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A SPECTROSCOPIC AND CATALYTIC INVESTIGATION OF ACTIVE
PHASE-SUPPORT INTERACTIONS

Progress Report

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Gary L. Haller

Department of Chemical Engineering
Yale University
New Haven, CT 06520

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ABSTRACT

Active catalytic phases (metal, mixed metals, oxide or mixed oxides) interacting with oxide support on which the active phase is dispersed can affect the percentage exposed, the morphology of supported particles, the degree of reducibility of cations, etc., in a variety of ways. Our objective is to characterize the physical chemistry of the active phase-oxide support interaction by spectroscopic methods and to correlate this structure with catalytic function.

The three systems discussed in this progress report are Ag/TiO₂, Ru-Cu/SiO₂ and SiO₂/Al₂O₃. Silver interacts so strongly with TiO₂ following a high temperature reduction that all catalytic reactions are suppressed. Because there is evidence for the formation of a surface phase of AgTiO₂, it is proposed that this surface phase consumes or covers the Ag inhibiting catalytic reactions of Ag metal.

The morphologies of Ru-Cu are very different when supported on different silicas. Using a combination of EPR, IR and X-ray absorption, we have concluded that these different morphologies result from a different interaction of Cu precursors on the two silicas (Cab-O-Sil HS5 and M5) and likely involves surface hydroxyl groups since dehydroxylation of the silicas tends to diminish differences in catalytic activity and in the IR spectra of adsorbed CO.

We have used the test reactions cumene cracking and the parallel double bond and methyl shift isomerization of 2-methyl-2-pentene as measures of catalytic acidity. The activities of these two reactions can be correlated with the ²⁹Si NMR shift and this correlation can be used to deduce the average local structure around Si in the amorphous silica-aluminas. From this correlation and the known chemical shifts of ²⁹Si as a function of the number of Al-O ligands in the first coordination sphere one can conclude that the acidity is increasing as one moves from Si(4Al) to Si(1Al) and that the latter, Si(AlO)(SiO)₃, is the most acidic.

I. INTRODUCTION AND BACKGROUND

Active catalytic phases (metal, mixed metals, oxide or mixed oxides) interacting with oxide support on which the active phase is dispersed can affect the percentage exposed, the morphology of supported particles, the degree of reducibility of cations, etc., in a variety of ways. Our objective is to characterize the physical chemistry of the active phase-oxide support interaction by spectroscopic methods and to correlate this structure with catalytic function. An important corollary to this objective is an understanding of the interaction chemistry between the active phase precursors and the oxide supports using the same spectroscopies used to characterize the final active phase.

We have investigated several disparate systems which have in common only the techniques used to probe the interaction between active phase-oxide support and the philosophy of our approach. The techniques we are using are element specific and provide information on the local structure about a given element without the requirement of any long-range order. These are X-ray absorption (near edge structure, XANES, and extended fine structure, EXAFS) and solid state NMR. We will briefly review our progress on three projects which sample three main kinds of active phase-support interactions (metal-oxide, mixed metal-oxide and oxide-oxide) and propose a parallel set to which we wish to extend our work. The three systems discussed in the progress review are Ag/TiO₂, Ru-Cu/SiO₂ and SiO₂/Al₂O₃.

II. PUBLISHED REPORTS

In the last two years, five papers which recognize DoE support have been published [1-5]. In addition, an **Adv. Catal.** review of earlier work [6], and research not yet published in the open literature, is summarized in one dissertation [7].

These are listed, respectively, below.

'XANES Evidence for Direct Metal-Metal Bonding and Electron Transfer in Reduced Rh/TiO₂ Catalysts', D. E. Resasco, R. S. Weber, S. Sakellison, M. McMillan and G. L. Haller, **J. Phys. Chem.**, 92, 189 (1988).

