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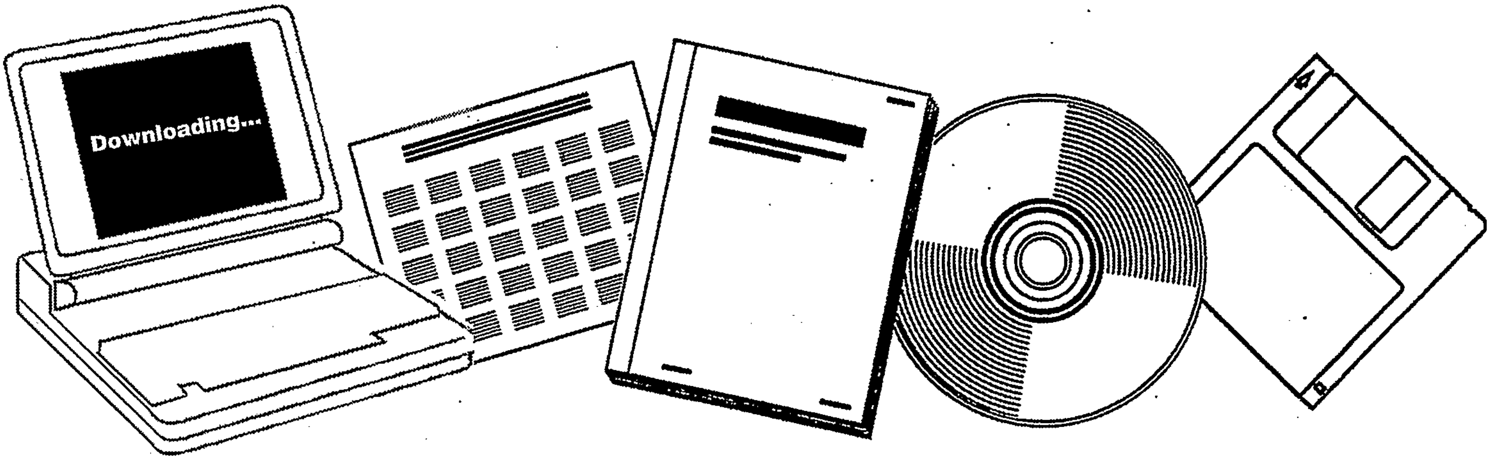

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CHEMICAL INTERACTIONS IN MULTIMETAL/ZEOLITE CATALYSTS

PROGRESS REPORT

FOR PERIOD JANUARY 7, 1990 - JANUARY 6, 1991

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Project Title:

Chemical Interactions in Multimetal/Zeolite Catalysts

Principal Investigator: W. M. H. SACHTLER
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During the project year, novel guidelines which had appeared in the preceding period from our research on bimetal/zeolite catalysts were pursued further. In addition, new concepts have emerged and were identified. They appear to reveal a novel type of chemistry with potentially strong impact on heterogeneous catalysis, even beyond the field of zeolite supported systems.

In this report four subjects areas will be focused briefly.

Subject Area 1: PtCu/NaY and Pd/Cu/NaY Catalysts.

Previously we had shown that bimetal particles are formed in supercages of NaY. With increasing Cu/Pt ratio at given Pt loading of the zeolite the rate of ring opening of methylcyclopentane decreases, but the rate of ring enlargement to benzene and cyclohexane increases. The former result is attributed to the dilution of the Pt ensembles, the latter result is due to the increasing acidity, since two protons of high Brønsted acidity are created by the reduction of each Cu^{2+} ion. This concept has now been confirmed by studying the nature of the carbonaceous deposit which is formed during use as catalyst. The temperature programmed oxidation technique, which we developed earlier, identifies coke in contact with metal sites by a peak at low temperature and coke on acidic sites by a peak at higher temperature. Our results show that with increasing Cu content the former peak decreases but the latter peak increases. An unexpected result is that the low temperature peak vanishes for catalysts which are still able of catalyzing the hydrogenation of benzene, though with a low rate. This result suggests that coke deposition on Pt is a "structure-sensitive" reaction, requiring a large ensemble of contiguous Pt atoms.

A second group of results shows that the reduction of Cu^{2+} ions in this zeolite is reversible. At high temperature the protons, which were formed during reduction, selectively reoxidize the Cu atoms, without apparently affecting the Pt atoms. The Cu^{2+} ions escape to small zeolite cages, where they have been identified by EXAFS. In the case of PdCu/NaY this "leaching" of Cu atoms out of the alloy particles results in pure Pd particles which we can detect *in situ* by their ability of forming Pd hydride, in contrast to the original PdCu particles. This hydride is easily detected by its characteristic temperature programmed desorption peak.

