pt(NH₃)₄²⁺, will be exchanged for two Na⁺ ions in the zeolite. The ammine ligands are subsequently destroyed by heating in O₂, the so-called "calcination step", and naked Pt²⁺ ions will be formed. Such ions can be reduced, for instance in a flow of hydrogen:



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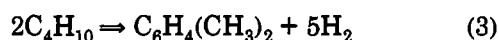
(2) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, 2nd ed.; Butterworth: London, 1987.

As a result, small clusters or even isolated atoms of the transition metal are formed. Coproducts of such reduction are protons which act as strong acid sites. The material thus exposes two types of catalytically active centers: platinum atoms and protons. Such *bifunctional catalysts* are capable of catalyzing many reactions, including the isomerization of alkanes. Zeolite-supported Rh and Pd have been found to catalyze the conversion of synthesis gas ($\text{CO} + \text{H}_2$) to alcohols, ethers, and hydrocarbons. These reactions consist of several steps, some catalyzed by metal, others by acid sites.

When protons are not desired, calcination can be programmed in such a way that some of the ammine ligands are kept intact; they will neutralize the protons formed in reaction 2. This procedure leads to a *monofunctional* catalyst, containing metal clusters as the only active sites. Many variants of this basic chemistry are possible, so that the ratio of metal sites to acid sites in a zeolite can be varied from zero to infinity; moreover, it is possible to exchange ions of more than one metal and thus obtain bi- or multimetal catalysts.

In some metal/zeolite catalysts of interest the introduced metal ions are not completely reduced. We mention two examples:

(1) A catalyst containing gallium or zinc ions in the channels of the zeolite H-ZSM5 is able to convert light paraffins to aromatics (benzene, toluene, and xylenes).³⁻⁶ This dehydrocyclodimerization is a complicated process; in a greatly simplified form the dominant reaction can be written as follows:



There are indications that Ga^{3+} ions in this zeolite are present in their hydrolyzed form as gallyl ions, $(\text{GaO})^+$. Under reaction conditions some of these will be reduced to Ga^+ ions.⁷

(2) A catalyst holding high promise for the abatement of nitrogen oxides contains Cu ions and Cu oxide particles inside the channels of, again, zeolite H-ZSM5.⁸ It permits reduction of NO_x with cheap hydrocarbons as the reductants. Unlike other catalysts used for this purpose, it does so even in the presence of O_2 , which is an inevitable ingredient of the exhaust gas of power stations or diesel engines; in fact the rate of reducing NO to N_2 is substantially *enhanced* by O_2 .⁹

In numerous catalysts at least one of the zeolite-supported elements is completely reduced to the zerovalent state. For such systems we shall briefly discuss evidence for (1) stereoselective catalysis, (2) catalysis by isolated Pt atoms, (3) formation of metal-proton adducts, and (4) bimetallic catalysts.

Stereoselectivity

It will come as no surprise that materials which are highly specific molecular sieves will also promote

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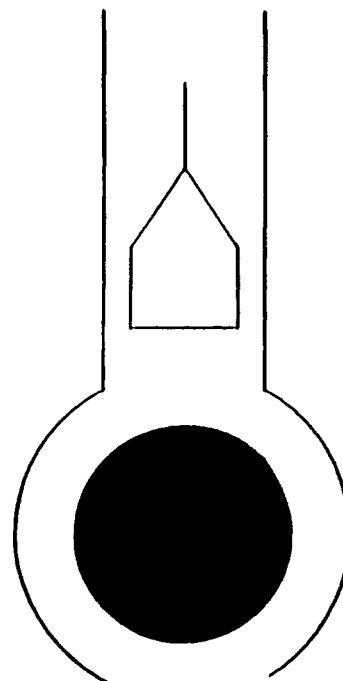


Figure 2. Collimation of methylcyclopentane molecule in a zeolite channel; the impact of the molecule's flat bottom on a Pt particle explains that among the three possible ring opening products 2-methylpentane is formed in a higher than statistical quantity.

stereoselective catalysis. In their acidic mode zeolites exhibit three basic types of stereoselectivity: (a) only those molecules which are capable of entering the zeolite channels will reach active sites; (b) when several products are formed simultaneously, those with the highest rate of diffusion will preferentially escape, while the remaining molecules may be trapped inside the zeolite or converted further; (c) formation of transition states which require only one molecule will be preferred over bimolecular transition states.

