SELECTIVITY, ACTIVITY AND METAL-SUPPORT INTERACTIONS OF GROUP VIII BIMETALLIC CATALYSTS. PROGRESS REPORT, 15 AUGUST 1984-15 OCTOBER 1985

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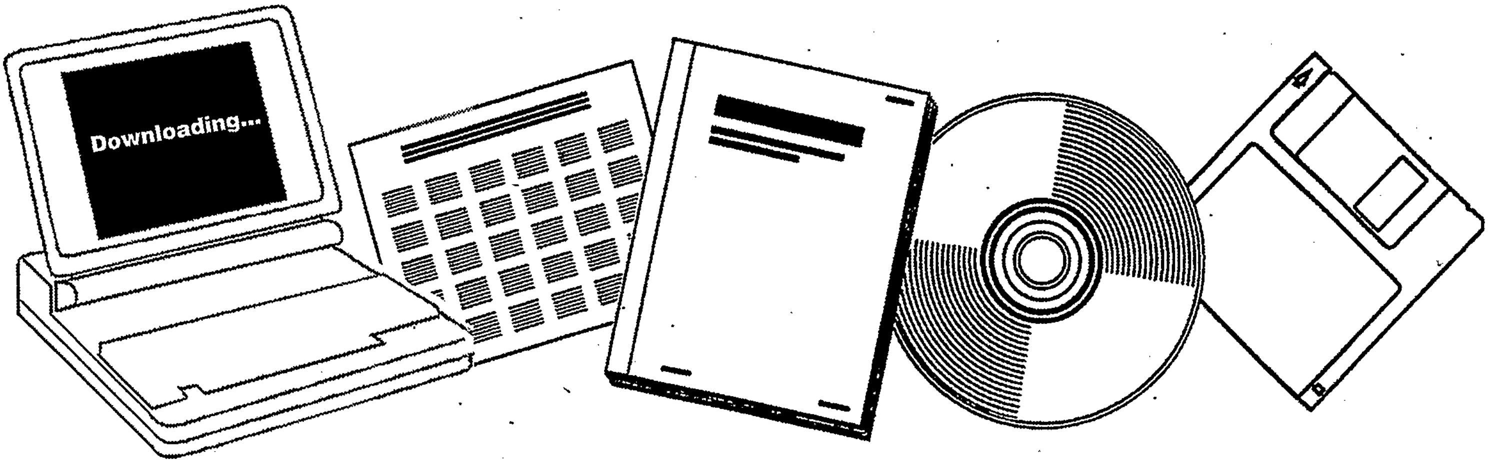

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SELECTIVITY, ACTIVITY AND METAL-SUPPORT INTERACTIONS OF GROUP VIII BIMETALLIC CATALYSTS

Progress Report

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ABSTRACT

In this report, we outline progress during the last year on our program to investigate bimetallic interaction in the systems Rh-Pt and Ru-Cu. In both cases, we are primarily interested in the effect of support on the nature and degree of interaction. For Rh-Pt, the interacting support is TiO_2 and the reaction used to probe the interaction is CO hydrogenation. The strong metal-support interaction induced by high temperature reduction is reversed by the reaction products of CO hydrogenation on both metals, but the stoichiometry of this reaction is quite different and this may indicate a fundamental difference in the mechanism of interaction between TiO_2 and the two metals. As we had previously deduced from the investigation of hydrogenolysis, the relative activity of the Rh-Pt/TiO_2 series for CO hydrogenation is consistent with there being Rh enrichment on the small bimetallic clusters. For the Ru-Cu bimetallic system the support of interest is SiO_2. The degree of interaction between the metals depends on the kind of SiO_2 used. Hydrogen chemisorption, cyclohexane hydrogenolysis and dehydrogenation were used as the catalytic probes of support effects on metal-metal interaction. As a part of our continuing investigation of support influence on bimetallic interaction, the metal-oxide interaction of Rh/TiO_2 and Rh/V_2O_3 have been compared. While the gross features of and effects on this interaction are the same, the mechanism is apparently different.

INTRODUCTION

In our last report, we described a part of our investigation of Rh-Pt bimetallic catalysts supported on SiO_2, Al_2O_3 and TiO_2. Some aspects of the mechanistic effects of metal-metal interaction on hydrogenolysis reactions over a range of compositions of the Rh-Pt system have recently been published [1,2]. During this report period we have concentrated on the characterization of the Rh-Pt/TiO_2 for CO hydrogenation, a structure insensitive reaction which might be expected to have quite different behavior relative to hydrogenolysis, a structure sensitive reaction, as a function of bimetallic composition.

