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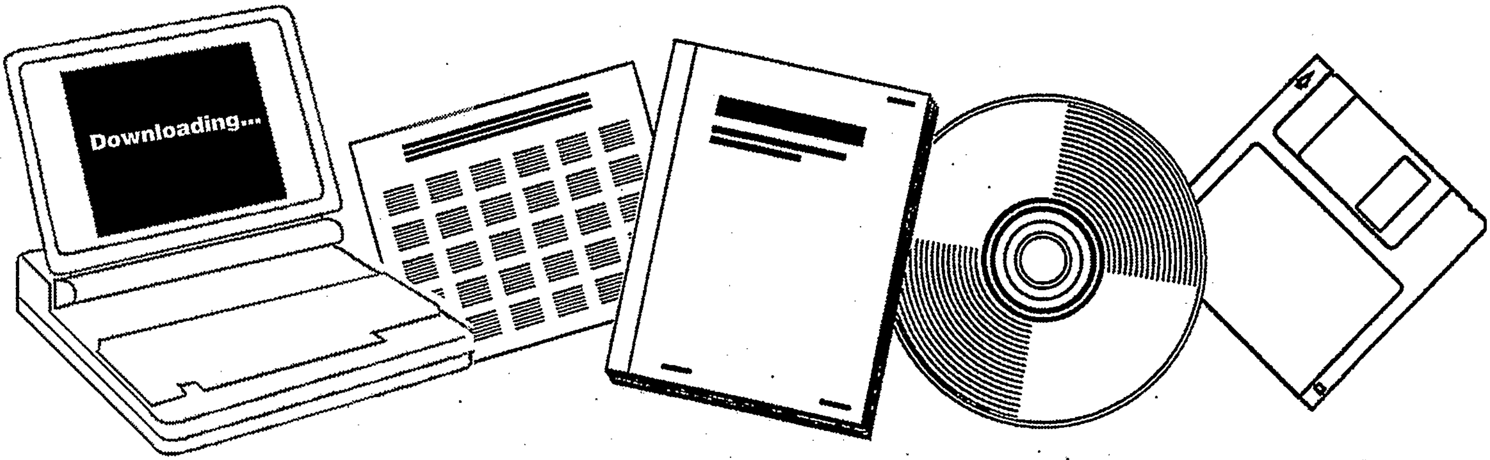

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PROGRESS REPORT

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6. Descriptive Summary

Research is proposed on two groups of zeolite based catalysts that contain two transition elements. In one group both metals are fully reduced, in the other group one element is left as a positive ion; it can act as a "chemical anchor", or as a catalyst promoter for the reduced metal. The objective is to explore the potential of such materials for designing superior catalysts for synthesis and conversion of hydrocarbons and other energy carriers. ENDOR, EXAFS, CO-FTIR and TPD will be used to identify the interaction of Mn^{2+} ions with Rh_n particles in the same zeolite cage. EXAFS at the K-edge of Fe and Pd, FTIR and Mössbauer spectroscopy will be used to characterize Fe ions and alloyed Fe atoms in PdFe/NaHY. The catalysts will be probed with CO hydrogenation and conversion of hydrocarbons.

Methods which proved successful in our study of Y supported bimetal systems will be applied to identify the state of Pt and Cu in ZSM-5, a catalyst system holding large promise for NO abatement, even in the presence of oxygen.

Renewal Proposal: DOE project DE FG02-87ERA 13654

Chemical Interactions in Multimetal/Zeolite Catalysts

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Abstract

Research is proposed on zeolite catalysts that contain two transition elements of different reducibility. In one group of catalysts the active sites are ensembles of atoms on the surface of well reduced bimetal or "true alloy" particles. In another group one transition metal is reduced to the zerovalent state, but the other element is left as a positive ion; it can act as a "chemical anchor", lowering the mobility of the reduced metal, or as a catalytic "promoter", interacting with molecules that are adsorbed on the metal particle. Chemical anchoring and catalyst promotion are of large importance in catalysis but little understood; zeolite supported systems offer unique possibilities to study them. ENDOR, EXAFS, CO-FTIR and TPD will be used to identify the interaction of Mn^{2+} ions with Rh_n particles in the same zeolite cage. This research will be the first application of ENDOR in this field. The catalysts will be probed for CO hydrogenation. For PdFe/NaY, EXAFS, both at the K-edge of Fe and Pd, and Mössbauer spectroscopy will be used to identify interactions in PdFe/NaHY.

