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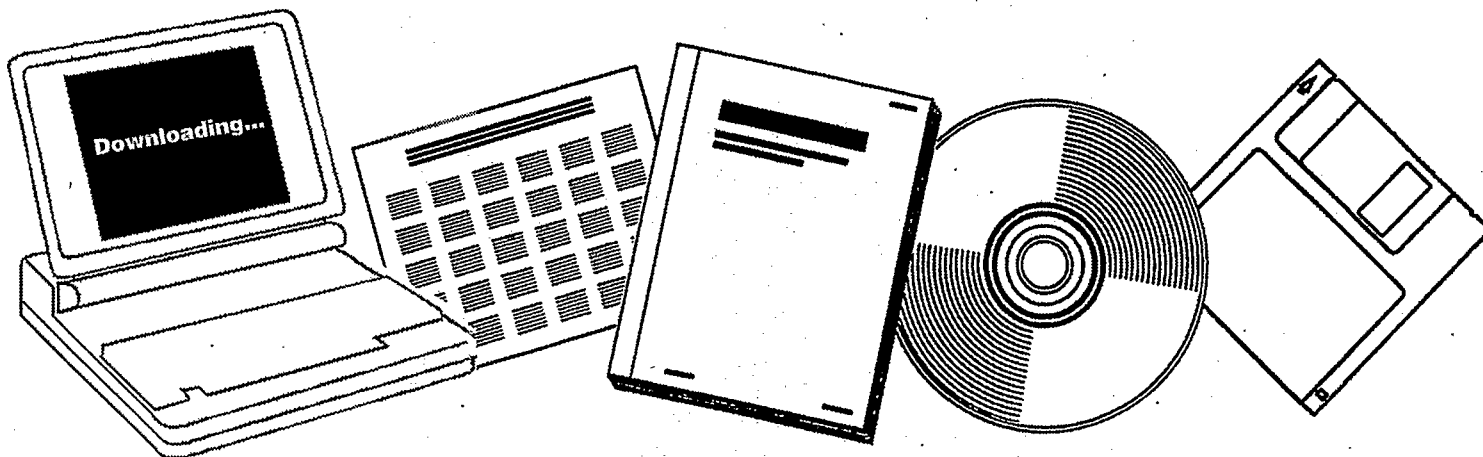
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**SELECTIVITY, ACTIVITY AND METAL-SUPPORT
INTERACTIONS OF GROUP VIII BIMETALLIC
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SELECTIVITY, ACTIVITY AND METAL-SUPPORT INTERACTIONS
OF GROUP VIII BIMETALLIC CATALYSTS

Progress Report

for Period 15 August 1983 - 15 August 1984

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ABSTRACT

Progress on our investigation of supported bimetallic catalysts and the development of techniques for the characterization of supported catalysts is reported. Three bimetallic systems were studied: Rh-Pt, Ru-Cu and Rh-Ag. In all three systems our goal has been the determination of the effect of the support on the kind and degree of metal-metal interaction. Small particles of Rh-Pt are found to be enriched in Rh on all supports, the degree of enrichment increasing in the order $\text{SiO}_2 < \text{Al}_2\text{O}_3 < \text{TiO}_2$. The kind of SiO_2 used to support Ru-Cu is found to have a large influence on the change in the H/Ru ratio when Ru and Ru-Cu/ SiO_2 catalysts are compared although the effect on ethane hydrogenolysis is comparable. For pure Rh supported on TiO_2 and reduced at high temperature, extended X-ray Absorption Fine Structure (EXAFS) analysis suggests direct Rh-Ti bonding following a high temperature reduction. EXAFS also indicates that there is a stronger interaction between Ag and TiO_2 than Ag and SiO_2 and clearly demonstrates that there is greater metal-metal interaction for Rh-Ag supported on TiO_2 than for Rh-Ag supported on SiO_2 . A fourth system, NiMoP/ Al_2O_3 , is not a bimetallic but was chosen as an interesting and convenient catalyst on which to initiate magic angle spinning NMR research. ^{27}Al NMR proves that formation of the surface compound $\text{Al}_2(\text{MoO}_4)_3$ on Mo/ Al_2O_3 is induced by calcination but on NiMoP/ Al_2O_3 this compound formation is inhibited and AlPO_4 is formed instead.

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INTRODUCTION

Five topics involving the investigation of bimetallic supported catalysts or the development of physical techniques for their characterization are reported here. We have previously reported on a mechanistic study of hydrogenolysis over Rh-Pt/SiO₂ catalysts [1]. This project has now been extended to include Al₂O₃ and TiO₂ supported Rh-Pt catalysts where our objective was to determine the effect of the support on the degree of metal-metal interaction. Preliminary work [2] on the influence of preparation variables on the degree of metal-metal interaction for the system of Ru-Cu/SiO₂ has been continued giving special attention to non-porous silicas and the relation between the change in hydrogen chemisorption and ethane hydrogenolysis activity when Cu is added to Ru. Using Extended X-ray Absorption Fine Structure (EXAFS) analysis, we believe we have produced the first evidence for direct Rh-Ti bonding for Rh/TiO₂ catalysts reduced at high temperature and that this provides a mechanism for transport of a suboxide of titania over the metal particles as proposed in our model for metal-oxide interaction in these systems [3]. In addition to each of these three topics, we will briefly summarize progress in the development of two different experimental approaches for the characterization of bimetallic catalysts. One technique involves the detailed analysis of the temperature dependence of the Debye-Waller term of the EXAFS interference function to deduce metal-metal interaction in systems where the nearest neighbor distance of the pure and bimetallic are nearly identical, e.g., Rh-Ag. The second technique involves magic angle spinning ²⁷Al NMR to investigate active component-support interaction in NiMoP/Al₂O₃ catalysts.

SUPPORT EFFECTS ON Rh-Pt INTERACTION

For two series of Rh-Pt bimetallics supported on SiO₂, one porous and one non-porous, we found no evidence for surface enrichment of one of the metals [1].

