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Studies of the Hydrogen Held by Solids

XXVI. Proton Resonance from Alumina and Molybdena–Alumina Catalysts

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Wide-line NMR techniques have been used to investigate the dehydroxylation of γ-alumina and an 8% molybdena–alumina. Second moments for surface hydroxyl groups were calculated based on the model proposed recently by H. Knözinger and P. Ratnasamy (*Catal. Rev.* 17, 31, 1978). The decrease in the percentage of hydroxyls observed by NMR with increasing temperature of dehydroxylation suggested a strong interaction between the "unobservable" hydroxyls (shown to be present by D_2-exchange measurements) and the ^{27}Al ions exposed at the surface by the removal of water. Restoration of these hydroxyl groups to detection by NMR upon adsorption of D_2O supported this hypothesis. The details of the reduction of the molybdena–alumina catalyst were investigated by studying the nature of the hydrogen species held by this solid. Although new hydroxyl groups were introduced by the reduction (H_I), the fraction detectable by NMR decreased. This was attributed to the introduction of paramagnetic centers by reduction, e.g., Mo^{+5}. Calculation showed, however, that the number contributing to the NMR signal was larger than possible were the paramagnetic centers and surface hydroxyls uniformly distributed over the catalyst surface, suggesting clustering. The nature of the high-temperature reversibly held hydrogen (H_R) was further defined by an isothermal desorption technique, which demonstrated that this species can be removed as H_2 quantitatively only at the reduction temperature. Furthermore, readsorption of H_R was slow. NMR studies showed that the removal of H_R is accompanied by a decrease in the integrated intensity of the NMR line corresponding to the disappearance of a single hydroxyl group per molecule of hydrogen removed. This is in agreement with recent infrared evidence and strongly suggests that formation and removal of H_R is a heterolytic process.

INTRODUCTION

The presence of hydroxyl groups on the surface of alumina and molybdena–alumina catalysts has been demonstrated by various methods (*1–4*). These hydroxyl groups, which are necessary to terminate the lattice, hold the key to the surface chemistry. Since dehydroxylation occurs during activation of the catalysts, models describing their surface chemistry must take this process into account. In the present paper, the recently proposed model of Knözinger and Ratnasamy (*5*) for the alumina surface has been used as a basis for comparison between the theoretically predicted and the actually measured second moments of the NMR lines arising from the surface hydroxyl groups on a γ-Al_2O_3 sample. Moreover, the effects on the hydroxyl signal brought about by the addition of the molybdena layer have been deduced and are presented and discussed. These data bear on the nature of the molybdena layer and, when compared with the proposed models, suggest that the epitaxial monolayer model (*6–9*) cannot be entirely correct. The results suggest that patches of a multilayer molybdena phase (*10, 11*) form which nevertheless retain some of the properties of the bound monolayer (*12*).

New hydroxyl groups (H_I) are introduced on reduction of molybdena–alumina catalysts (*9*); these are bound to the alumina surface and replace those removed when the catalyst is formed (*4*). Another form of

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(adsorbed) hydrogen (H_R) has been described (*9, 12*) but not investigated thoroughly. It is introduced during reduction, but may be removed as H_2 by evacuation at the reduction temperature (~500°C). This is in contrast with the H_I form which cannot. Both volumetric and NMR data are presented herein defining some of the properties of this chemisorbed hydrogen.

Millman *et al.* (*4*) found that the bond between the molybdenum atom and the surface oxygen of the alumina support is attacked during reduction and that H_2O is removed from the sublayer as the reduction proceeds. However, the resulting molybdena species probably must remain bound to the alumina, since reduction below Mo(IV) is difficult and the original catalyst is regenerated easily by reoxidation. The infrared evidence (*4*) suggested that H_R was formed by a heterolytic cleavage of H_2 into an hydroxyl group and another species which was not detectable. This conclusion is supported by the present NMR data.

EXPERIMENTAL

The γ-Al_2O_3 was Ketjen CK-300 which had a surface area of 192 m^2/g (N_2, BET). Its chief impurities were Ca, Cr, Cu, Mg, and Si; fewer than 50 ppm paramagnetic impurities were present and a total impurity content was less than 100 ppm.

The 8% molybdena–alumina catalyst has been the subject of earlier investigations (*4, 9, 12*); it was prepared by the incipient wetness technique using a solution of ammonium paramolybdate. The samples were dried at 120°C for several hours and calcined in air at 550° for 16 hr; these samples were cooled in a desiccator. The surface area of the final catalyst was 185 m^2/g (N_2, BET) and did not change on reduction with H_2 up to 550°C.