Our recent discoveries on the causes of catalyst deactivation motivate us to study chemical anchoring by TM ions in ZSM-5 supported Pd. EXAFS and FTIR will be used

in appropriate cases, in addition to catalytic study, to characterize $PdX^{y+}/ZSM-5$ catalysts where X is a second transition metal ion.

Cu and PtCu in ZSM-5 hold large promise for NO abatement, even in the presence of oxygen. The oxidation state of both metals and their interaction are still a mystery which needs to be solved; we accept this challenge and propose to use the same methods which we previously found to be so successful in our study of Y supported bimetal systems.

I. Research Objectives

By utilizing our experience in producing bimetallic clusters of controlled composition in zeolite supports, the proposed research herein will explore the catalytic potential of two forms of bimetallic clusters, *viz.*: (a) "true alloy" clusters consisting of two zerovalent transition metals and (b) "metal-metal ion" clusters in which one transition metal is zerovalent, while the other is present as a positive ion in direct contact with the former. For clusters of the latter category, (b), two functions of the positive ion will be identified: (b-1) the *catalyst promoter* function, i.e. modification of the catalytic activity and selectivity of the reduced metal, and (b-2) the *chemical anchor* function, i.e. preventing or delaying agglomeration of clusters of the reduced metal.

II. Background and Incentive

IIa."True Alloy" Clusters

In previous research we have demonstrated that alloy clusters exhibit distinctly different catalytic activities from physical mixtures of the clusters of the pure components. The present PI introduced the concepts of "*ensemble effect*" and "*ligand effect*" into the scientific literature on heterogeneous catalysis.[1] More recently, to rationalize the unusual catalytic propensities of alloys such as PtRe, PdNi, PdCo or PdAu, the concept of "*mixed ensembles*" has been used.[2]

Our current DOE sponsored work on zeolite supported bimetallic clusters has resulted in a number of novel strategies for the design of bimetallic clusters in zeolite cages. For instance we were able to control the location, ligancy, and reducibility of less reducible ions as well as control the composition and morphology of the reduced bimetal clusters in systems such as PtCu, PdCu, PdNi or PdCo in faujasite-type zeolites.[3] It was found that a proximity of the more readily reducible ions and those of less reducible ions is crucial for the enhanced reduction of the latter and, therefore, essential for the formation of bimetal clusters; This proximity requirement can be achieved via a carefully designed calcination program prior to metal reduction. Specifically, we can control the number of ligands in each ionic component and consequently the ions are either separated in different cages or forced into the same cages, by exploiting the tendency of naked multivalent cations to migrate from large to small zeolite cages with high negative charge density.

More recently we explored a different strategy. The ions of both components are forced to migrate from the "hidden" sites to the large cages after calcination at high temperature. Upon reduction, true alloy clusters are formed in the large cages. The key "trick" is to provide potential ligands such as H_2O or NH_3 to the transition metal ions, i.e. creating a thermodynamic driving force for the formation of complexes (hexaquo or tetrammine) that can only exist in large cages. By exploring this chemistry we have been able to dramatically change the selectivity of CO hydrogenation over PdCo/NaY catalysts from mainly hydrocarbons to oxygenates.[4] The same basic principle, ion migration from small to large cages, has been exploited in our catalyst rejuvenation project. In this case, exposure to ammonia was essential for regulating migration of Pd^{2+} ions, a step which is decisive for the successful redispersion of large to small Pd particles in zeolite Y.[5]

Another successful strategy employed by us was to hydrolyze the less reducible ions in the supercages prior to calcination. Upon reduction, true alloy clusters are formed in the supercages.