While on thermodynamic grounds one would expect the more volatile metal, Pt, to enrich the surface, this has not been observed even for a model system of supported bimetallic films reduced at 873K [4]. However, a 48% Rh/52% Pt film exhibited enrichment in Rh by as much as a factor of 3 after oxidation at 873K and, once established, enrichment was not easily reversed by subsequent heating in H₂. This result suggested that one might observe surface enrichment of bimetallic Rh-Pt particles if supported on oxides which preferentially interacted with one of the metals. To test this hypothesis, we have prepared Rh-Pt catalysts supported on Al₂O₃ and TiO₂ to be compared to the SiO₂ supported catalysts. We have used the hydrogenolysis of ethane and of isopentane as test reactions to probe the composition of the surface of the metal particles. Both reactions are structure sensitive. In the case of ethane hydrogenolysis, the rate on Rh is of the order of 10⁵ greater than on Pt so that Pt behaves as a relatively inert surface component. Thus, for example, if the surface is covered randomly with half Rh and half Pt, one expects the rate to be much less than the average of the pure Rh and pure Pt catalysts since the Pt would not only be relatively inert but would breakup Rh ensembles rendering them inactive also. In fact, the rate of ethane hydrogenolysis on the catalysts with a 1:1 atomic ratio of Rh:Pt exhibit rates which exceed the average of the two metals on all of the supports but the magnitude of the rate appears to increase in the order SiO₂ < Al₂O₃ < TiO₂. (The result in the case of TiO₂ is complicated by the deactivation of the metals for hydrogenolysis by the metal-oxide interaction [3].) We believe that this may be evidence for a stronger interaction of Pt with the oxide supports than for Rh which in turn induces a surface enrichment of Rh.

SUPPORT EFFECT ON Ru-Cu INTERACTION

Our investigation of Rh-Ag bimetallic interaction lead us to a comparative investigation of Ru-Ag and Ru-Cu [5]. In the process of this investigation we

observed an unexpected effect of silica texture and anion of impregnation solution effect on the characteristics of Ru-Cu which has now been published [2]. While the effect of added Cu on the ethane hydrogenolysis activity was very much as would have been expected on the basis of Sinfelt's published work [6], hydrogen chemisorption was not. In particular, it was observed that the addition of Cu to a 1 wt% Ru catalyst to give a 1:1 atomic ratio of Ru:Cu at constant Ru loading of Ru resulted in an increase in the H/Ru ratio while Sinfelt's work always showed a decrease in H/Ru as well as a suppression of ethane hydrogenolysis rate. To elucidate this apparent contradiction in experimental observations, we initiated a comparative study of two non-porous silica supports, Cab-O-Sil HS5 which had been used in the original Sinfelt work [6] and Cab-O-Sil M5 which had been used in our preliminary study [2]. A part of our results is shown in Table 1 below.

TABLE 1

CATALYST	ANION OF Ru	SUPPORT	H/Ru	
			Co-Impregnation	Sequential
Ru	Cl ⁻	M5	0.09	
Ru-Cu	Cl ⁻	M5	0.21	0.06
Ru	NO ₃ ⁻	M5	0.16	
Ru-Cu	NO ₃ ⁻	M5	0.24	0.15
Ru	Cl ⁻	HS5	0.29	
Ru-Cu	Cl ⁻	HS5	0.16	0.26
Ru	NO ₃ ⁻	HS5	0.57	
Ru-Cu	NO ₃ ⁻	HS5	0.50	0.41

There are several observations worth noting. Firstly, the only known difference between these two silicas is their surface areas which are 200 and 325 m²/g, respectively, for the M5 and the HS5. The higher surface area silica

results in a higher dispersion of Ru, an observation consistent with that reported when M5 (non-porous, 200 m²/g) was compared to Davison 923 (porous, 600 m²/g). Also, the nitrate anion of the salt Ru(NO)(NO₃)₃ generally gives a higher dispersion than the chloride salt, RuCl₃. However, the observation which is difficult to explain is that addition of Cu by co-impregnation on the HS5 support deceases hydrogen chemisorption as one expects if Cu covers the surface of Ru particles as proposed by Sinfelt while Cu addition to Ru supported on M5 increases hydrogen chemisorption. In fact, we have found the latter to be the more general finding which applies not only to the non-porous Cab-O-Sil M5 but also to Davison 62, 923 and 952 silicas. However, it should also be noted that there is a very small and similar effect of Cu on H/Ru using sequential impregnation (Ru first) on all silicas and all silica supported Ru catalyst behave qualitatively the same when the effect of added Cu on ethane hydrogenolysis activity is measured, i.e., addition of Cu dramatically reduced the hydrogenolysis rate but the activation energy remains about constant around 30 Kcal/mole for all catalysts. Clearly the simple picture of Cu covering the surface of Ru decreasing the hydrogen chemisorption capacity and a simple correlation of H/Ru with the breakup of Ru ensembles necessary for hydrogenolysis sites needs to be re-investigated in the light of these findings.

EXAFS OF TiO₂ SUPPORTED Rh CATALYSTS

The discovery that group VIII metals supported on TiO₂ [7] and other reducible oxides [8] can produce dramatic, reversible effects on chemisorption and catalysis has stimulated widespread interest in these systems [9]. This effect has been labeled a Strong Metal-Support Interaction (SMSI), and initial interpretations attributed the chemisorption and catalytic effects to an electronic interaction [10]. Because of the parallel behavior between group VIII-group Ib and Rh-TiO₂ interaction effects on structure-sensitive and

structure-insensitive reactions, we have proposed a model involving migration of a reduced species of the support onto metal particles which results in a geometric effect as well [3]. Several model system studies of Fe/TiO₂ [11], Ni/TiO₂ [12-14], Pt/TiO₂ [15-17] and Rh/TiO₂ [15,18] have provided direct physical evidence for migration of a (reduced) titanium species onto metal particles during heating and reduction by H₂. Such a migration clearly implies a chemical interaction or bonding which provides the thermodynamic driving force for the movement of the titanium entity from the surface of TiO₂ to the surface of the metal particle. This migration must result in both a geometric and electronic perturbation of the metal surface. Thus, two of the most important unanswered questions about the SMSI effect are concerned with the nature of the titanium species which migrates (metallic or oxidized) and the kind of bonding between this species and the group VIII metal.

We have studied the metal-oxide interaction as a function of reduction temperature of a catalysts prepared by ion exchange. The metal loading measured by HCl extraction and atomic absorption was 0.47% and the H/Rh chemisorption measured by our standard procedure was 1 ± 0.05 [19]. X-Ray absorption spectra were obtained at the Cornell High Energy Synchrotron Source. All spectra reported here were obtained at liquid N₂ temperature.