The different interaction between Ru-Cu supported on different silicas has been probed in a preliminary fashion using Cu EXAFS. As a catalytic probe for the of nature metal-metal interaction, we have used a comparitive investigation of the hydrogenolysis and dehydrogenation of cyclohexane and have attempted to correlate our results with the recent study of the model system, Cu deposited on single crystal Ru.

In the future, we plan to extend our program to bimetallic systems supported on other active supports, e.g., V_2O_3. Vanadia is a reducible support which exhibits metal-oxide interaction similar to that of TiO_2. Here we report progress on experiments to directly compare the pure metals Rh and Pt on TiO_2 and V_2O_3.

SUPPORT EFFECTS ON Rh-Pt INTERACTION OVER TiO_2

As has been observed by others, the support has a large influence on the turnover frequency for CO hydrogenation on Pt and Rh. Our results for the two metals on 4 supports are summarized in Table 1.

TABLE 1

Relative Turnover Frequencies for CO Hydrogenation at 350°C

Catalyst	Pt	Rh
SiO_2, Davison 923	1.0*	5.5
SiO_2, Cab-O-Sil M5	2.0	120
Al_2O_3, Degussa C	8.3	150
TiO_2, Degussa P25	9.6	390

*This turnover frequency is 0.203 molecules per hydrogen atom adsorption site per sec using a 1:3 ratio of $CO:H_2$ and a total pressure of one atmosphere.

The ordering of the rate by supports is qualitatively in agreement with previous reports, SiO_2 Al_2O_3 SiO_2, e.g., see Vannice and Twu [3]. The support effect on Rh is substantially greater than it is on Pt, but the ordering of the supports is the same. When the rates across the full range of Rh-Pt is considered, one observes a monotonic, non-linear decrease in rate from pure Rh to pure Pt with the rates exceeding that predicted by a straight line extrapolation between the two metals. This behavior is the same as observed for hydrogenolysis reactions [2] and would be consistent with surface enrichment of Rh on the bimetallic clusters. Such surface enrichment is not what would be expected based on simple thermodynamic models taking into account only the relative surface free energies but is in agreement with emperical observations for a model system of supported bimetallic films reduced at 600°C [4].

We have concentrated our attention on the Rh-Pt/TiO_2 system because TiO_2 support produces both the highest rates and the greatest difference in rates between the two metals. Because the so called strong metal support interaction [5] is reversed by oxidation, one does not expect it to survive under CO hydrogenation reaction conditions where water is a product. In deed, this has been confirmed by comparing pulse reaction with steady state flow reaction. The degree of activity suppression of the structure insensitive CO hydrogenation following high temperature reduction is very much smaller than for the structure sensitive hydrogenolysis reaction. Using a high temperature reduction of 510°C and a reaction temperature of 250°C on Rh/TiO_2, the yield per pulse increases about a factor of five with sequential pulses following the initial pulse. However, the steady-state rate of CO hydrogenation on such catalysts is comparable to that in the first pulse. The reason for this is carbon buildup during steady-state reaction, i.e., one may conclude that the initial suppression by strong metal support interaction is comparable to suppression by carbon deposition after steady-state is reached. Using the same catalyst reduced at low temperature (250°C) and following reaction at 250°C as a function of sequential pulses, one observes only a steady decay in activity to the steady-state rate which is about a factor of 15 lower than that in the first pulse. Removal of this carbon residue as methane and water by H_2 pulsing indicates that it has an average composition of about CH_2.

Alternating pulses of CO and H_2 clearly shows that there is a net oxygen consumption from the interaction of CO with either Rh/TiO_2 or Pt/TiO_2 after high temperature reduction, i.e., a H_2 pulse following a CO pulse only produces CH_4 initially but after several pulses also produces the stoichiometrically required amount of H_2O. We have carefully measured the stoichiometry of this oxygen comsumption for both metals and several bimetallic catalysts using alternating pulses of O_2 and H_2. On Rh/TiO_2 about one oxygen atom is comsumed per surface

Rh atom (measured by hydrogen chemisorption after low temperature reduction). This stoichiometry is in good agreement with that measured by Orita et al. [6] using a technique where the H_2 produced in the gas phase upon exposure of the high temperature reduced catalyst to H_2O at 160°C was measured. On Pt/TiO_2 oxygen comsumption is somewhat in excess of 2 atoms per surface Pt atom (again measured by hydrogen chemisorption after low temperature reduction). In this case, similar results have been obtained by Kunimori and Uchijima [7] measuring quantitatively the amount of oxygen consumed in a high temperature oxidation at 400°C (after a high temperature reduction) and ratioing this quantity to the increase in hydrogen chemisorption following this treatment. One conclusion one might draw from these results in that the mechanism of TiO_2 interaction with Rh and Pt is quantitatively different. This is very likely the case. One must be careful about the exact stoichiometry because the fraction of surface metal atoms in both cases was measured by hydrogen chemisorption, i.e., if the H/M stiochiometry were other than 1, this would explain a part of the difference. However, experimentally one finds that , to the extent that H/M differs on Rh and Pt, it is greater on Rh which would only increase the relative difference in the metal-oxide interaction reversal stoichiometry.