IIb. Combinations of clusters of a fully reduced transition metal with cations of a second transition metal

Reduction conditions have been found, for zeolites containing Pt+Fe, or Pd+Fe, such that Pd or Pt is quantitatively reduced to Pd^{o} or Pt^{o}, whereas the majority of the Fe^{3+} ions is only reduced to the Fe^{2+} state. The interaction of the reduced transition metal (TM1) particles with cations of another less reducible transition metal (TM2) has two important effects on the ultimate catalyst:

(a) *catalyst promotion* by the interaction of the decorating TM2 cation with molecules adsorbed on the TM1 particle.

(a) *chemical anchoring* of the primary TM1 particles to the zeolite cages by TM2 cations.

A novel strategy for obtaining zeolite encaged TM1 clusters in close contact with one or more cation(s) of TM2 has been recently discovered in our lab. In this strategy both metals are first co-reduced to form alloy particles inside zeolite cages; the alloy is then forced to react with zeolite protons. In the case of Pd_xCu_y the following reaction steps have been discerned:

1. $Pd_xCu_y + yH^+ \;\; ====> Pd_x + yCu^+ + y/2\ H_2$
2. $yCu^+ + y\ H^+ \;\; ====> Cu^{2+} + y/2\ H_2$

This process will later be called *proton leaching*. Evidence has been obtained which suggests that the Cu^+ ions at the end of step (1) are still in contact with the Pd_x particles, whereas at the end of step (2), the Cu^{2+} ions migrate to smaller cages.[6] *Proton leaching* has also been observed for PtCu and PdNi; we assume that this is a rather general phenomenon which can be exploited to create adducts of TM1 clusters with TM2 cations. In view of the vast importance of *catalyst promotion* and *chemical anchoring* for industrial catalysis, we propose to study both phenomena systematically.

Extensive literature has shown that *catalyst promotion* of TM1 catalysts by TM2 cations is crucial in CO hydrogenation. Ichikawa, Ponec, Shriver and other groups, including our own, have shown that the catalytic activity and selectivity of Rh and Pd catalysts in the hydrogenation of CO to methane, higher hydrocarbons, methanol, higher alcohols, ethers and aldehydes is dramatically changed by TM2 ions on the surface.[7,8] The systems Rh + Mn^{2+} and Rh + V^{4+} have received special attention.[9,10] Often the promoter ion is initially present as a supporting oxide. Upon partial reduction the lower valent ions together with charge compensating oxide ions decorate the surface of the reduced TM1 particle. For this procedure the term *SMSI*, acronym for "Strong Metal-Support Interaction", has been proposed by Tauster.[11] In the case of zeolite supports the matrix carries the negative charge; it is challenging to design procedures to position a reduced TM1 cluster and a TM2 cation into the same zeolite cage. As vanadium is known to cause zeolites destruction, we propose to concentrate on the $Rh+Mn^{2+}$ and the $Pd+Fe^{2+}$ systems for this study.

A catalyst for which electronic interaction between metal particles and cations has often been proposed is the Pt/K,Ba-L-zeolite system, the best known catalyst for the dehydrocyclization of n-hexane to benzene. No research is known to us, where the Ba^{2+} ions, supposedly located in cancrinite cages, are replaced by TM cation.

Chemical Anchoring of Pt or Rh particles to zeolite cage walls by means of Fe^{2+} or Cr^{3+} ions was the focus of our research under this DOE contract during the first phase. Three discoveries which we made since that time justify returning to that topic:

1. We found that zeolite protons can act as reasonably strong anchors; as a consequence true metal dispersion after identical reduction conditions is higher in H-zeolites than e.g. in Na-zeolites.[12]

2. The phenomenon of CO induced migration of clusters was discovered; adsorbing CO displaces zeolite protons as ligands on a metal cluster; the anchor-less carbonyl clusters swiftly migrate through zeolite channels even at room temperature and coalesce to larger carbonyl clusters characterized by highly structured IR spectra. This coalescence process continues until the critical size of the carbonyl cluster is attained where the metal

core is no longer able to traverse through the cage windows. In the case of Pd in Y zeolites this stage is reached for clusters of 13 Pd atoms, but in zeolite 5A Pd_6 carbonyl clusters are unable to pass through the smaller windows.[13]