EXAFS above the K edge of Rh at 24.224 eV was normalized to the atomic absorption coefficient of Rh after subtraction of the atomic absorption coefficient. The resulting interference function was weighted by the wave vector cubed and Fourier transformed over the range of wave vectors 3 to 13 Å⁻¹. The magnitude of the Fourier transforms of the EXAFS of the oxidized catalyst is shown in Figure 1. In Figures 2, 3 and 4 we show the magnitude of the Fourier transforms after in situ reduction at 494K for 90 min, 628K for 60 min and 775K for 90 min.

FIGURE 1

The EXAFS Fourier transform for the ion exchanged Rh/TiO₂ after oxidation at 673K.

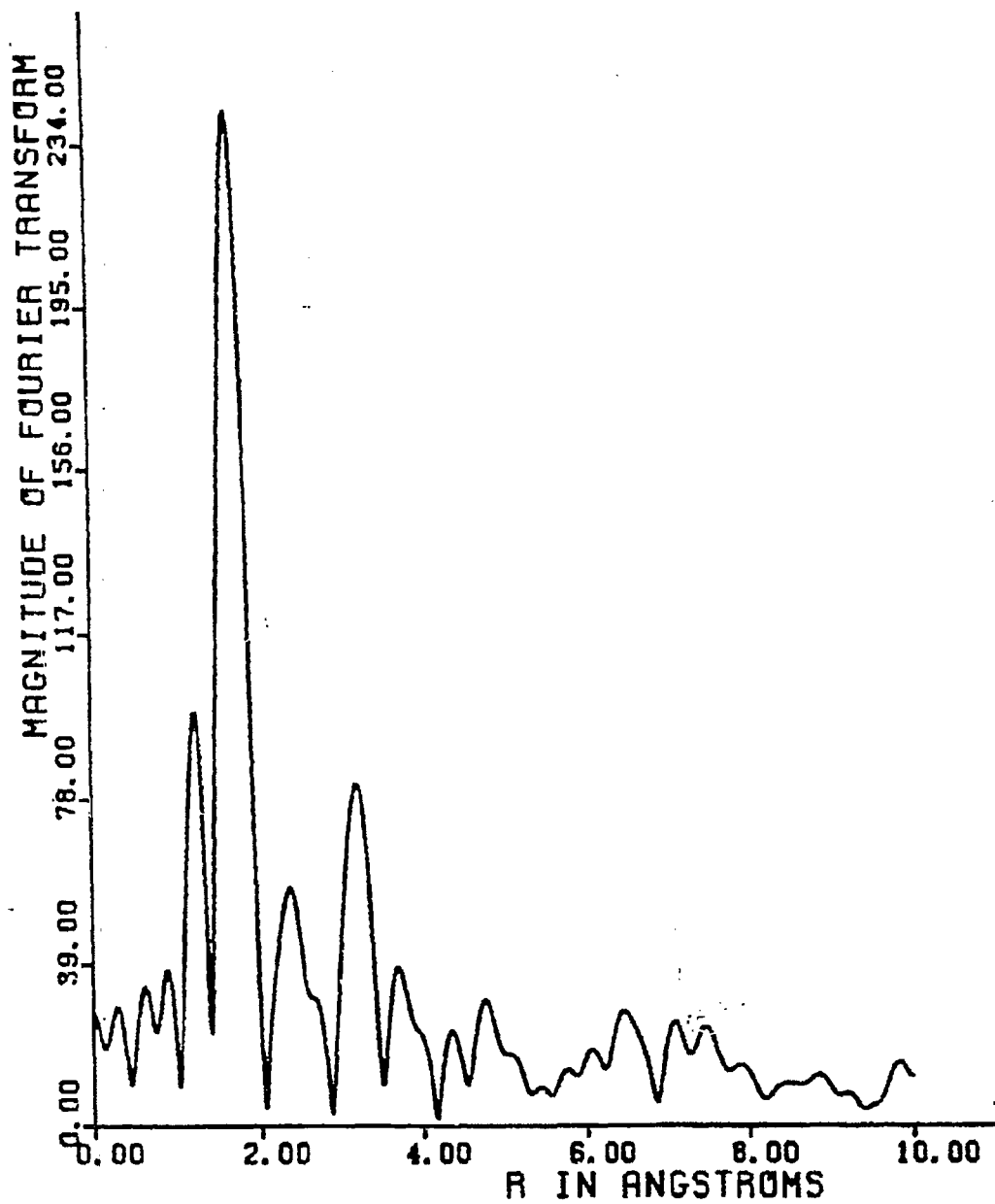


FIGURE 2

The EXAFS Fourier transform for the ion exchanged Rh/TiO₂ after reduction at 494K for 90 min.

