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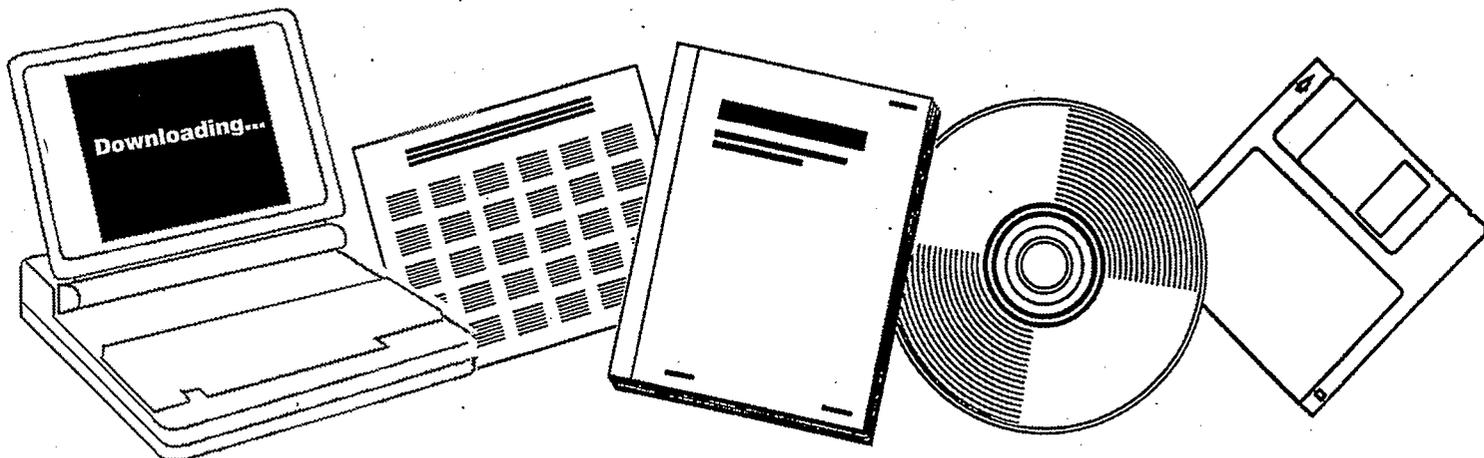
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**SELECTIVITY, ACTIVITY AND METAL-SUPPORT  
INTERACTIONS OF GROUP VIII BIMETALLIC  
CATALYSTS: FINAL TECHNICAL PROGRESS  
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SELECTIVITY, ACTIVITY AND METAL-SUPPORT INTERACTIONS  
OF GROUP VIII BIMETALLIC CATALYSTS

FINAL TECHNICAL  
Progress Report

for Period 15 January, 1985 - 15 July, 1987

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#### ABSTRACT

Titania supported Rh Catalysts characterized by EXAFS and XANES analyses indicate that there is direct Rh-Ti bonding with electron transfer from Ti to Rh in these catalyst after high temperature reduction. When coverage of metal particles, which is driven by this bonding, is avoided, there does not appear to be a major effect of the electronic interaction on H<sub>2</sub> and CO chemisorption. However, a comparison of Rh/TiO<sub>2</sub> and Rh/V<sub>2</sub>O<sub>3</sub> which undergo similar metal-oxide interaction does suggest that there are catalytic consequences of this interaction which are of an electronic nature. A comparison of Rh and Pt supported on TiO<sub>2</sub> (or V<sub>2</sub>O<sub>3</sub>) demonstrates that the stoichiometry, strength and temperature of initiation of the interaction is different for the two metals on the same support.

Chemisorption, catalytic reactions of different structure sensitivity and X-ray absorption spectroscopies indicate that the morphology of Ru-Cu clusters supported on different silicas is different. On Cab-O-Sil HS5 the Cu is more uniformly spread over a Ru core and inhibits surface oxidation and preferentially inhibits the more structure sensitive reactions. On Cab-O-Sil M5 Cu physically encapsulates the Ru core of particles blocking both structure sensitive and structure insensitive reactions, but these clusters are less resistant to surface oxidation.

The interaction of MoO<sub>3</sub> and SiO<sub>2</sub> with Al<sub>2</sub>O<sub>3</sub> has been studied by <sup>27</sup>Al and <sup>29</sup>Si NMR. Mo reacts with the surface of Al<sub>2</sub>O<sub>3</sub> to form Al<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> but this reaction is inhibited by P, probably by the formation of AlPO<sub>4</sub> at temperatures below where MoO<sub>3</sub> reacts with Al<sub>2</sub>O<sub>3</sub>. Low wt% SiO<sub>2</sub> added as a surface modifier forms a surface species which is either a meta silicate or more likely Si atoms which are in a very strained Si(Al-O)<sub>4</sub> surface environment. The amount of this species correlates with increased structural stability of the modified alumina.