The same geometric principles that govern stereoselectivity of zeolites in their acidic mode remain valid for zeolites containing metal clusters; i.e., there are constraints for reactants, transition states, and products. In addition, nonspherical molecules tend to become oriented with their long axis parallel to that of the channel when they diffuse through narrow pores; they will then hit a metal particle end-on.¹⁰ This collimation concept might explain some observations on the ring-opening catalysis of methylcyclopentane (MCP), as illustrated in Figure 2. Hydrogenolytic ring opening of MCP can lead to any of the three C_6H_{14} isomers *n*-hexane, 2-methylpentane, and 3-methylpentane; the head-on collision of an oriented MCP molecule with a Pt particle as suggested in Figure 2 is thought to preferentially open the ring at its flat bottom, so that 3-methylpentane is the preferred product.^{11,12} A different situation arises in a linear channel, if very small Pt clusters or individual Pt atoms are located in side pockets of the channel walls: In this case one can imagine that the five-membered ring is preferentially cut open at its sides, so that 2-methylpentane is formed

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in higher than statistical quantities, as has indeed been observed.¹³

Catalysis by Isolated Pt Atoms

Researchers in heterogeneous catalysis have often tried to disperse valuable metals on a support to such an extent that metal atoms are isolated from each other and easily accessible to molecules in the gas phase. For amorphous supports this is probably not possible. In zeolites, however, metal atoms can be prevented from coalescing with each other by combining chemical and geometric methods. For instance, in a Y zeolite this can be achieved by first chasing Pt^{2+} ions into the small cages, so that there is only one Pt^{2+} in any cage; subsequent reduction under relatively mild conditions results in isolated Pt atoms. They are very reactive: unlike bulk platinum or multiatomic Pt_n clusters, isolated Pt atoms are easily reoxidized by protons to Pt^{2+} ions in reversal of eq 2. The resulting H_2 evolution permits convenient identification of such isolated Pt atoms. In addition, there is "negative evidence", e.g., the absence of XRD lines or EXAFS modulations that are typical for multiatomic particles or clusters.

While Pt atoms that are engaged in small zeolite cages will be inaccessible for most molecules, some recent research focuses on isolated Pt atoms in another zeolite: mordenite. That zeolite has no cages but only linear channels; however, as mentioned above, the channel walls have "side pockets". It appears possible to "anchor" isolated Pt atoms via protons in these niches. In this case the Pt atoms are accessible to CO molecules, and a very characteristic sharp infrared band appears at 2123 cm^{-1} . It disappears upon neutralizing the protons; it is also absent when reduction is carried out at high temperature.¹⁴ Whereas FTIR bands due to CO adsorbed on multiatomic particles are known to shift with degree of CO coverage, due to mutual dipole-dipole coupling of CO molecules, the 2123-cm^{-1} band behaves as a true singleton: neither frequency nor line width depends on CO coverage. When such Pt/H-mordenite is probed as a catalyst for the isotope exchange of the H atoms in cyclopentane, a highly unusual distribution pattern of partly exchanged molecules is found; it agrees with the pattern predicted for monoatomic Pt sites but strongly differs from that found for multiatomic sites.¹⁵

Formation of Metal-Proton Adducts

In 1973 Dalla Betta and Boudart reported an unusually high hydrogenation activity of small Pt particles in zeolite Y. They ascribed this to an electron transfer from the Pt clusters to the zeolite; i.e., the Pt atoms were assumed to become "electron-deficient".¹⁶ Later studies with zeolite-supported Pt, Pd, and Rh showed that the electron deficiency is related to the proton concentration of the zeolite and that it disappears when the protons are neutralized.¹⁷⁻¹⁹ The results suggest

that transition metal clusters in zeolites interact with zeolite protons and form *metal-proton adducts*.^{20,21} In these complexes the positive charge of the protons is shared with the metal atoms. The resulting partial positive charge and its dependence on the proton concentration have been detected by X-ray photoelectron spectroscopy (XPS). It was found that the binding energy (BE) of the Pd $3d_{5/2}$ electrons in the palladium atoms in Pd/NaHY is significantly increased with respect to normal Pd. The shift in BE is largest for isolated Pd atoms in sodalite cages; the XPS data indicate that its charge is nearly equal to that of the Pd^+ ion.²² Likewise, Pd^+ ions and small charged clusters Pd_y^{x+} ($y > x$) have been detected in NaHX by ESR and XPS.^{23,24} The XPS data, moreover, suggest that, in zeolites with high proton concentration, metal clusters are linked to more than one proton in the same cage;²⁵ i.e., in adducts of the type $[\text{M}_n\text{-H}_x]^{x+}$, x may be > 1 .

A molecule which is quite popular for probing metal-catalyzed reactions is neopentane, $\text{C}(\text{CH}_3)_4$. Since it is not able to form secondary or tertiary carbenium ions or olefins in one step, its conversion is not accompanied by extensive formation of carbonaceous deposits, which often deactivate the catalyst with other hydrocarbon probes. Neopentane can be isomerized to isopentane or hydrogenolyzed to isobutane plus methane. When clusters of Pt, Pd, or Rh inside zeolites form adducts with protons, the activity for neopentane conversion is markedly increased.^{19,26,27} For instance, in a series of supported Pd catalysts, the reaction rate per exposed Pd site was almost 2 orders of magnitude higher for Pd supported in a Y zeolite with high proton concentration than on a proton-free zeolite or amorphous support.