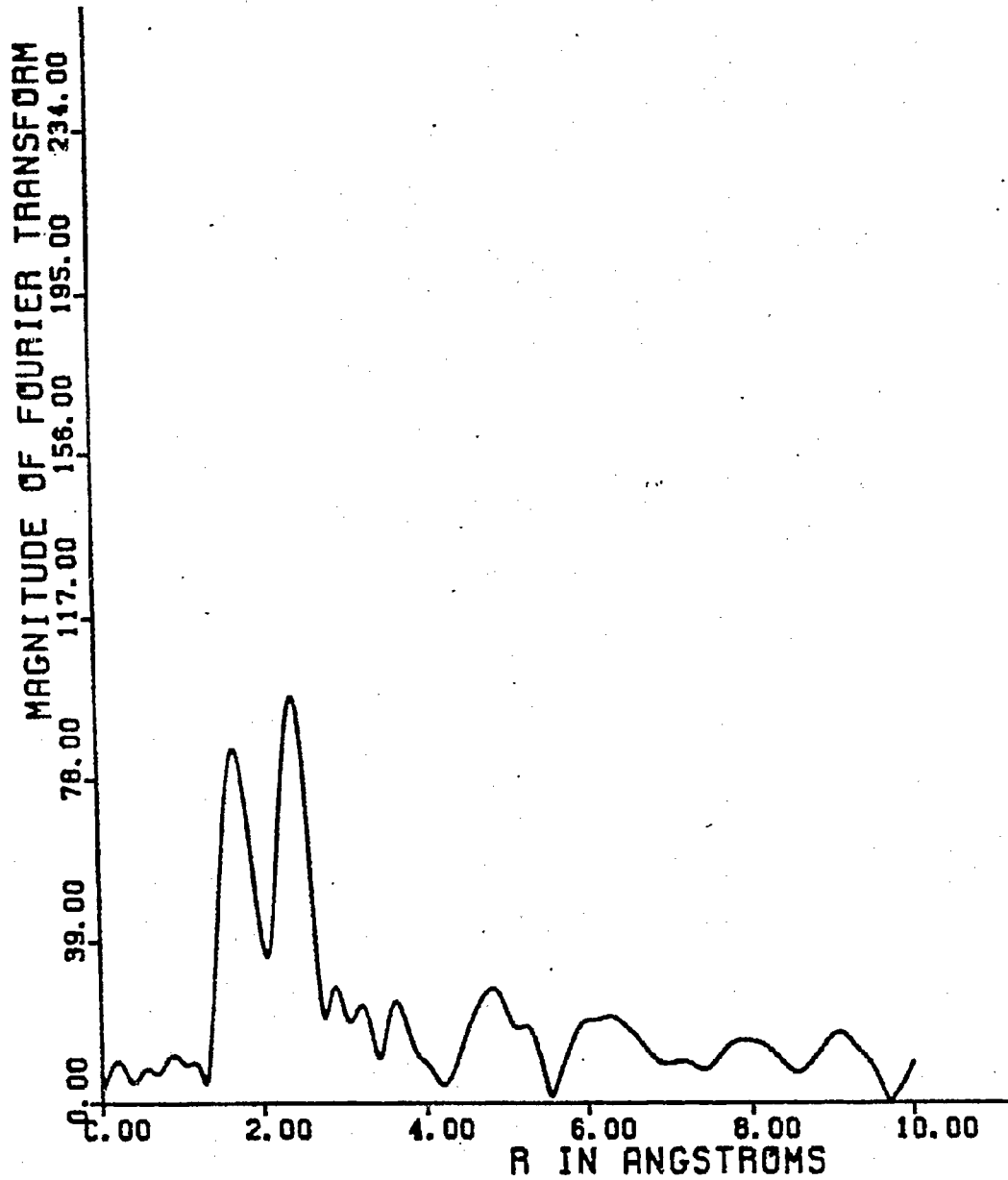


FIGURE 3

The EXAFS Fourier transform for the ion exchanged Rh/TiO₂ after reduction at 628K for 60 min.