'Characterization of RuCu/SiO₂ Catalysts by Chemisorption, Catalysis and Spectroscopy', A. J. Hong, B. J. McHugh, L. Bonneviot, D. E. Resasco, R. S. Weber and G. L. Haller, **Proc. 9th Intern. Congr. Catalysis**, (Eds., M. J. Phillips and M. Ternan), Vol. 3, p. 1198, Chemical Instit. of Canada, 1988.

'EPR Characterization of Ti⁺³ Ions at the Metal-Support Interface in Pt/TiO₂ Catalysts', L. Bonneviot and G. L. Haller, **J. Catal.**, 113 96 (1988).

'Metal-Support Effects in Pt/L-Zeolite Catalysts', G. Larsen and G. L. Haller, **Catalysis Letters**, 3, 103 (1989).

'A ²⁹Si NMR Investigation of the Structure of Amorphous Silica-Alumina Supports', M. McMillan, J. S. Brinen, J. D. Carruthers and G. L. Haller, **Colloids and Surfaces**, 38, 133 (1989).

'Metal-Support Interaction: Group VIII Metals and Reducible Oxides', G. L. Haller and D. E. Resasco, **Advances in Catalysis**, 36, 173 (1989).

'Metal-support Interaction in Silver/Titania Catalysts', Yuejin Li, Ph. D. Thesis, Yale University, 1989.

III. PROGRESS REVIEW

A. Interaction of Ag with TiO₂ Support

In our recent review [6], we discussed in some detail the relative strength of interaction of Rh and Pt with TiO₂ and V₂O₃ supports. Platinum has much the stronger interaction with these two supports. This is evidenced by a lower temperature of onset of the interaction and a higher oxidation temperature to reverse the interaction (particularly evident for V₂O₃). While the catalytic consequences of the interaction are similar, the stronger interaction of Pt results in a morphology change which is much less evident for Rh and the stoichiometry of reductant and oxidant required to produce and reverse the metal support interaction is about twice as large for Pt as it

is for Rh. This observation suggested that the strength of transition metal interaction with reducible oxides increases as one moves from left to right in the periodic table. This prompted us to investigate Ag/TiO₂ catalysts. An even stronger interaction of Ag with TiO₂ than observed for group VIII was observed [7]. Indeed, we find that a surface compound is formed which deactivates Ag for all reactions, including CO oxidation.

The dispersion of Ag/TiO₂ was measured by hydrogen-oxygen titration at 170°C following either an oxidation pretreatment at 400°C or a reduction pretreatment at 500°C. Two Ag loadings of 1 and 10 wt% on TiO₂ were studied and these were compared to similar catalysts using a SiO₂ support. The dispersion was always substantially greater on TiO₂ than on SiO₂ for a given pretreatment (see Table 1 below for results on the 1 wt% catalysts), but the effect of pretreatment has the opposite effect with the two supports. Oxidation results in a pronounced increase in dispersion on SiO₂ but a very modest effect on TiO₂.

Table 1

Catalyst	1%Ag/TiO ₂		1%Ag/SiO ₂	
Pretreatment, R = 500°C red. O = 400°C ox.	R	O	R	O
Dispersion	0.41	0.35	0.051	0.22

However, even though TiO₂ gives higher dispersion of Ag, this material is not very active catalytically. As is shown in the following Figure, all catalysts supported on SiO₂ have turnover frequencies that are equivalent to unsupported Ag but the rates of CO oxidation are suppressed when Ag is supported on TiO₂ and the degree of suppression is more pronounced on the catalyst of lower loading which has a higher dispersion.

Using a pulsed chemisorption technique, we have been able to measure the steady-state oxygen and CO coverage at reaction temperatures. On Ag/SiO₂, oxygen coverages are high in the temperature range 60 - 140°C and they increase with temperature. On Ag/TiO₂, oxygen coverages are very low and, where they can be measured, they decrease