Because the stoichiometry of the reversal of metal-oxide interaction by oxygen is about that of pure Rh until catalysts with an overall Pt composition greater than 50% are reached and then there is a monotonic approach to the Pt stoichiometry, one obtains a clear indication that there is Rh enrichment of the bimetallic clusters. Thus we appear to have three independent indications of Rh enrichment: the relative rates of a structure sensitive reaction, hydrogenolysis;

the relative rates of a structure insensitive reaction, CO hydrogenation; and the relative stoichiometry of the reversal of the metal-TiO_2 interaction.

SILICA SUPPORT EFFECT ON Ru-Cu INTERACTION

In our last progress report and a publication [8] we have drawn attention of the fact that the kind of silica support used to prepare Ru-Cu bimetallic catalyst can have a pronouced influence on the behavior of these catalysts. This is particularly evident when the H/Ru ratio measured by room temperature chemisorption is compared for the Ru/SiO_2 and Ru-Cu/SiO_2 catalysts using the same silica. For example, on Cab-O-Sil HS5, the silica used by Sinfelt in his original work on supported Ru-Cu, addition of Cu causes a depression of H/M relative to Ru/SiO_2 prepared on the same silica. However, the opposite behavior, i.e., an increase in H/M with addition of Cu, is observed for Cab-O-Sil M5. The latter result is more general and has been observed for all silicas investigated except for HS5.

Samples of Ru-Cu/HS5-SiO_2 and Ru-Cu/M5-SiO_2 have been examined by Cu EXAFS.[1] In the oxidized state there are obvious differences. The Cu in the air exposed Ru-Cu/HS5-SiO_2 is indistinguishable from CuO. The air exposed Ru-Cu/M5-SiO_2 appears to be less susceptable to oxidation and retains Ru-Cu bonds. However, the two catalysts cannot be distinguished by Cu EXAFS after reduction. Neither appear to have Cu-Cu bonds sugesting that most Cu is interacting with Ru. A more complete analysis will require a combined Cu and Ru edge EXAFS analysis, experiments which are comtemplated during the next year.

[1] The EXAFS experiments were carried out at the University of Delaware by Alison D. Pratt under the direction of Professor Robert S. Weber.
significant amount of Cu-Cu bonding suggesting that the Cu is mostly

The Ru-Cu system represents a system of metals in which there is very little bulk miscibility. The inital evidence for interaction between the two metals was provided by chemisorption and catalysis where it was shown that the presence of the Cu in the catalysts led to substantial inhibition of H_2 chemisorption by the Ru and also to a marked suppression of the catalytic activity of the Ru for ethane hydrogenolysis [9]. Chemisorption, catalysis and X-ray photoelectron spectroscopy studies on unsupported Ru-Cu aggregates [10-13] indicate that a typical aggregate consists of a core of Ru covered by Cu, i.e., that Cu effectively chemisorbed on the surface of the Ru particles. This picture has been confirmed for the Ru-Cu/SiO_2 catalysts by an extended X-ray absorption fine structure (EXAFS) analysis [14]. The effect of this chemisorption of Cu on Ru is to block H_2 chemisorption and, in the case of hydrogenolysis, to break up ensembles of Ru which constitute sites such that a relatively small fractional coverage of the Ru surface by Cu, as measured by H_2 chemisorption, can result in a dramatic reduction of hydrogenolysis sites. How then can one explain an **increase** in H_2 chemisorption when Cu is added to Ru? We suggested that there may be H_2 spillover from Ru to Cu [15]. Such H_2 spillover has been unequivalently shown to occur in the model system of Cu evaporated onto (0001) Ru by Peden and Goodman [16]. However, these same investigators observe that Cu forms two dimensional islands on Ru(0001) using their low temperature evaporation approach which results in a one-to-one site blocking of H_2[17]. This is in constrast to the observation of Shimizu et al. [18] and Vickerman and Christman [19] who concluded that a single Cu atom blocked approximately 10 and 4 hydrogen bonding sites, respectively. Perhaps the latter work involved a more uniform spreading of Cu over the Ru because of the high temperature at which the Ru was held during evaporation of Cu. Peden and Goodman [20] have also performed ethane hydrogenolysis on the model system and observe a modest, linear decrease in rate to about 75% of the clean Ru rate upto 0.25 monolayers of Cu beyond which there is less effect of added Cu, i.e., the rate at one monolayer of added Cu is 50% of the clean Ru rate. This would seem to imply Cu island formation upto 0.25 monolayers and the onset of three dimensional growth at higher coverages. A very similar effect of Cu on CO hydrogenation rate is observed but this reaction is known not to be structure sensitive so island formation or uniform distribution at below monolayer coverage would be expected to give similar results. The hydrogenolysis results are not entirely consistent with the temperature-programed desorption of Cu from Ru(0001) which suggests the onset of three dimensional growth does not occur until the total Cu deposited approaches a monolayer [16].