## INTRODUCTION

This progress report is intended to summarize results for the period beginning with the contract initiation date, 15 January, 1985, through the renewal date, 15 July, 1987. Additional details can be found in two annual Progress Reports [1,2], the eight papers published (or in press) since the initiation date which acknowledge DOE support under the current contract [3-10] and the five theses complete during the contract and listed below.

'Metal-Metal Interaction on Supported Ir-Pt, Rh-Pt Bimetallic Catalysts', Louis Chintyen Chang, May, 1985.

'Support Induced Geometric and Electronic Effects for Rhodium Supported Titania Catalysts as Studied By EXAFS and Infrared Spectroscopies', Stanley John Sakellson, October, 1985.

'Hydrogen Adsorption Behavior and Strong Metal-Support Interaction (SMSI) on Rh-Pt Bimetallic Catalysts', Henton Hwang, May, 1986.

'Strong Metal-Support Interactions (SMSI) over Rh and Pt Catalysts Supported on Vanadia or Vanadia-Silica', You-Jyh Lin, May, 1987.

'EXAFS and MAS NMR Investigations of Active Phase-Support Interactions', Samuel Martin McMillan, Jr., May, 1987.

We will begin by reviewing the nature of metal-oxide interaction as exemplified by Rh/TiO<sub>2</sub> and characterized by extended X-ray absorption fine structure (EXAFS) [5] and X-ray absorption near edge structure (XANES) [9] analyses. The catalytic consequences of this interaction between a group VIII metal and a reducible support will be reviewed by reference to the differences between different group VIII metals (Rh and Pt) supported on TiO<sub>2</sub> and the same metal (Rh) supported on different reducible supports (TiO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>) [8].

The influence of the support (SiO<sub>2</sub> vs TiO<sub>2</sub>) on metal-metal interaction (between Rh and Ag) was the subject of an earlier publication [11] from work completed under the previous DOE contract. Here we will briefly outline the more recent work of the effect of different silica supports on the metal-metal interaction (Ru-Cu cluster morphology) and on chemisorption and catalytic activity [6].

We will conclude with some comments on oxide-oxide interaction (MoO<sub>3</sub> and SiO<sub>2</sub> interaction with Al<sub>2</sub>O<sub>3</sub> support) investigated by NMR [4]. The interaction

of catalytically active phases with oxide supports is one of the new directions which we wish to move.

#### PHYSICAL CHARACTERIZATION OF Rh-TITANIA INTERACTION

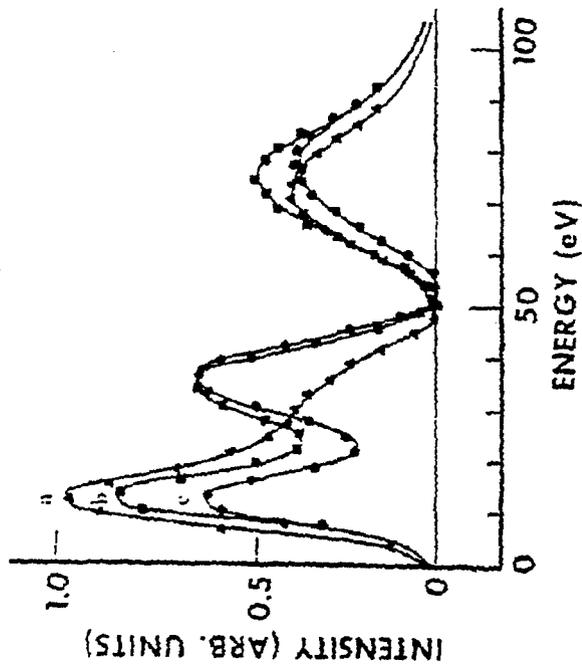
The bulk structure and electronic properties of the group VIII-Ti alloys have been studied for some time [12]. Among the stable intermetallics formed, the stoichiometric compounds  $M_3Ti$  and  $MTi$ , e.g.,  $Pt_3Ti$  and  $PtTi$ , have been widely investigated. Both theory [13] and experiment [14-17] indicate that there is d-d bonding between the group VIII metal and Ti with net transfer of charge from Ti to the group VIII metal.