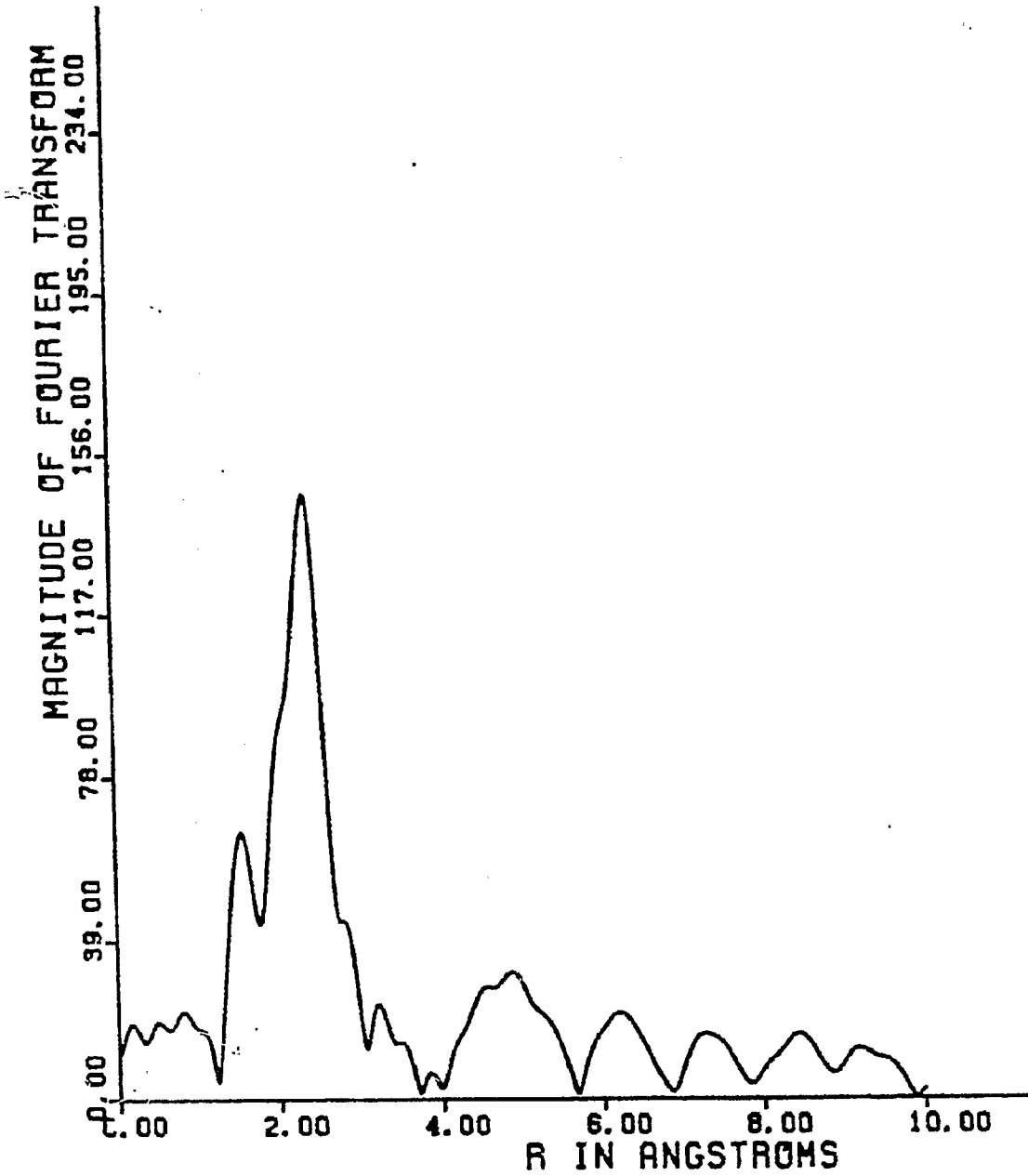
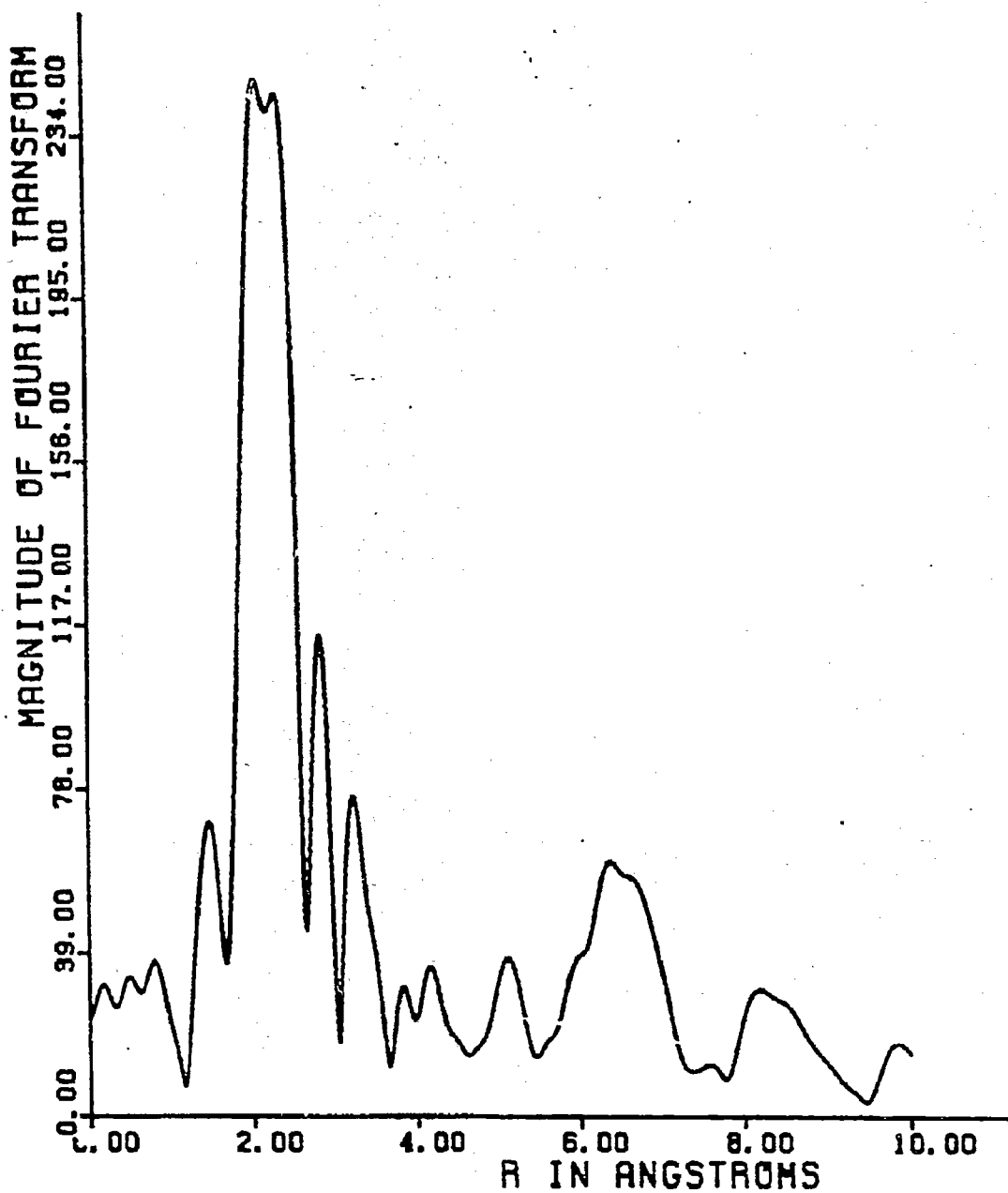


FIGURE 4

The EXAFS Fourier transform for the ion exchanged Rh/TiO₂ after reduction at 775K for 90 min.



The major peak in Figure 1 corresponds to Rh-O bond at 2.05Å after phase correction in the completely oxidized catalyst. However, the peak at about 3Å in Figure 1 does not correspond to Rh-O-Rh. We assign this peak to Rh-O-Ti bonding. After reduction at 488K a second nearest neighbor Rh peak appears which represents Rh-Rh bonding at 2.69Å (after phase correction) grows in as a result of reduction. This is the same bond distance as found in bulk Rh metal. The Rh-O-Ti peak completely disappears although Rh-O bonding is still very prominent. The relative magnitudes under the Rh-O peaks in Figures 1 and 2 suggest that not more than one third of the Rh has been reduced. This is unusual compared to well dispersed Rh supported on SiO₂ where complete reduction can be accomplished at 494K. Reduction remains incomplete at 628K, Figure 3, and there is evident the development of another peak as a shoulder on the Rh-Rh peak which becomes a distinct peak after reduction at 775K, see Figure 4. We believe that this peak is due to Rh-Ti metallic bonding. Using a Rh-Ti phase estimated on the basis of theory [20], we obtain a bond length of 2.63Å. Because we do not have a reference compound spectrum and the Rh-Rh and Rh-Ti peaks overlap and cannot be Fourier filtered, the error in the Rh-Ti bond length is likely to be relatively large, i.e., ±0.05Å is probable.

The Rh-Ti bond is very strong [21] and its formation could well provide the driving force for the migration of Ti species onto Rh particles. However, other work suggests that the species which migrates is a sub-oxide [18]. A more complete structural analysis will require EXAFS of both Rh and Ti on the same sample and perhaps additional physical characterization of local structure.