Subject Area 2: Reducibility of Ni in PdNi/NaY Catalysts

The presence of palladium has been found to strongly enhance the reducibility of nickel in NaY. Pretreatment conditions have a pronounced effect on the temperature programmed reduction (TPR) profiles of monometallic and bimetallic palladium/nickel catalysts. At high pH, Ni is hydrolyzed in supercages; at low pH, Ni^{2+} ions migrate to smaller cages. Reduced Pd particles in the supercages, in close contact with NiO clusters, enhance their reducibility; the protons formed during Pd reduction however, redisperse them to form Ni^{2+} ions, thus decreasing their reducibility.

As with PdCu/NaY, reduction is partly reversible: at elevated temperature and in the absence of gaseous H_2 zeolite protons selectively oxidize Ni atoms in NiPd particles. This phenomenon has been exploited to identify the mechanisms of the reducibility enhancement. After leaching of the Ni from the PdNi particles by the oxidizing action of zeolite protons, a situation is created where all Pd is present in the form of Pd particles, but all the Ni as Ni^{2+} ions in small cages.. Under reducing conditions at elevated temperature Ni^{2+} ions leave the small cages and adhere to Pd particles, where they are swiftly reduced by chemisorbed hydrogen; the hydrogen atoms lose their electron and become zeolite protons. Indeed TPR shows only one peak which can thus be assigned to this mechanism. The position of this TPR peak is identical with one of the three TPR peaks in the original reduction of the sample containing initially all Pd and Ni as ions. We thus conclude that the two other peaks reflect different reduction mechanisms. One of these peaks is located at a somewhat lower temperature than the TPR peak of the monometallic Pd/NaY system, it is therefore assigned to cation-cation bonding, similar to the situation encountered in our previous work with (Pd + Co)/NaY. The third peak is very likely due to interaction of Ni^{2+}ions with Pd° atoms. Summarizing it follows that three processes are responsible for the Pd enhanced reducibility of Ni: (1) interaction of Ni^{2+} with Pd^{2+}; (2) interaction of Ni^{2+} with Pd atoms; (3) interaction of Ni^{2+} with Pd particles.

Subject Area 3: CO Hydrogenation Over PdNi/NaY Catalysts

The PdNi/NaY catalysts are at present being tested for CO hydrogenation at elevated pressure. First results are quite exciting: the bimetallic catalysts are much more active than each of the corresponding monometallic counterparts, Pd/NaY and Ni/NaY. This statement also holds per metal atom in the catalyst and presumably per exposed metal atoms; the latter statement is, however, less clear, because the metal dispersion changes during the catalytic process. The selectivity (formation of methane; formation of normal alkanes via a Fischer-Tropsch mechanism; formation of branched alkanes via methanol and dimethyl ether in the bifunctional mode of the catalyst) deviates from that of the monometallic samples. It is also dependent on the PH of the washing procedure after ions exchange. We prefer, at this stage, to refrain from drawing firm conclusions, our impression is that mixed NiPd ensembles on the surface of the bimetallic particles are contributing to the enhanced catalytic activity.

Subject area 4: PdFe/NaY, Ga/H-ZSM5 and PtGa/H-ZSM5 Catalysts

In this category it appears that a reduced metal (Pd or Pt) is interacting with a metal ion of another element, without reducing the latter to the zerovalent state. The chemical interaction of Pd and Fe in NaY has been studied in cooperation with professor Dumesic in whose lab Mössbauer spectra were measured. The results have been published in Applied Catal. TPR results show that Pd strongly catalyzes the reduction of Fe^{3+} to Fe^{2+} by H_2. Mössbauer data prove that reduced Pd particles interact with Fe^{2+} cations in the zeolite. TPD of H_2 illustrates an increasing degree of interaction with increasing reduction temperature. FTIR spectra of adsorbed CO indicate that Fe cations populate the surface of the Pd particles, similar to Ti ions on TiO_2 supported group VIII metals in the SMSI state. EXAFS data show that, after high temperature reduction, the Pd coordination number is lower for PdFe/NaY than for Pd/NaY. This is attributed to inhibited Pd particle migration due coulombic interaction of the Fe cations that decorate the Pd particles, with the zeolite lattice.

As mentioned in our proposal, the Ga/H-ZM5 and PtGa/H-ZSM5 catalysts are intriguing because of their ability to catalyze the dehydrocyclodimerization of propane to benzene and of butane to akylbenzenes. Little is understood about the catalytic sites and the details of the mechanism. In 1990 we have started this part of our proposed program; we have succeeded in reproducing literature data and characterized both the monometallic Ga/H-ZSM5 and the bimetallic PtGa/H-ZSM5 catalysts by TPR. The results show that Pt strongly enhances the reducibility of Ga, without however forming an alloy. It also appears that the active form of these catalysts contains Ga^{1+} ions.

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