One must ask to what extent the bonding situation in the intermetallic compounds may carry over to metals supported on  $TiO_2$  and reduced at high temperature. Our own X-ray absorption measurements of Rh-Ti compounds exhibit suggestive similarities with the reduced Rh/ $TiO_2$  catalysts. First of all, the EXAFS analysis of high temperature reduced Rh/ $TiO_2$  (100% dispersed) catalyst provides evidence for the formation of Rh-Ti bonds [5]. An inspection of the near edge structure of the K edge of Rh reveals interesting features [9]. As illustrated in Fig. 1, the XANES of Rh foil,  $Rh_3Ti$  and  $RhTi$  show significant variation in the sizes of the peaks located at 10 and 35 eV above the edge. It is observed that both peaks decrease as Rh coordination is gradually replaced by Ti around each Rh atom when going from pure Rh to  $RhTi$ . The first peak can be related to symmetry allowed electronic transitions from the core level 1s to empty states above the Fermi level [18]. Thus, the decrease in the size of that peak from Rh to  $RhTi$  can be explained in terms of a filling of Rh valence states resulting from the formation of Rh-Ti bonds. The second peak after the edge reflects multiple scattering processes of the outgoing electron [18]. In agreement with multiple scattering calculations done for different cluster sizes [19,20] we have observed that this second peak increases with metal

particle size (number of ligands). Fig. 1 shows that it also varies with the kind of ligand because it decreases as Rh scatterers are replaced by Ti. In the case of the highly dispersed Rh/TiO<sub>2</sub> catalyst, see Fig. 2, it was observed that as the reduction temperature was increased the size of the first peak gradually decreased, very much like for the series Rh, Rh<sub>3</sub>Ti, RhTi. This strongly suggests that the same type of Rh-Ti interactions occurring for the Rh-Ti alloys, i.e., rehybridization of d-orbitals and electron transfer from Ti to Rh, does occur for the high temperature reduced Rh/TiO<sub>2</sub> catalysts. It is worth repeating that this is very likely bonding between Rh particles and Ti cations and thus not identical to the bonding in the intermetallic compounds.

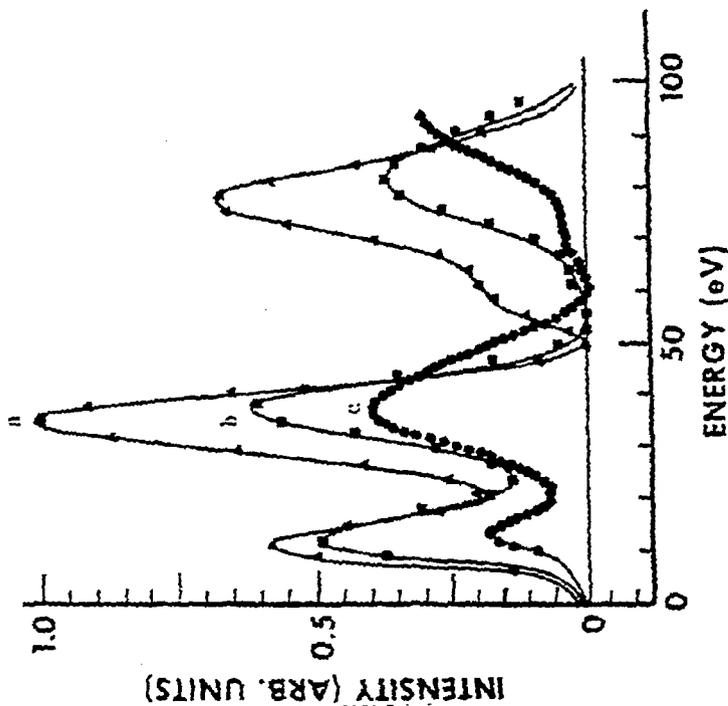
Assuming that the electronic interactions that accompany strong metal support interactions (SMSI) are similar to those in the intermetallic compounds, we must then ask if there are any significant effects on chemisorption or catalysis other than the effects of site blocking and ensemble break-up which have clearly been demonstrated to affect chemisorption capacity and activity for structure sensitive reactions, respectively. Sadeghi and Henrich have addressed this question by preparing Rh particles on a TiO<sub>2</sub> surface effectively reduced to Ti<sub>2</sub>O<sub>3</sub> [21]. The samples were prepared at low temperature to avoid migration and emphasize electronic interactions. Using several different electron spectroscopies, they conclude that there is electron transfer from the titania surface to the Rh particles. However, they find no evidence from an effect of this electron transfer on either the amount or kind of CO chemisorption as detected by UPS. This is not a very sensitive probe compared to other methods of investigation of chemisorption, e.g., TPD, or compared to catalytic probes.