EXAFS OF TiO₂ SUPPORTED Rh-Ag CATALYSTS

We have previously studied Rh-Ag/SiO₂ [22] and compared it to Rh-Ag/TiO₂ [23] with respect to the effect of the added group Ib metal on the activity of Rh for ethane hydrogenolysis. In the case of Rh-Ag/SiO₂ there was very little effect

the added Ag on Rh ethane hydrogenolysis activity while for Rh-Ag/TiO₂ added Ag markedly suppressed ethane hydrogenolysis activity, i.e., the latter system is quite analogous to Ru-Cu/SiO₂ [6]. We postulated that the difference between Rh-Ag on SiO₂ and on TiO₂ was the result of Ag islands covering Rh particles supported on SiO₂ while the Ag spread out over the Rh particles when the TiO₂ support was used.

One technique which has been used very successfully by Sinfelt and his co-workers [24,25] to study group VIII-group Ib interactions is EXAFS. However, in all of the systems so far studied, Ru-Cu, Rh-Cu and Os-Cu, the two metals have been from different rows of the periodic table and have had substantially different EXAFS phase shifts while for Rh and Ag they are about the same [20]. On the other hand Rh has a relatively high Debye-Waller temperature (a measure of the root-mean-square displacement), $\theta_D = 350\text{K}$ while Ag is relatively low, $\theta_D = 225\text{K}$ [26]. This suggests that one might be able to detect the interaction of these two metals by comparing the EXAFS magnitude as a function of temperature. However, the surface Debye-Waller temperature is always about half that of the bulk, 260 and 104K respectively for Rh and Ag, so that the magnitude of the EXAFS radial distribution curve will decrease with particle size and the temperature dependence may also vary with particle size. The observed magnitudes in arbitrary units and the change in the EXAFS Debye-Waller term between 77 and 298K for three standards (foil and two supports) for each metal and two bimetallic catalysts on the two supports are presented in Table 2.

The first observation is that the magnitude of the first nearest neighbor peak for either Ag or Rh at both 77K and 298K decreases when the supported metals are compared to the foils. This is expected due to the small particles. In the case of Rh the magnitudes are about the same for both supports. However, for Ag the magnitude is smaller for Ag/TiO₂ relative to Ag/SiO₂ at 298K but larger for Ag/TiO₂ relative to Ag/SiO₂ at 77K. This is a clear indication that the change

TABLE 2

		AG EDGE EXAFS		RH EDGE EXAFS		
T, K	Magnitude	% Decrease $(\sigma_{298}^2 - \sigma_{77}^2) \times 10^3$		Magnitude	% Decrease $(\sigma_{298}^2 - \sigma_{77}^2) \times 10^3$	
		Ag Foil			Rh Foil	
77	1225	75.1	5.93	2250	43.3	2.14
298	305			1275		
		Ag/SiO ₂		Rh/SiO ₂		
77	705	68.1	4.83	990	45.1	2.87
298	245			544		
		Ag/TiO ₂		Rh/TiO ₂		
77	1020	76.7	7.50	960	41.7	2.58
298	238			560		
		Rh-Ag/SiO ₂		Rh-Ag/SiO ₂		
77	538	68.0	4.38	970	—	—
298	170			—		
		Rh-Ag/TiO ₂		Rh-Ag/TiO ₂		
77	930	60.2	5.09	1137	55.6	3.10
298	370			515		

in the magnitude is sensitive to both the particle size and the metal interaction with the support. From an independent measure of particle size by X-ray line broadening, we know that Ag forms smaller particles on TiO₂ than on SiO₂. Thus the large magnitude for Ag/TiO₂ at 77K must be a result of the strong interaction of the Ag small particles with TiO₂ compensating for the fact that more Ag atoms are on the surface in small particles. Additional evidence for this interpretation can be found in the temperature dependence of the Debye-Waller term, $\sigma_{298}^2 - \sigma_{77}^2$, which is greater for Ag/TiO₂ than for Ag foil. When the EXAFS of either metal in Rh-Ag/SiO₂ is compared to Ag/SiO₂ or Rh/SiO₂, both the magnitude and temperature dependence of the Debye-Waller term are comparable for the bimetallic and the pure metals. This is in marked contrast to Rh-Ag/TiO₂. In

this bimetallic catalyst the temperature dependence of the Debye-Waller term for Rh is greater than Rh/TiO₂ or Rh foil, i.e., it is more like Ag. At the same time the temperature dependence of the Debye-Waller term for Ag is less than Ag/TiO₂ or Ag foil, i.e., it is more like Rh. In fact the Ag in Rh-Ag/TiO₂ has a magnitude, when measured at 298K, which is greater than Ag foil, i.e., it apparently has a coordination number in the small particles of the catalyst which exceeds that in the bulk. A more reasonable interpretation of this result is that the average Ag atom in the catalyst has several Rh atoms in its coordination sphere and Rh is a better backscatterer than Ag. This is also consistent with the temperature dependence of Ag. The temperature dependence of the average Rh atom suggests that it has several Ag atoms in its coordination sphere. Our conclusion is that there is more metal-metal interaction between Rh and Ag when supported on TiO₂ than when supported on SiO₂ and that the Ag is not just chemisorbed on the surface of Rh particles like Cu in on Ru particles [6]. The latter conclusion is based on the mutual interaction of the two metals on each others temperature dependent Debye-Waller term.

²⁷Al NMR OF NiMoP/Al₂O₃ CATALYSTS

High resolution NMR spectroscopy of solids is now a well recognized structural tool [27,28] and there have been several recent applications to catalysts per se. Slichter and his co-workers have applied ¹⁹⁵Pt NMR to Pt/Al₂O₃ catalysts [29-31] and several groups have investigated ²⁹Si in zeolites [32-38]. The NMR of ²⁷Al in zeolites has also been examined [39,40]. For zeolites, it was noted that ²⁷Al NMR is much more structure sensitive than ²⁹Si NMR which is first nearest-neighbor dependent [39]. Specifically, Al can exist in both octahedral and tetrahedral coordination and, when the ligands are oxygen, the chemical shift of ²⁷Al differs by 55-80 ppm for these different coordinations [41,42]. Thus, ²⁷Al NMR can, in principle, be very useful for following the

tetrahedral/octahedral ratio in alumina supports as a function of thermal treatment as we will show below.

Even with magic angle spinning of highly crystalline α -alumina (corundum), the NMR linewidth of ^{27}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 NiMoP/ Al_2O_3 hydrodesulfurization catalyst, at least, an 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.