Another catalytic probe used to detect "electron-deficient" metal clusters inside zeolites is the competitive hydrogenation of toluene and benzene.^{28,29}

The formation of metal-proton adducts has consequences also for multistep reactions in *bifunctional* catalysts. Reaction intermediates which would otherwise have to shuttle between metal and acid sites can undergo several reaction steps while being attached to the same adduct. As a result the reaction rate is much higher for a catalyst that contains metal clusters and protons inside the same zeolite than for a physical mixture of zeolites, each containing only one type of site.³⁰

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Also the *selectivity* of catalysts might be affected by the proximity of metal clusters and protons in the same zeolite cage. As mentioned above, the five-membered ring of methylcyclopentane (MCP) is opened by C–C fission on metal sites, but when platinum and protons coexist in the same catalyst, ring enlargement to cyclohexane and benzene occurs. If in catalysts containing metal and acid sites these sites were separated one from another, ring opening and ring enlargements would be expected to be additive at low conversion. In reality they are not, but the turnover frequency for ring enlargement increases and that for ring opening decreases with increasing ratio of acid to metal sites, n_A/n_{Pd} .³¹ Addition of acid sites to a metal/zeolite catalyst apparently not only opens an additional reaction path but also modifies the metal sites. This concept is also consistent with findings by the group of Guisnet, who studied the conversion of *n*-heptane, e.g., over Pt/NaHY catalysts with various ratios of Pt/H⁺. With this test three major reaction types can be identified: isomerization, hydrogenolysis, and cracking. With high metal loads, hydrogenolysis was found to be catalyzed preferentially, whereas a high concentration of acid sites enhances cracking. Remarkably, the rate of isomerization passes a maximum at intermediate values of Pt/H⁺.³² This suggests that an intimate proximity of metal and acid sites is required for this reaction, which is also the most desired one in industry. Metal and acid function thus appear to modify each other rather than acting independently.

Since protons in metal–proton adducts are bridging between metal atoms and oxygen ions of the zeolite wall, they also act as *chemical anchors*.^{33,34} An important consequence is that a high metal dispersion, even monoatomic metal atoms, can be achieved in zeolites with high proton concentrations. This has been demonstrated by electron microscopy: whereas, after careful reduction in a proton-rich zeolite, extremely small Pt particles are formed, neutralization of these protons, followed by reduction at the same temperature, results in large particles. They are actually larger than the zeolite channels, so that local destruction of the zeolite takes place. Protons can, however, be displaced from the metal by molecules which form stronger bonds to it, for instance, carbon monoxide: its adsorption on Pd₁ atoms or Pd₄ clusters cuts the anchor, and the clusters start migrating even at room temperature. When they meet each other, larger Pd clusters are formed. The ultimate size of these particles depends on the width of the cage windows: in a Y zeolite, Pd₁₃ clusters, surrounded by CO ligands, are readily formed, but in zeolite 5A, with much smaller windows, coalescence of the primary particles stops at the stage of a Pd₆ core, surrounded by CO ligands. Cutting the “anchor” thus sets the “ship” free in both cases; once clusters are mobile, their growth is limited by the zeolite geometry. In this case one can even see the displaced “anchor”: the protons detached from the adduct show up in IR spectroscopy as added intensity to the IR band characteristic of the vibration between zeolite O²⁻ and