Figure 2



Near edge X-ray absorption difference spectra of a 100% dispersed Rh/TiO<sub>2</sub> catalyst following reduction at a) 473K; b) 523K and c) 773K.

Figure 1



Near edge X-ray absorption difference spectra of a) Rh foil; b) Rh/Ti and c) Rh/Tl.

NOTE: The difference spectra are obtained by subtraction of an arctangent function constrained to pass through the inflection point (taken as zero energy) of the Rh K edge and the second minimum in the near edge structure about 50 eV above the edge.

## CHEMICAL CHARACTERIZATION OF Rh-TITANIA INTERACTION

### Comparison of Rh and Pt Interaction with Titania

Electron energy loss spectroscopy (EELS) demonstrates that the  $Ti^{+4}$  in  $TiO_2$  islands formed on  $Pt_3Ti$  by  $O_2$  chemisorption at 650K (which may contain some  $Ti^{+3}$  defects) can be reduced by CO desorption at 450K [22]. This is a very important observation because it suggests that the  $Ti^{+3}$  detected by XPS or Auger on catalysts subjected to  $CO/H_2$  reaction mixtures and evacuated at the reaction temperature may not have had detectable  $Ti^{+3}$  under reaction conditions, but it was formed by the desorption of CO above 450K. This may be the case in the work of Dwyer et al. [23] who report that  $Ti^{+3}$  is formed on  $TiO_2$  promoted Pt black by  $H_2$  reduction at 450 K and is also detected by XPS on the same catalyst after 16 hours of reaction at 625K in a one atm 3:1 mixture of  $H_2:CO$ . We note that the surface of single crystal  $Ti_2O_3$  is readily oxidized even at ambient temperature by  $O_2$  [24]. Even  $H_2O$  will dissociatively adsorb on defect  $Ti_2O_3$  to partially oxidize the surface to  $Ti^{+4}$  at room temperature, although perfect (047)  $Ti_2O_3$  only associatively adsorbs  $H_2O$  with accompanying transfer of electrons from the  $Ti\ 2p$  band [25]. Since the mechanism of CO hydrogenation to  $CH_4$  is generally believed to involve dissociative adsorption of CO [26], it would seem that the oxygen atoms formed would oxidize any  $Ti^{+3}$  under reaction conditions. This picture is in accord with pulse experiments we have performed at 535 K using alternating CO and  $H_2$  pulses, i.e., CO pulses are adsorbed and react with a subsequent pulse of  $H_2$  to produce  $CH_4$  but no  $H_2O$  is produced until one O atom per surface Rh atom (measured by  $H_2$  chemisorption after LTR) has been consumed, see Table 1 [27]. There will always exist some  $Ti^{3+}$  at steady state (or equilibrium) conditions which will depend on the  $H_2/H_2O$  and/or  $CO/CO_2$  ratios and temperature. Unfortunately we do not have an in situ measurement of the  $Ti^{3+}$  concentration under reaction conditions but our prejudice is that its concentration is unlikely to be significant.

TABLE 1

Hydrogen/Oxygen Stoichiometry to Produce/Reverse SMSI

	Rh	Pt	Ref.
H <sub>2</sub> consumed to produce interaction	1.7	5.2	32,33
O <sub>2</sub> consumed to reverse interaction (O <sub>2</sub> /H <sub>2</sub> titration)	1.2	2.2	27
Ratio, H <sub>2</sub> /O <sub>2</sub>	1.42	2.36	-
O <sub>2</sub> consumed to reverse interaction (CO/H <sub>2</sub> titration)	1.1	-	27
Anger O(508 eV)/Ti (385 eV) ratio	1.1	0.6	34

Once it has been accepted that the nature of SMSI is best understood in terms of chemical bonding, albeit bonds between metal atoms on the surface of a particle with cations of an oxide, it follows that the details of such bonding and its consequences will be a strong function of the partners. That is, the details of the metal-oxide interaction will change when two different noble metals supported on the same reducible oxide are compared or when the same metal on two different reducible oxides, e.g., TiO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub>, are compared. We will make this point by comparing metal-oxide interactions in the Rh/TiO<sub>2</sub> or Pt/TiO<sub>2</sub> systems.

Using our operational definition of SMSI, i.e., inhibition of hydrogen and CO chemisorption following high temperature reduction, Rh/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> do appear to behave in an analogous manner. However, when one considers a macroscopic property that can be directly observed by electron microscopy, the effect of SMSI on particle morphology, it is clear that Rh and Pt respond quite differently to interaction with TiO<sub>2</sub>. Very early in the literature on SMSI, Baker et al. [28,29] reported that Pt particles spread out to form thin pill-box particles during reduction. Meriaudeau et al. [30] and Singh et al. [31] performed similar electron microscopic investigations of Rh/TiO<sub>2</sub> and reported

that there was no observed change in Rh particle shape with reduction.