Figure 5 shows the spectra of θ , γ , δ and α aluminas (all except γ were X-ray diffraction standards [43]). These have been referenced to $\text{Al}_2(\text{MoO}_4)_3$ which is shifted down-field from $\text{Al}(\text{H}_2\text{O})_6^{3+}$ by 11 ppm [41]. The $\gamma\text{-Al}_2\text{O}_3$ in Figure 5b exhibits tetrahedral and octahedral Al_{3+} at about 85 and 11 ppm, respectively. This is a somewhat larger chemical shift difference than previously reported [44,45] but the tetrahedral to octahedral ratio is about the 1:3 ratio expected [46]. A part of the intensity is probably in transitions other than the $-1/2$ to $1/2$, and the amount will depend on pulse width and the distortion from ideal tetrahedral and octahedral symmetry [47]. Thus it might not be possible to simply obtain quantitative tetrahedral to octahedral ratios without careful consideration of the effects of pulse width on the peak integrals. The agreement between NMR measurements and X-ray structure predictions of the tetrahedral/octahedral ratios of γ - and $\eta\text{-Al}_2\text{O}_3$ [45] suggests that this need not always be a serious problem. However, the ratios reported by John et al. [45] were probably the result of similar distortions from cubic symmetry for all sites because when the distortion is very different as in $[(\text{Al}_{13}\text{O}_4(\text{OH})_{25}(\text{H}_2\text{O})_{11})\text{Cl}_6]$, only the central Al-O tetrahedron was detected while

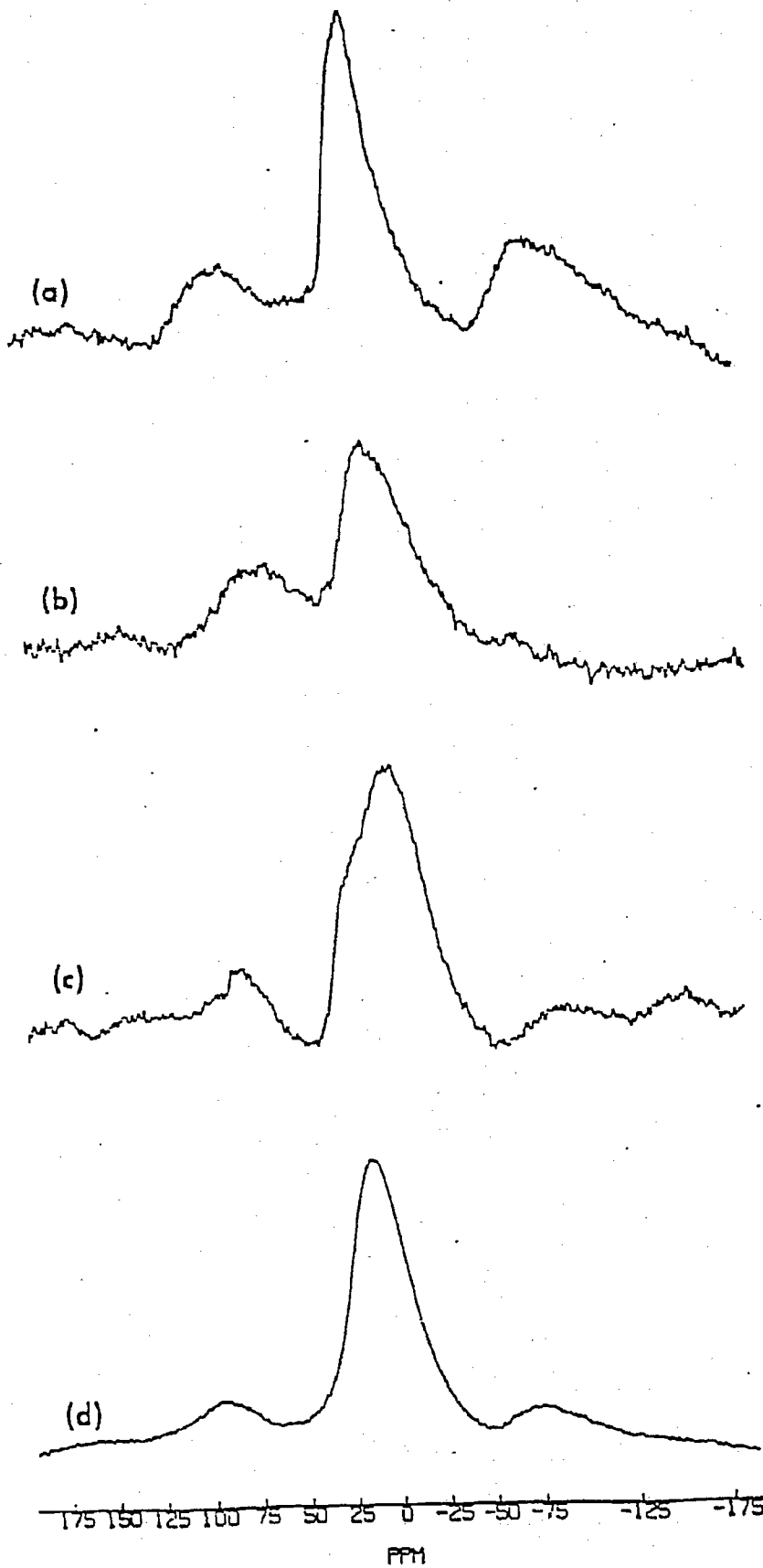


FIGURE 5

^{27}Al NMR spectra of aluminas: a) θ , b) γ , c) δ , and d) α . The chemical shift is set to zero for the reference compound $\text{Al}_2(\text{MoO}_4)_3$, see Figure 6d.

the twelve distorted octahedra were not [41]. In an example of severe distortion effects on ^{27}Al signals, the tetramer of aluminum isopropoxide which has a central non-distorted octahedral AlO_6 unit and three distorted tetrahedral AlO_4 units, the correct integrated intensity ratio was observed but the line width of the tetrahedral Al peak was 10 times that of the octahedral Al peak [48].