3. During a catalytic reaction, such as conversion of methylcyclopentane (MCP), metal migration is usually accompanied by formation of carbonaceous overlayers. Recently we found, however, that Pd/ZSM-5 is exceptional; MCP conversion over this catalyst does not lead to measurable formation of coke, which we usually identify by temperature programmed oxidation or NMR spectroscopy. This discovery opens the opportunity to study metal agglomeration and its suppression by chemical anchoring in the absence of the second cause of catalyst deactivation, coking. Most remarkably we found that with cyclopentane (CP) the rate of Pd agglomeration is much lower than with MCP at identical reaction conditions. This exciting result indicates that the tertiary carbon in MCP is essential in the agglomeration of primary Pd particles. We assume that MCP reacts with the proton anchored Pd clusters, forming a metal-carbocation-adduct:

$$[Pd_n\text{-}H]^+ + C_6H_{12} \;{=}{=}{=}{=}{>}\; [Pd_n\text{-}C_6H_{11}]^+ + H_2$$

which deprives the Pd cluster of its proton anchor, so that metal agglomeration is facilitated because the carbocation does not anchor the primary Pd particles. This conclusion was further supported by the observation that Pd particles also grow significantly when the reduced Pd/HZSM-5 catalysts is exposed to a NH_3/H_2 mixture at reduction temperature so that the protons are converted into NH_4^+ ions. These results provide a strong incentive to study more stable chemical anchors of TM1 particles which retain the anchoring effect under actual catalytic conditions. Research is therefore proposed with ZSM-5 supported bimetal catalysts. We also hope to find the cause of the remarkable differences in metal migration rate between elements which are quite similar, such as platinum and palladium.

In the above analysis of the present state of our scientific understanding of these fields we have made a distinction between fully reduced TM alloy systems and combinations where TM2 element remains in an oxidation state > 0. This distinction is conceptually valuable, but in reality the two categories will be less sharply divided. For instance, in PdCo/NaHY a certain fraction of the Co may be alloyed to Pd, while another fraction remains unreduced. During the catalytic process part of the alloyed Co will be oxidized by *proton leaching*, so that the ratio Co^{o}/Co^{2+} will decrease with time on stream. The same holds, *mutatis mutandis*, for PtCu, PdNi, PtFe or PdFe.

A bimetal system of high potential interest is the group of NO abatement catalysts such as PtCu/ZSM-5 for large scale application. We have been studying the monometal Cu/ZSM-5 system and are intrigued by its ability to catalyze the reduction of NO by propane even in the presence of comparatively large concentrations of O_2.[14] As Somorjai observed a similar enhancement by O_2 on the reduction of NO with NH_3 over Pt catalysts,[15] we intend to study NO reduction with C_3H_8 and/or NH_3 over ZSM-5 supported bimetal combinations such as PtCu. Under steady state conditions it is conceivable that the Pt will be predominantly Pt^0, but part of the Cu will be present as Cu^+ or Cu^{2+}. We have identified Cu^+ by the strong adsorption of CO with FTIR. The Cu-Pt interaction will be identified by EXAFS. Besides understanding the fundamental chemistry of NO abatement catalysis, we will be searching for the optimum NO abatement catalyst.

III. Research Strategy

To achieve the objectives specified above we shall:

(1) *Prepare* zeolite supported bimetal clusters using the experimental "tricks" outlined above, including forced ion migration followed by reduction or decomposition of a volatile metal carbonyl of one TM element in contact with reduced zeolite encaged clusters of the other TM element;

(2) *Characterize* the bimetal cluster by the arsenal of chemical, spectroscopic, and physical techniques used in our previous work, to which we will now add EPR, ENDOR, SENFR (spin echo ferromagnetic nuclear resonance) and Mössbauer spectroscopy in collaboration with professors Brian Hoffman , Joe Budnik and James Dumesic;

(3) *Probe as catalysts* these materials, using three basic test reactions specified below;

(4) *Determine the extent of metal agglomeration* at elevated temperature and under conditions of catalytic application, identify its mechanism and the effect of chemical anchors to prevent or delay this process.