Perhaps the most direct proof that the interaction between Rh and  $\text{TiO}_2$  is different from the Pt and  $\text{TiO}_2$  interaction comes from experiments which probe the stoichiometry of the metal-oxide interaction chemistry. The hydrogen consumed to produce interaction has been measured by Miessner et al. [32] for Rh/ $\text{TiO}_2$  and by Kunimori and Uchijima for Pt/ $\text{TiO}_2$  [33]. We have measured the oxygen consumption to reverse the interaction on both catalysts using alternating  $\text{H}_2$  and  $\text{O}_2$  pulses at 423K and monitoring the consumption of  $\text{O}_2$  which did not result in  $\text{H}_2\text{O}$  as a product [27]. In all chemisorption experiments the  $\text{H}_2$  or  $\text{O}_2$  consumption has been normalized to the  $\text{H}_2$  chemisorption after LTR with the assumption that the stoichiometry here is  $E/M_{\text{SUR}} = 1$  and that this is an approximate measure of the fraction of the metal on the surface. These results along with some Auger O/Ti ratios for  $\text{TiO}_x$  on the two foils measured by Ko and Gorte [34] are collected in Table 1.

The expected ratio of  $\text{H}_2$  consumed to produce the SMSI state to  $\text{O}_2$  consumed to reverse it would be 2, of course, if the reduction produced  $M_{\text{SUR}}\text{TiO}_x$  and  $(2-x)\text{H}_2\text{O}$ . Obviously this ratio is low for Rh and high for Pt, but one must keep in mind the reactions were not done on the same samples, that the  $\text{H}_2$  chemisorption is not an exact measure of exposed surface metal atoms and that the percentage exposed will change if a change in morphology accompanies SMSI as it almost certainly does for Pt. What one is able to conclude from these experiments is that the SMSI surface complex,  $M_{\text{SUR}}\text{TiO}_x$  is likely to be more oxygen rich on Rh than on Pt and this is confirmed by the O/Ti Auger ratio for  $\text{TiO}_x$  on the surface of Rh and Pt foils. It should be added that this is not likely a simple compound, e.g.,  $\text{RhTiO}$ , but a mixture of stoichiometric surface compounds and may even contain a component of the intermetallic compounds  $\text{M}_3\text{Ti}$  and  $\text{MTi}$  [35]. Note also that the stoichiometry of  $\text{O}_2$  consumed to  $\text{Rh}_{\text{SUR}}$  is

independent of the source, i.e., we obtain the same stoichiometry when CO is the oxidant (alternate H<sub>2</sub> and CO pulses producing CH<sub>4</sub> and H<sub>2</sub>O after complete oxidation of TiO<sub>x</sub>) or when O<sub>2</sub> is the oxidant [27].

Anderson et al. [36] have performed similar experiments where hydrogen and oxygen consumed in chemisorptive titration (as opposed to consumed to form and break the SMSI state) was measured on Rh/TiO<sub>2</sub> and Pt/TiO<sub>2</sub>. These results cannot be directly compared to those presented in Table I because they used a higher LTR (573K instead of 423K) than Huang [27], but they come to complementary conclusions. They find that Pt enters into the SMSI state more easily (at a lower temperature or in a shorter time) than Rh and that the SMSI state for Pt/TiO<sub>2</sub> is more difficult to reverse than Rh/TiO<sub>2</sub>.

#### Comparison of Rh/TiO<sub>2</sub> and Rh/V<sub>2</sub>O<sub>3</sub> Interaction

The investigation of both TiO<sub>2</sub> supported small Rh particles [37] and a model system of Rh evaporated films on single crystal TiO<sub>2</sub> (110) [38] 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<sub>2</sub> is also consistent with a migration model. However, only for ion-exchanged Rh/TiO<sub>2</sub> do we observe EXAFS evidence for direct Rh-Ti bonding which provides the thermodynamic driving force for the interaction.