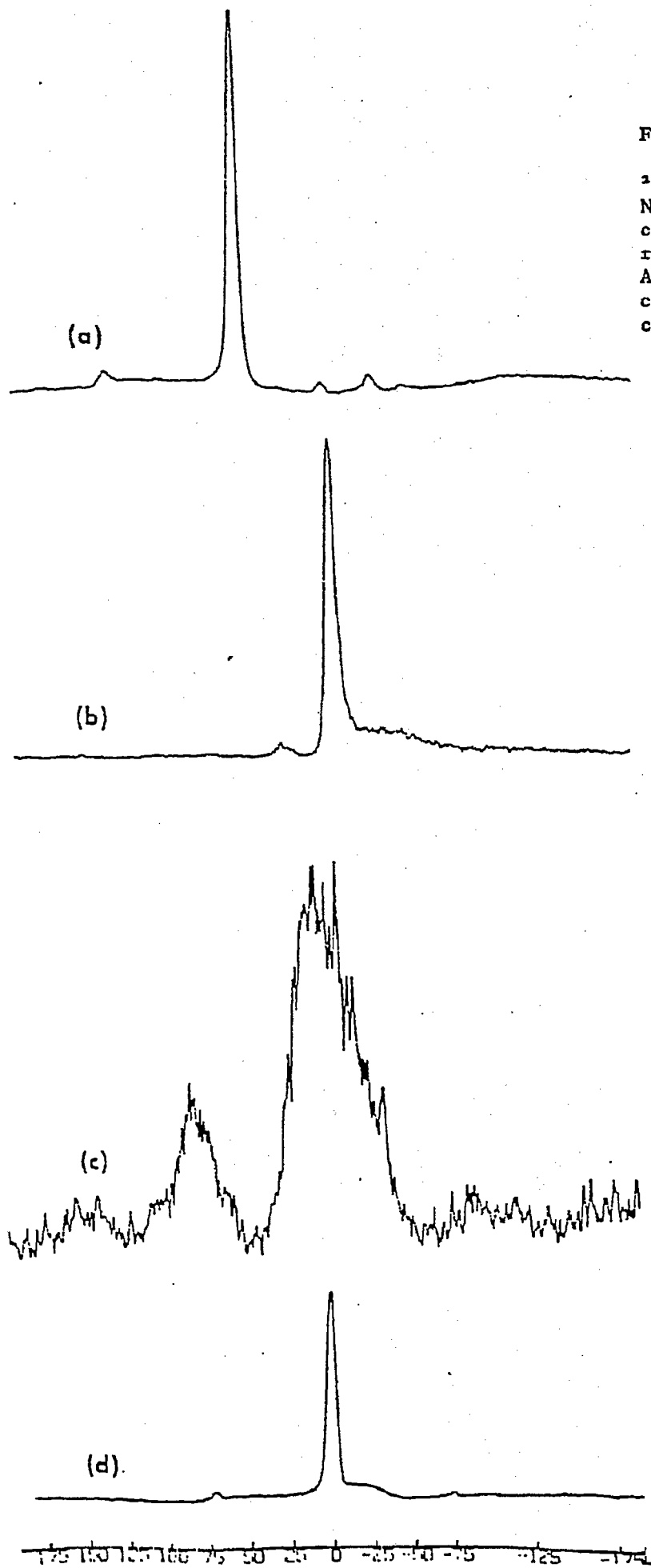
The $\delta\text{-Al}_2\text{O}_3$ is almost devoid of Al_{3+} in tetrahedral sites. What appears to be two kinds of octahedral sites is more likely the result of a large distortion from cubic symmetry and the line shape therefore reflects the strong quadrupole interactions [47]. The $\alpha\text{-Al}_2\text{O}_3$, of course, has only octahedral sites and, except for a somewhat greater width and asymmetry, $\theta\text{-Al}_2\text{O}_3$ cannot easily be distinguished from $\alpha\text{-Al}_2\text{O}_3$ except by its chemical shift (compare a and d of Figure 5).

Figure 6 shows the ^{27}Al NMR spectra of three catalysts prepared by impregnation and calcined at 980K in air. We realize that this calcination temperature exceeds that which is optimum for the precursors to good hydrodesulfurization catalysts. However, it is at this temperature that the sharpest NMR signals were obtained, and these may be related to surface structures which lead to catalyst deactivation. We have used the compound $\text{Al}_2(\text{MoO}_4)_3$, Figure 6d, as a reference because it produces a single sharp NMR resonance, and it may be expected to form when MoO_3 and Al_2O_3 are heated together. The $\text{NiMoP}/\text{Al}_2\text{O}_3$, Figure 6a, was 3.1% NiO, 19.8% 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, Figures 6b and 6c, were 18% MoO_3 and 3.1% NiO, respectively.

A complete X-ray structure of $\text{Al}_2(\text{MoO}_4)_3$ does not appear to have been published, but Coldish [49] 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 [50]. This structure consists of WO_4 tetrahedra and AlO_6 octahedra which extend into an infinite three-dimensional

FIGURE 6

^{27}Al NMR spectra of a) $\text{NiMoP}/\text{Al}_2\text{O}_3$, b) $\text{Mo}/\text{Al}_2\text{O}_3$, c) $\text{Ni}/\text{Al}_2\text{O}_3$ and the reference compound $\text{Al}_2(\text{MoO}_4)_3$. The three catalysts were each calcined in air at 980K.



network by corner sharing. By comparing the NMR chemical shift of $\text{Al}_2(\text{MoO}_4)_3$, Figure 6d, with that of $\alpha\text{-Al}_2\text{O}_3$, Figure 5d, and a large number of aluminates with both tetrahedral and octahedral Al_{3+} coordination, we can unequivocally conclude that 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 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 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}P signal develops in parallel with ^{27}Al , and the chemical shifts of both ^{27}Al and ^{31}P are identical to 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 $\gamma\text{-Al}_2\text{O}_3$. (The ^{27}Al signal of $\gamma\text{-Al}_2\text{O}_3$ underlies that of the surface compounds in both Figures 6a and 6b, but its intensity is so small relative to the surface compounds that it is lost in the noise.) 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 P, 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 AlPO_4 begins to decompose, and at sufficiently high temperatures, all of the Mo_{6+} is converted to $\text{Al}_2(\text{MoO}_4)_3$.

In summary, we emphasize that the observation of the NMR of ^{27}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 [32-40]. 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. However, care must be taken in analyzing the relative amount of such phases based on a simple integration of peak areas until a proper study of peak area and shape as a function of excitation pulse length has been performed.

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