Among the bimetal systems which we propose to study, four prototypes can be identified:

(1) PdFe/Y. In this system the Pd will be completely reduced. To study clusters which also have the Fe in the zerovalent state, we shall decompose $Fe(CO)_5$ selectively on prereduced Pd clusters in analogy to our previous work with zeolite supported PtRe, where reductive decomposition of $Re_2(CO)_{10}$ on Pt/NaY and Pt/HY was found extremely

successful.[16]

These preparations will be compared with others where Fe is originally present as a positive ion and co-reduced with Pd, and those where part of the reduced Fe is re-oxidized by *proton leaching*. The effect of complexing agents such as NH_3, NO, and CO to enforce migration of Fe ions from small to large cages will be studied.

(2) RhMn/NaHY. This will be our prototype of a cluster where TM1 metal (Rh) is completely reduced, whereas the TM2 element (Mn) will remain cationic. It seems an optimal system for identification by ENDOR, since the Mn^{2+} ions have a well defined EPR signal, while Rh has a natural abundance of 100% of the isotope with nuclear spin 1/2. It is a fortunate coincidence that this system provides an avenue for research on the promoter effects in CO hydrogenation. Models of the Mn^{2+} promotion of Rh have been published and widely discussed.[17] FTIR of adsorbed CO and EXAFS will be extensively used besides ENDOR to identify the interaction of Rh and Mn and their effect on the adsorption of CO.

(3) PdX^{y+}/HZSM-5 catalysts will be studied during conversion of MCP and CP in order to identify the effect of TM anchors in delaying or preventing Pd metal agglomeration. Fe, Cr, and Mn are primary candidates for the anchoring element X, but others, including lanthanides will also be tested.

(4) PtCu/ZSM-5. As mentioned, Cu/ZSM-5 is unique in NO reduction by C_3H_8 because O_2, in contrast to most other catalysts, does not act as poison but actually accelerates the NO reduction.[18] We will be using our testing equipment for the bimetal catalysts and identify the Pt-Cu interaction by EXAFS and the techniques which we have been applying

to Cu/ZSM-5.[13]

The catalytic probe reactions which will be used in the proposed research are:

(1) CO hydrogenation. This reaction is chosen in view of the mission of DOE to convert natural gas or coal into liquid energy carriers, but also in view of the characteristic response in selectivity from changes in the nature of the active sites. Moreover the FTIR data of adsorbed CO can be applied rather directly to mechanistic interpretations of this reaction.

(2) MCP and CP conversion. This is a well proven reaction typical of hydrocarbon reactions on mono- and bifunctional catalysts. This reaction will also reveal by its proven stereoselectivity the intricacies of the microgeometry of metal/zeolite systems.[19]

(3) NO decomposition and NO reduction with hydrocarbons or ammonia are obvious probe reactions for catalysts of the PtCu/ZSM-5 system.

IV Plan of Work

IVa PdFe/NaY Catalysts.

These will be used for CO hydrogenation. In one series PdFe/NaY samples with zero valent Fe will be prepared by first reducing Pd/NaY at low temperature, neutralizing the protons formed during reduction by ion exchange with NaOH, followed by mild reduction, and subsequently subliming $Fe(CO)_5$ onto the Pd/NaY. The CO ligands will be removed by purging with Ar. In parallel work zeolite encaged PdFe clusters will be made by starting with neutral Pd(allyl-cyclopentadienyl) and $Fe(CO)_5$ clusters.