Ion-exchange prepared Rh/TiO<sub>2</sub> and Ir/TiO<sub>2</sub> catalysts are 100% dispersed and, when reduced at high temperature (773 K), they exhibit a unique activity for n-butane isomerization and dehydrogenation [39]. Hydrogenolysis, greatly suppressed on these catalysts, has an unusual 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<sub>2</sub>O<sub>3</sub> 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 [8]. While Rh interaction with either TiO<sub>2</sub> or V<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> and Rh/V<sub>2</sub>O<sub>3</sub> have comparable hydrogenolysis activities, n-butane dehydrogenation is a factor of three higher on Rh/V<sub>2</sub>O<sub>3</sub> while n-butane dehydrogenation is a factor of ten higher on Rh/TiO<sub>2</sub>. 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<sub>2</sub> and decreases significantly on Rh/V<sub>2</sub>O<sub>3</sub> after a high temperature reduction. Rh/V<sub>2</sub>O<sub>3</sub> is also much less sensitive to oxygen and water impurities (which induce a recovery of hydrogenolysis activity) than is Rh/TiO<sub>2</sub>. We conclude that the mechanism of metal-support interaction for TiO<sub>2</sub> and V<sub>2</sub>O<sub>3</sub> 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.

#### SILICA SUPPORT EFFECT ON Ru-Cu INTERACTION

In a previous publication [40] we have drawn attention of the fact that the kind of silica support used to prepare Ru-Cu bimetallic catalyst can have a pronounced 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<sub>2</sub> and Ru-Cu/SiO<sub>2</sub> 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 [41], addition of Cu causes a depression of H/M relative to Ru/SiO<sub>2</sub> 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 [6].

The Ru-Cu system represents a system of metals in which there is very little bulk miscibility. The initial 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<sub>2</sub> chemisorption by the Ru and also to a marked suppression of the catalytic activity of the Ru for ethane hydrogenolysis [41]. Chemisorption, catalysis and X-ray photoelectron spectroscopy studies on unsupported Ru-Cu aggregates [42-45] 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<sub>2</sub> catalysts by an extended X-ray absorption fine structure (EXAFS) analysis [46]. The effect of this chemisorption of Cu on Ru is to block H<sub>2</sub> 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<sub>2</sub> chemisorption, can result in a dramatic reduction of hydrogenolysis sites. How then can one explain an increase in H<sub>2</sub> chemisorption when Cu is added to Ru? We suggested that there may be H<sub>2</sub> spillover from Ru to Cu [47]. Such H<sub>2</sub> spillover has been unequivocally shown to occur in the model system of Cu evaporated onto (0001) Ru by Feden and Goodman [48]. 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<sub>2</sub> [49]. This is in contrast to the observation of Shimizu et al. [50] and Vickerman and Christman [51] 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. Feden and Goodman [52] 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 programmed 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 [48].

The Ru-Cu system is clearly a complex system where the degree of metal-metal interaction depends on the preparation and treatment. Supported Ru-Cu is probably even more complex than the model system because one must deal with varying particle sizes, varying distribution of particle sizes and even separate Cu particles not interacting with Ru. [53]. By comparing the effects of three reactions which have varying structure sensitivity in the order ethane hydrogenolysis > cyclohexane hydrogenolysis > benzene hydrogenation one can deduce the difference in the gross morphology of Ru-Cu clusters on HS5 and M5 silicas [6]. On HS5 these reactions have relative rates (rate on pure Ru ratioed to the rate on a 1:1 mixture of Ru:Cu) in the ratio 250:10:5, respectively, while on M5 the ratios are 160:810:100. Because all three reactions are greatly affected by added Cu on the M5 support and this effect does not follow the expected order of structure sensitivity, we postulate that the Ru particles are effectively encapsulated by Cu on M5. On the other hand, addition of Cu to Ru on HS5 behaves more like one might predict, i.e., the relative rates are in the order of structure sensitivity and would accord with

a simple breaking up of Ru ensembles by Cu. However, to obtain a mass balance (account for all the Cu) on the HSS support and to rationalize H<sub>2</sub> spillover from Ru to Cu on M5 but not on HSS, we were obliged to postulate that the bimetallic Ru-Cu clusters have outer layers that are effectively a Cu rich mixture or surface alloy [6]. This postulate goes beyond that proposed by Sinfelt et al. [46] based on EXAFS where their model pictured the Cu as more or less chemisorbed on the surface of Ru particles. A re-investigation of both the EXAFS and XANES of the Ru-Cu on HSS and M5 supports is in progress. What is immediately clear from the XANES is that Cu protects the underlying Ru from oxidation on HSS (in agreement with the EXAFS results of Sinfelt et al. [46]), but it does not on M5 even though the rates of varying structure sensitive reactions suggests that the Ru particles are more completely encapsulated on M5 support. The morphologies of Ru-Cu are clearly different but the detailed differences must await a careful XANES and EXAFS analyses.