Keeping in mind Sinfelt's previous work on silica supported Ru-Cu and the observations of the model system studies, we suggest the following tentative interpretation of the silica support effect. On HS5 the Cu spreads reasonably uniformly over the Ru particles; these chemisorbed Cu atoms do not act as hydrogen adsorption sites via spillover and any Cu not interacting with Ru must form a separate phase. On M5 the Cu not interacting with Ru must be in contact with Ru particles to allow for spillover. (One cannot invoke an increase in the Ru dispersion in the presence of Cu because hydrogenolysis suppression on M5 tends to exceed that on HS5 even though H_2 chemisorption is increased on M5 and decreased on HS5 by the addition of Cu.) Cyclohexane reaction on these catalysts also exhibits interesting behavior. On M5 addition of Cu increases the dehydrogenation rate normalized to mass of Ru relative to pure Ru while on HS5 there is a very modest suppression of dehydrogenation activity. (If the rates of dehydrogenation are normalized to hydrogen chemisorption there is an apparent increase in dehydrogenation activity on both M5 and HS5 in agreement with Sinfelt's [9] previous observation.) Sinfelt has suggested the effect of Cu on dehydrogenation activity made be due to a weakened bonding of the product benzene on the Ru-Cu bimetallic clusters. However, the close correlation between effect of Cu on H_2 chemisorption and cyclohexane dehydrogenation may also implicate Cu in the reaction either by H_2 spillover or spillover of chemisorbed cyclohexane derived species, e.g., benzene desorption from Cu sites.

COMPARISON OF Rh/TiO_2 AND Rh/V_2O_3 INTERACTION

The investigation of both TiO_2 supported small Rh particles [21] and a model system of Rh evaporated films on single crystal TiO_2 (110) [22] have indicated that there is a Ti containing species which migrates over the metal particles. Extended X-ray Absorption Fine Structure (EXAFS) analysis of Pt/TiO_2 is also consistent with a migration model. However, only for ion-exchanged Rh/TiO_2 do we observe EXAFS evidence for direct Rh-Ti bonding which provides the thermodynamic driving force for the interaction.

Ion-exchange prepared Rh/TiO_2 and Ir/TiO_2 catalysts are 100% dispersed and, when reduced at high temperature (773 K), they exhibit a unique activity for n-butane isomerization and dehydrogenation [23]. Hydrogenolysis, greatly suppressed on these catalysts, has an unusal positive order in hydrogen and a relatively high selectivity for terminal vs. central C-C bond breaking of n-butane compared to impregnated Rh and Ir catalysts. When V_2O_3 is used as a support for Rh or Pt, even catalysts prepared by impregnation and of low dispersion exhibit high alkane isomerization and dehydrogenation activity. While Rh interaction with either TiO_2 or V_2O_3 causes orders of magnitude depression of n-butane hydrogenolysis, a comparison of activities suggest that their role is more than simple suppression of hydrogenolysis so that alkane isomerization and dehydrogenation can be observed. For example, after high temperature reduction Rh/TiO_2 and Rh/V_2O_3 have comparable hydrogenolysis activities, n-butane dehydrogenation is a factor of three higher on Rh/V_2O_3 while n-butane dehydrogenation is a factor of ten higher on Rh/TiO_2. Moreover, the activation energies for reactions of n-butane are about the same on the two supports after a low temperature reduction (when hydrogenolysis is the dominant reaction) but increases slightly on Rh/TiO_2 and decreases significantly on Rh/V_2O_3 after a high temperature reduction. Rh/V_2O_3 is also much less sensitive to oxygen and water impurities (which induce a recovery of hydrogenolysis activity) than is Rh/TiO_2. We conclude that the mechanism of metal-support interaction for TiO_2 and V_2O_3 are different and that interaction between noble group VIII metals and reducible oxides, which produces alkane isomerization and dehydrogenation activity, involves electronic as well as geometric effects.

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