In a second series the same procedure will be followed, but omitting the neutralization step. Heating in Ar will induce oxidation of part of the Fe by zeolite protons; this phenomenon will be monitored by measuring the released hydrogen. In a third series, conventional ion exchange will be applied to bring Fe ions into the zeolite, subsequent reduction will leave part of them in the Fe^{2+} oxidation state while another part will be reduced to form a PdFe alloy. TPR will reveal the reduction peaks and the total amount of H_2 consumed. We propose to systematically study the reducibility of the Fe ions in the presence of Pd as a function of the pH of the ion exchanging solution and the subsequent washing. It is known that the pH has a very strong effect on the reducibility of Co and Ni in zeolites, the same is to be expected for Fe. Likewise, the calcination and reduction programs are crucial for the reducibility of multivalent cations. Special attention will be focused on the effect of potential ligands such as NO, CO, NH_3, and H_2O, to which the calcined sample will be exposed prior to reduction. In an alternative strategy we will also use Mg^{2+} or Ca^{2+} ions to block small zeolite cages for Fe ions, following our previous work with PdNi/MgY catalysts. The purpose is, again, to force the Fe ions into the supercages where they can be reduced by the action of the noble TM.

All samples will be probed as catalysts and analyzed by physical methods. These include Mössbauer, EXAFS, FMR, XPS, XRD, SEFNR, CO FTIR spectroscopy and magnetic susceptibility measurements. Published data show that Fe has a very strong effect on the magnetic properties of Pd. PdFe alloys have been reported to be ferromagnetic even with trace amounts of Fe. Since the Curie temperature depends on the Fe concentration in the alloy phase, this will be used for the detection of true PdFe alloy particles in zeolites. The transition from superparamagnetism to ferromagnetism can be observed with Mössbauer, spin-echo ferromagnetic nuclear resonance (SEFNR), FMR and magnetic susceptibility measurements. Mössbauer spectroscopic study will be carried out in collaboration with Professor Dumesic at the University of Wisconsin. SEFNR and magnetic susceptibility study will be performed in the laboratory of Professors Budnick and Hines at the University of Connecticut. FMR work will be done at the laboratory of Professor Hoffmann at Northwestern University. The bulk composition of the PdFe phase can be deduced from the published literature where various Fe concentrations in such alloy were reported. The relative surface concentration of the PdFe alloy particles will be probed with CO FTIR. Comparison of the FTIR spectra of the PdFe alloy particles will be made with those of pure Pd and Fe. The FTIR spectra of Pd carbonyl clusters ranging from Pd_6, Pd_{13}, and larger Pd particles have been reported in the laboratory of the present PI. Those of Fe carbonyl clusters are well documented in literature. The structure and particles sizes of the PdFe alloy will be determined with EXAFS. The relative concentration of Fe° and Fe^{2+} will be investigated with XPS. After Fe proton leaching, the magnetic properties of the alloy particles are expected to vary strongly; moreover the propensity of Pd to form hydrides is known to change drastically with the presence of an alloy partner. In our previous work on PdCu/NaHY we used this detection of the Pd hydride by TPD to monitor proton leaching of Cu from these alloys; the same will be done with PdFe alloys. The amount of H_2 released in proton leaching provides important information on the composition of the PdFe alloy.

By performing EXAFS on the K-edge of each individual component of the bimetal systems, we plan to use the difference in bond distance between Pd-Fe° and Pd-Fe^{2+} to distinguish the alloy bond and the promotional metal-ion pair. We will also use FMR and ESR to characterize the $PdFe^{x+}$ systems.

CO hydrogenation with PdFe/NaY catalysts will be carried out at high pressure under conditions similar to those used previously with PdCo and PdNi catalysts. Fe was reported to change the selectivity of Rh/SiO_2 catalysts from CH_3CHO and CH_3COOH to C_2H_5OH. Catalysts will be characterized physically at various stages of preparation, and after catalytic reaction. The expected change in particle size during reaction will be analyzed by XRD which will also detect formation of carbides as in our previous work, which showed that formation of Pd carbide is suppressed by small admixtures of Co.

In previous work we showed that Fe^{2+} ions act as chemical anchors for Pt clusters in zeolites. This phenomenon will now be studied for PdFe/Y catalysts. As Pd, unlike Pt, swiftly migrates and coalesces when exposed to CO, it will be of great interest to see whether Fe can suppress this agglomeration of Pd.