#### OXIDE-OXIDE INTERACTION IN SUPPORTED OXIDES STUDIED BY NMR

##### Interaction of MoO<sub>3</sub> with Al<sub>2</sub>O<sub>3</sub>

High resolution NMR spectroscopy of solids is now a well recognized structural tool [54,55] and there have been several recent applications to catalysts per se. Slichter and his co-workers have applied <sup>195</sup>Pt NMR to Pt/Al<sub>2</sub>O<sub>3</sub> catalysts [56] and several groups have investigated <sup>29</sup>Si in zeolites [57]. The NMR of <sup>27</sup>Al in zeolites has also been examined. For zeolites, it was noted that <sup>27</sup>Al NMR is much more structure sensitive than <sup>29</sup>Si NMR which is first nearest-neighbor dependent [58]. Specifically, Al can exist in both octahedral and tetrahedral coordination and, when the ligands are oxygen, the chemical shift of <sup>27</sup>Al differs by 55-80 ppm for these different coordinations [59,60]. Thus, <sup>27</sup>Al NMR can, in principle, be very useful for following the tetrahedral/octahedral ratio in alumina supports as a function of thermal treatment.

Almost all of the solid state NMR of oxide catalysts has involved crystalline zeolites [57]. Our attention has been focused on oxides supported on an amorphous support, i.e.,  $\gamma$ - $\text{Al}_2\text{O}_3$ , which are more difficult to study because their lack of crystallinity and distortions result in broader lines than found in the zeolites. We will briefly outline our findings for a commercial hydrodesulfurization catalyst studied by  $^{27}\text{Al}$  NMR [4] and for several silica modified alumina supports [61] which were studied by  $^{29}\text{Si}$  NMR.

Even with magic angle spinning of highly crystalline  $\alpha$ -alumina (corundum), the NMR linewidth of  $^{27}\text{Al}$  is quite broad. This would lead one to surmise that it would not be feasible to observe the formation of surface compounds of the alumina support or active catalytic phases since the NMR signal of the surface phase would be masked by the bulk if the two phases were of comparable linewidth. However, we have demonstrated that the surface and bulk phases of alumina need not have the same linewidth. In the case of a  $\text{NiMoP}/\text{Al}_2\text{O}_3$  hydrodesulfurization catalyst, at least, an  $\text{Al}^{3+}$  containing surface phase is formed during calcination which can easily be distinguished from the bulk  $\gamma$ - $\text{Al}_2\text{O}_3$  support.

We have obtained the  $^{27}\text{Al}$  NMR spectra of three alumina supported catalysts containing  $\text{NiO}$ ,  $\text{MoO}_3$  and the mixed oxides prepared by impregnation and calcined at several temperatures between 800 and 1100 K in air [4]. We have used the compound  $\text{Al}_2(\text{MoO}_4)_3$  as a reference because it produces a sharp NMR resonance, and a surface phase of this compound may be expected to form when  $\text{MoO}_3$  and  $\text{Al}_2\text{O}_3$  are heated together. The  $\text{NiMoP}/\text{Al}_2\text{O}_3$  was 3.1%  $\text{NiO}$ , 19.8%  $\text{MoO}_3$  and 2.5% P on  $\gamma$ - $\text{Al}_2\text{O}_3$ . The  $\text{Mo}/\text{Al}_2\text{O}_3$  and  $\text{Ni}/\text{Al}_2\text{O}_3$  catalysts were 18%  $\text{MoO}_3$  and 3.1%  $\text{NiO}$ , respectively.

A complete X-ray structure of  $\text{Al}_2(\text{MoO}_4)_3$  does not appear to have been published, but Goldish [62] states that it is isostructural with a large class