with increasing temperature. These results can be used to rationalize both the suppression of CO oxidation activity on Ag/TiO₂ and the fact that there is a maximum in the Arrhenius function as seen in Figure 1. We attribute this oxygen adsorption suppression to the formation of a surface compound between Ag and TiO₂. The evidence for this conclusion comes from EXAFS and XANES analysis. The EXAFS of Ag/SiO₂ is essentially that of Ag metal independent of pretreatment, but the EXAFS of oxidized 1%Ag/TiO₂ is not that of Ag metal or of silver oxide. (The reduced 1%Ag/TiO₂ is a mixture of Ag metal and the new phase.) We have tentatively identified this new phase as AgTiO₂. This is not a known bulk phase compound and, indeed, we observe no phases other than TiO₂ (rutile) in the X-ray diffraction of oxidized 1%Ag/TiO₂, i.e., this is the reason that we refer to this as a surface compound.

B. Silica Support Effect on Ru-Cu Interaction

In a previous publication [8] we have drawn attention to 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/SiO₂ and Ru-Cu/SiO₂ 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 [9], addition of Cu causes a depression of H/M relative to Ru/SiO₂ 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 [10].

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 H₂ chemisorption by the Ru and also to a marked suppression of the catalytic activity of the Ru for ethane hydrogenolysis [9].

Figure 1

Activities of Silver Catalysts for CO Oxidation

- R - reduced at 500 °C for 2 hours; O - oxidized at 400 °C for 2 hours.
- + Ag Powder.
 - ◻ 1%Ag/Silica, R.
 - ◻ 1%Ag/Silica, O.
 - ▲ 10%Ag/Titania, R.
 - △ 10%Ag/Titania, O.
 - 10%Ag/Silica, R.
 - 10%Ag/Silica, O.
 - ⊕ 1%Ag/Titania, R.
 - ◆ 1%Ag/Titania, O.

Chemisorption, catalysis and X-ray photoelectron spectroscopy studies on unsupported Ru-Cu aggregates [11-14] 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/SiO₂ catalysts by an EXAFS analysis [15]. The effect of this chemisorption of Cu on Ru is to block H₂ 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 H₂ chemisorption, can result in a dramatic reduction of hydrogenolysis sites. How then can one explain an **increase** in H₂ chemisorption when Cu is added to Ru? We suggested that there may be H₂ spillover from Ru to Cu [16]. Such H₂ spillover has been unequivocally shown to occur in the model system of Cu evaporated onto (0001) Ru by Goodman and Peden [17] and more recently by NMR of high area supported Ru-Cu catalysts [18]. However, these same investigators observe that Cu forms two dimensional islands on Ru(0001) using Yates et al. low temperature evaporation approach which results in a one-to-one site blocking of H₂ [19]. This is in contrast to the observation of Shimizu et al. [20] and Vickerman and Christman [21] 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 [22] 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 [17].

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 [23]. 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 [10]. 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 HS5 support and to rationalize H₂ spillover from Ru to Cu on M5 but less so on HS5, we were obliged to postulate that the bimetallic Ru-Cu clusters have outer layers that are effectively a Cu rich mixture or surface alloy [10]. This postulate goes beyond that proposed by Sinfelt et al. [15] based on EXAFS where their model pictured the Cu as more or less chemisorbed on the surface of Ru particles. A re-investigation of the X-ray absorption of the Ru-Cu on HS5 and M5 supports has been performed [2]. What is immediately clear from the XANES is that Cu protects the underlying Ru from oxidation on HS5 (in agreement with the EXAFS results of Sinfelt et al. [15]), 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. Using a combination of EPR, IR and X-ray absorption, we have concluded that these different morphologies result from a different interaction of Cu precursors on the two silicas and likely involves surface hydroxyl groups since dehydroxylation of the silicas tends to diminish differences in catalytic activity and in the IR spectra of adsorbed CO [2].

C. NMR of Amorphous Silica-Alumina

We have used magic angle spinning NMR to investigate the structure of silica which increases the thermal stability of alumina supports [5]. We have continued this investigation in a direction which seeks correlations between acidity and the ^{29}Si and ^{27}Al NMR chemical shifts of a variety of amorphous silica-aluminas. Three methods were used to modify the surface structure of amorphous silica-alumina (varying the silica content, calcination temperature and preparation method). Cumene cracking and reaction of 2-methyl-2-pentene [24] were also used to investigate the Brønsted acidity and the overall acid site strength.