While not being a primary objective we shall also study zeolite supported clusters of RhFe, PdPt, PdRh and PtRh alloys, the last mentioned in view of its importance for the "three-way" autoexhaust catalyst.

IVb RhMn/NaY

While this system is a prototypical "metal-metal ion" bimetal clusters, it will be of interest to study fully reduced RhMn alloys in zeolites as a reference. For the preparation we intend to use $Mn_2(CO)_{10}$. In view of its toxicity, this preparation will be performed under a fumehood in a glovebag. A solution of $Mn_2(CO)_{10}$ in an organic solvent will be used to impregnate the complex into dehydrated reduced Rh/NaY. As $Mn(CO)_5^-$ is a well-known negatively charged species and positive Rh ions are stable in zeolites, it is visualized that novel bimetal carbonyl clusters form in the zeolite cages as a side product of this research. FTIR of adsorbed CO will be applied to the neutral RhMn/NaY samples to monitor the possible formation of RhMn bimetal in carbonyl clusters. The stability and activity of such clusters will also be tested in CO hydrogenation reaction.

The RhMn catalysts prepared in this way or by conventional ion exchange will be probed for CO hydrogenation. In the case of true PdMn alloy it is possible that Mn is oxidized to MnO by the water produced which is, of course, a reaction product.

The well documented promoting action of Mn in Rh/SiO_2 catalysts for CO hydrogenation uses a chemical environment where Mn is predominantly present as an oxide. In contrast to this, Mn in a zeolite can be prepared in the form of Mn^{2+} ions which should be in direct contact with the Rh. As the Mn^{2+} ion will also serve as a chemical anchor it should suppress the agglomeration of Rh. Finally, Mn^{2+} ions might block small zeolite cages and thus enhance the reducibility of the Rh.[20] We shall therefore focus on the effects on selectivity, reducibility and rate of metal agglomeration.

As cage blocking does not necessarily require a TM ion we shall also use a third non-promotional cation in combination with Rh +Mn. Ca, Mg and lanthanides are obvious candidates. As mentioned, characterization methods will include EXAFS, ENDOR, CO-FTIR, magnetic susceptibility, TPR and TPD.

Even though there has been considerable research activity using ENDOR on Mn^{2+} electron spin and the nuclear spin of other light elements, application of this technique to study the interaction with a reduced transition metal is novel to the best of our knowledge. We expect that information gained in this way will be extremely valuable for the fundamental understanding of the catalyst promotion mechanism.

CO hydrogenation will be performed under conditions used previously for PdNi and PdCo catalysts; i.e., about 10 bar of total pressure of CO and H_2 mixture with varying space velocity. The reaction temperature range will be the same as for PdNi/NaY and PdCo/NaY.

IVc PdX^{y+}/ZSM-5

A prerequisite for anchoring TM ions ,X^{y+}, is that they interact with Pd strongly and that they are not consumed during the reaction. While there is no *a priori* prediction, which ions other than Fe, Mn or Cr will be optimum for such purpose, we propose to also include alkaline earth ions and less reducible multivalent TM ions, including lanthanide ions. Since coke does not form in ZSM-5 under our reaction conditions, the changes in the Pd particle size will be primarily monitored by the change in activity of PdX^{y+}/ZSM-5 catalysts with time on stream during conversion of CP or MCP, with verification in appropriate cases by XRD and EXAFS.

It is conceivable that anchoring ions will also modify the catalytic activity and selectivity. The result may lead to the identification of the promotional effect of the second ions, which is one of the main goals in the present proposal. Once such anchoring metal ions are identified, research on the mixed proton-metal ions will be conducted to optimize the catalytic performance of the Pd-based catalysts in ZSM-5 zeolite support. It is hoped that the results of this research can be generalized to other transition metals and other zeolites.

IVd PtCu/ZSM-5

In ongoing work we have developed the reactor and the analytical technique to study the decomposition and the reduction of NO over Cu/ZSM-5. The same equipment will be used to study the bimetal catalysts; CO-FTIR will be used to identify mixed ensembles and Cu^+ ions; The interaction of Cu and Pt will be studied by means of EXAFS.

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