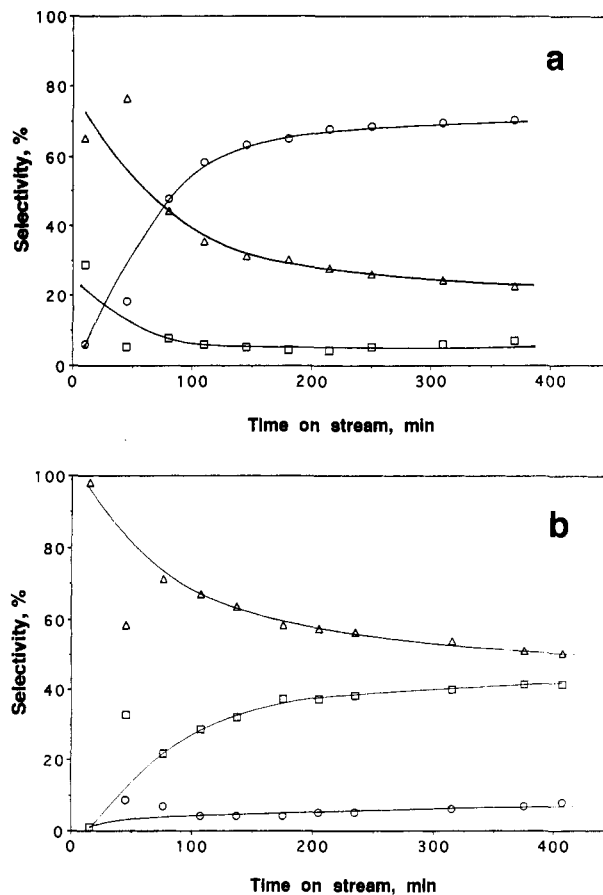


Figure 3. Selectivity of CO hydrogenation over PdCo/NaY catalyst. If the calcined catalyst precursor is reduced without delay, the oxygenate products, methanol and dimethyl ether, prevail (a). If, prior to reduction, the calcined precursor is exposed to a moist atmosphere during several days, methane and higher hydrocarbons prevail (b). (The catalyst contains 9 Co and 9 Pd atoms per unit cell of the zeolite. Reaction conditions: 250 °C, 10 bar, H₂/CO = 1/1. For details see ref 38; O, oxygenates; Δ, methane; □, C₂₊ hydrocarbons.)

H⁺.³⁵ If subsequently part of the CO is removed by purging the catalyst with argon, some protons in the vicinity of a Pd₁₃ cluster form again a chemical bond with the metal; this process results in a decreasing intensity of the same IR band due to the O–H vibration.³⁶

Bimetal Clusters in Zeolites

Catalysis with zeolites containing two metals is anything but additive. With many preparations metals such as Ni or Co are virtually inactive, because the precursor ions escape into very small zeolite cavities where they cannot be reduced at temperatures compatible with the stability of the zeolite. In the presence of a second metal, e.g., Pt or Pd, and a calcination program which keeps the atoms of both elements in close proximity, nearly complete reduction is possible at fairly low temperatures and alloy particles are formed. At elevated temperature, for instance during use as a catalyst, the composition of the alloy particles will change again, because zeolite protons selectively oxidize the atoms of the less noble metal, leaving pure clusters

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of the more noble metal in larger cages.³⁷ This "leaching" by protons is thus another card up the chemist's sleeve to control the composition of bimetal particles in zeolites.

For bimetal catalysts containing palladium and cobalt in zeolite Y it was found that subtle changes in the preparation conditions have dramatic consequences in the catalytic performance. These catalysts catalyze the conversion of synthesis gas to methane, higher hydrocarbons, methanol, and dimethyl ether. In Figure 3 is shown the product pattern for two catalysts, both containing the same quantities of Pd and Co. Both were calcined and reduced at the same temperature. Still, the catalyst selectivity is strikingly different; over one catalyst the oxygenates (methanol, dimethyl ether) prevail, but over the other catalyst they are almost negligible and production of hydrocarbons predominates.³⁸

To understand this result one must recognize one difference in the preparation programs of the two catalysts. In one sample the precursor was reduced immediately after calcination; in the other case it was allowed to stand in an atmosphere containing some moisture. As cobalt ions form very stable hexaquo complexes, this moisture was apparently sufficient to induce migration of Co ions out of the small cages and back into the large supercages. This relocation and mobilization of the cobalt ions has important consequences: during reduction of the Pd²⁺ ions in the supercages, the cobalt ions migrate to the metal nuclei so that they are reduced together with the Pd, and alloy

particles rich in Co are formed. As cobalt is known to be an efficient Fischer-Tropsch catalyst, it is plausible that such particles will catalyze predominantly the formation of hydrocarbons.

The same chemistry of bringing metal ions back to large cages by offering attractive potential ligands has potential for other applications. For instance, this idea has been applied in the rejuvenation of aged metal/zeolite catalysts.³⁹

Conclusions

Metal/zeolite catalysts offer challenging perspectives for catalysis; as an object of fundamental research they have helped to revive the debate on some general concepts. In the present Account the authors present his personal views, based on the available experimental facts. Metal-proton interaction in zeolites and anchoring of metal clusters by protons are phenomena supported by independent data. The formation of isolated Pt atoms, in sodalite cages of Y and in side pockets of mordenite, is possible at low metal loadings, low reduction temperatures, and high concentrations of protons. The catalytic characteristics of metal/zeolite catalysts can be manipulated by exploiting the chemistry which drives metal ions into small cages or stabilizes them with appropriate ligands in large cages. Hydrolysis of multipositive ions to oxo complexes of low effective charge, such as (GaO)⁺, improves the Coulomb interaction with widely spaced negative charges in the zeolite. Formation of "alloy" clusters in bimetallic catalysts is controlled, among other things, by reoxidation of one metal by zeolite protons at elevated temperatures.

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