Using cumene cracking, it has been demonstrated that the silica which imparts structural stability (and has a chemical shift of -78 ppm with respect to TMS) has low Brønsted acidity which is comparable to pure alumina. This suggests that any correlation between catalytically significant acidity and NMR intensity should first be corrected for intensity with a chemical shift at -78 ppm. It must also be corrected for intensity at -109 ppm, the chemical shift for ^{29}Si in pure silica which is also of relatively low Brønsted acidity.

As an example of the procedure which we have developed, we will consider three samples where the surface area, porosity and acidity has been varied by varying the calcination temperature. The sample was 10% silica and was calcined at 500, 1000 and 1175°C. The ^{29}Si NMR spectra of these three samples is shown in Figure 2. In the case of the sample calcined by 1175°C, the two peaks due to non-acidic silica that

Figure 2

The ^{29}Si NMR Spectra of 10%-Silica-Alumina

Calcined at Three Differ Temperatures (SA500 = 500° calcination)

were subtracted (dotted curve) and the resulting corrected NMR intensity (dashed curve) is also shown. When the activity is normalized to the surface area only, the apparent activity for the three samples changed by 300%. When it was also normalized to the NMR intensity, as described above, it varied by only 50%. These results are summarized in Table 2.

TABLE 2
Activity of Cumene Cracking at 450°C

Sample(calincation T°C)	SA(500)	SA(1000)	SA(1175)
Surface Area (m ² /g)	347	217	120
Activity			
mole/g-sec	4.0x10 ⁻⁵	3.0x10 ⁻⁵	5.7x10 ⁻⁵
mole/m ² -sec	1.2x10 ⁻⁷	1.4x10 ⁻⁷	4.8x10 ⁻⁷
above rate normalized to NMR ²⁹ Si intensity and relative to SA(1000)	1.3x10 ⁻⁷	1.4x10 ⁻⁷	1.9x10 ⁻⁷

While this is a substantial improvement, if the NMR corrected intensity had been a true measure of site density and acidity of the site, the NMR normalized activity should have been constant. While the corrected NMR intensity is approximately positioned at -93 ppm, its width is not constant which suggests that there is more than one kind of mixed Si-O-Al sites represented. Thus, it will be necessary to be able to fully deconvolute this intensity and attach a relative acidity (activity) for each component of this NMR measure of acid site density.

Because cumene cracking does not measure the very weak acidity (the activity of those silica-aluminas with less than 5% SiO₂ have less activity than γ-Al₂O₃), we have sought another reaction to correlate acidity. Recently, Kramer et al. [24] have recommended the reaction of 2-methyl-2-pentene isomerization to probe the relative acidity of a series of silica-aluminas. Specifically, they suggest the use of the ratio of 3-methyl-2-pentene to 4-methyl-2-pentene (3M2P/4M2P) ratio, the ratio of a

methyl shift to a double bond shift, respectively. This ratio was found to be linearly correlated to the MAT activity (micro activity test, an industrial measure of cracking activity that involves the cracking of a gas oil under ASTM prescribed conditions). We have used this reaction to measure the acidity of a wide variety of silica-aluminas. The 3M2P/4M2P ratio is plotted against the chemical shift of ^{29}Si in Figure 3 along with the MAT number (not measured, taken from the correlation given in Ref. [24]). There is a remarkable linear correlation between this measure of acidity and the ^{29}Si chemical shift. From this correlation and the known chemical shifts of ^{29}Si as a function of the number of Al-O ligands in the first coordination sphere (also shown in Figure 3) one can conclude that the acidity is increasing as one moves from Si(4Al) to Si(1Al) and that the latter, Si(AlO)(SiO)₃, is the most acidic.

Figure 3

The relation between the acid strength and the local structure of silicon in amorphous silica-alumina.

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