of molybdates and tungstates of the scandium tungstate type and, in particular, with  $\text{Al}_2(\text{WO}_4)_3$  which has been analyzed [63]. This structure consists of  $\text{WO}_4$  tetrahedra and  $\text{AlO}_6$  octahedra which extend into an infinite three-dimensional network by corner sharing. By comparing the NMR chemical shift of  $\text{Al}_2(\text{MoO}_4)_3$  with that of  $\alpha\text{-Al}_2\text{O}_3$  and a large number of aluminates with both tetrahedral and octahedral  $\text{Al}^{3+}$  coordination, we can unequivocally conclude that  $\text{Al}^{3+}$  in  $\text{Al}_2(\text{MoO}_4)_3$  is in a pure octahedral environment. By a similar analysis, we conclude that the surface compound of  $\text{Al}^{3+}$  formed in the  $\text{NiMoP}/\text{Al}_2\text{O}_3$  catalyst when calcined at 980K is in a pure tetrahedral environment. We assign this peak to  $\text{AlPO}_4$  because it is not formed in either  $\text{Mo}/\text{Al}_2\text{O}_3$  or  $\text{Ni}/\text{Al}_2\text{O}_3$ ; the  $^{31}\text{P}$  signal develops in parallel with  $^{27}\text{Al}$ , and the chemical shifts of both  $^{27}\text{Al}$  and  $^{31}\text{P}$  are identical to  $\text{AlPO}_4$ . The  $\text{Mo}/\text{Al}_2\text{O}_3$  forms the surface structure of  $\text{Al}_2(\text{MoO}_4)_3$  and the NMR of  $\text{Ni}/\text{Al}_2\text{O}_3$  calcined at 980K is almost that of  $\gamma\text{-Al}_2\text{O}_3$ . Since  $\text{Al}_2(\text{MoO}_4)_3$  forms on  $\text{Mo}/\text{Al}_2\text{O}_3$  but not on  $\text{NiMoP}/\text{Al}_2\text{O}_3$  at 980K we conclude that the formation of  $\text{Al}_2(\text{MoO}_4)_3$  is probably inhibited by the formation of  $\text{AlPO}_4$ , even though Ni's influence remains unclear. If the  $\text{NiMoP}/\text{Al}_2\text{O}_3$  catalyst is calcined at temperatures above 1000K, the surface compound of  $\text{AlPO}_4$  begins to decompose, and at sufficiently high temperatures, all of the  $\text{Mo}^{6+}$  is converted to  $\text{Al}_2(\text{MoO}_4)_3$ .

#### Interaction of $\text{SiO}_2$ with $\text{Al}_2\text{O}_3$

Low percentages of silica are often added to alumina as a modifier to stabilize the pore structure [61]. There are a variety of ways that this is done, e.g., during precipitation of the alumina, impregnation of the precipitated alumina, etc., but there is very little known about the manner in which the silica becomes distributed over and bonded to the alumina surface. We have studied several silica modified aluminas by  $^{29}\text{Si}$  NMR. These supports were prepared by American Cyanamid by post precipitation impregnation of alumina by a base stabilized silica sol and were 1-6 wt% silica.

Very little of the silica in these modified alumina had Si in an environment with one, two, three or four Al cations bonded in a normal tetrahedral geometry, i.e., much of the silica has a chemical shift (-110 ppm with respect to TMS) which can only be assigned to Si bonded to four other Si-O units [64]. A surprising result is that the next most abundant Si species has a chemical shift of -77 ppm which is out of the range expected for Si surrounded by any number of Al-O- ligands, the highest frequency shift of Si(OAl)<sub>4</sub> normally falling between -81 to -92 ppm. The -77 ppm shift is very close to that observed for solid meta silicate Na<sub>2</sub>SiO<sub>3</sub> and essentially identical to the cyclic meta silicate species found in basic solution [65]. Both of these seem chemically unlikely on the surface of alumina. A third possibility is that this species is bonded to three or four AlO in a very distorted environment. Newsam [66] has identified a Si(AlO)<sub>4</sub> at -76 ppm in a synthetic Li sodalite and inferred that the origin of this low field shift is caused by a smaller Si-O-Al bond angle (126°) compared to its Na analog (138°). The <sup>29</sup>Si NMR of various mineral shows that in at least one phyllosilicate (margarite) where Si is Si(AlO)<sub>3</sub>(SiO), the resonance lies at -76 ppm and a correlation between deshielding and distortion of the SiO<sub>4</sub> tetrahedra was noted [67].

The peak at -77 ppm in these spectra could thus be Si(AlO)<sub>4</sub> in a strained environment, perhaps near the surface of the alumina rather than a meta silicate. This may explain why the -77 ppm peak appears after calcination in some samples or appears to grow after calcination and may signal that the species is near the surface of the alumina which is likely to be a highly strained environment. The practical observation is that there appears to be a good correlation between the stabilization of the alumina porosity and the amount of the -77 ppm species formed by silica addition.

We have performed cumene cracking, a good test reaction for characterizing Brønsted acidity, over several of these silica modified aluminas. While there is an exponential increase in cracking activity with wt% silica, this does not correlate with either of the major kinds of silica species identified by NMR. It seems probable that only a small fraction of the silica is incorporated into the alumina surface in such a way that an acid site is created.

In summary, we emphasize that the observation of the NMR of  $^{27}\text{Al}$ , and probably that of other metal oxides sufficiently near the surface to be of catalytic interest, need not be restricted to the crystalline aluminosilicates. There may be a large class of catalysts where the active phase supported on an oxide may enter into chemical reaction and many of these surface phases may be distinguished from the bulk oxide phase by NMR.

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