The method of reduction has been described in detail elsewhere (*4, 9*). The extent of reduction will be symbolized herein as *e*/Mo. This term represents the average number of electrons by which Mo^{6+} is reduced and may be calculated as

$$e/\mathrm{Mo} = \frac{([\mathrm{O_2}]\ \mathrm{cm^3/g\ cat.})(2.69 \times 10^{19}\ \mathrm{molec/cm^3})(4\ e/\mathrm{O_2\ molec})}{(5.02 \times 10^{20}\ \mathrm{Mo/g\ cat.})} \qquad (1)$$

or

$$e/\mathrm{Mo} = 0.214[\mathrm{O_2}], \qquad (2)$$

where $[O_2]$ is the amount of oxygen needed to reoxidize the catalyst.

Dehydroxylation studies. Samples of catalyst were pretreated in flowing dry O_2 at 500°C overnight and evacuated for at least 2 hr at the same temperature; they were then cooled to room temperature and exposed to the ambient vapor pressure (~20 Torr) of doubly distilled, degassed water for 4–6 hr before a final evacuation at a selected temperture. When reduced catalysts were prepared for study, the reduction was carried out on the pretreated catalyst after the 500°C evacuation (before rehydration). Then, after removal of H_R by evacuation, the sample was isolated, cooled to room temperature, and exposed to H_2O as before. Finally, the sample was evacuated at room temperature until the pressure above the sample was about 5×10^{-5} Torr, before raising the temperature slowly, under continued evacuation, to the desired value. Previous catalytic studies (*13*) had shown that this procedure did not effect reoxidation of the catalyst. Also, both isotope dilution and NMR measurements had revealed (*4*) that evacuation for 11–13 hr at any chosen temperature between room temperature and 500°C was sufficient to allow the catalyst samples to attain a constant residual hydroxyl concentration on the surface.

Volumetric measurement of H_R. The amount of H_2 which could be desorbed from freshly reduced catalysts at the reduction temperature was measured volumetrically using a Sprengle pump which was capable of lowering the pressure above the catalyst to about 5×10^{-5} Torr over relatively long evacuation times and delivering the gas removed back into the volumetric system. The design of the pump is shown in Fig. 1. The error introduced in calibration experiments involving a 24-hr evacuation of an empty 500-ml volume was ≤ 0.04 cm^3, which was insignificant in our measurements. The efficiency of the pump could be increased by lowering the total pressure in the system. This was done by expanding the gas to be measured into a 500-ml volume prior to the evacuation, resulting in an overall residual gas pressure of several Torr. The placement of a liquid-nitrogen trap in the line between the pump and the measuring system assured that only a noncondensable gas was delivered, and subsequent mass spectrometric determinations showed that this was exclusively H_2. Only nominal amounts of H_2O were found in the trap after the evacuation of the catalyst.

NMR measurements. The spectra were determined by using the wide-line NMR attachment to a Varian E-115 spectrometer with the variable frequency oscillator at 35 mHz. A Northern Scientific NS-560 Computer of Average Transients was interfaced to allow accumulation and averaging of spectral data. Modulation corrections to the observed second and fourth moments were calculated from Andrew's treatment (*14*) and all linewidths were corrected for finite modulation using the usual formulary (*15*).

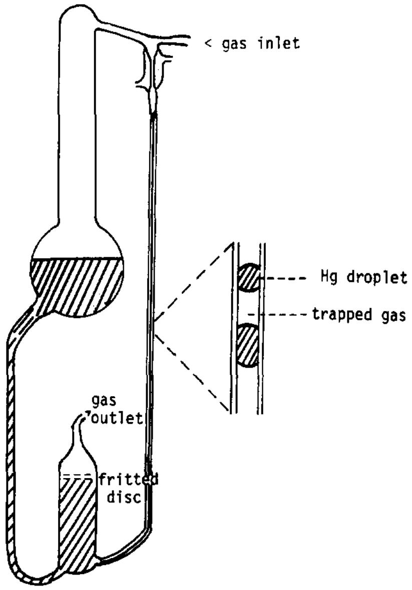


FIG. 1. Design of the Sprengle pump.

Relative spin concentrations were obtained by comparison of the area under the proton NMR line with one of similar width obtained from a 2.017 *M* solution of $MnSO_4 \cdot H_2O$ in 99.2% D_2O. These results were reproducible to within 12% relative error. In every case, at least three separate measurements were made.

NMR measurements were made using 15-mm (o.d.) Pyrex recirculation reactors containing about 5 g of sample and designed to allow sample pretreatment with flowing gases.

RESULTS

Dehydroxylation

Table 1 contains the summary of the data gathered in the dehydroxylation studies of both the pure γ-alumina and the 8% molybdena–alumina catalyst at various extents of reduction. The next to the last column contains the total hydrogen contents measured by D_2 exchange (*4*), and the last column shows the percentage of these hydroxyl groups observable by NMR. In all cases, the number of protons contributing to the NMR signal was significantly less than the number actually present. The possibility of saturation broadening was tested and was found not to occur under the conditions used in these experiments.

Addition of D_2O to samples which had been dehydroxylated at 500°C raised the percentage of the OH groups observed by NMR; this is shown in Table 2. For samples exposed to D_2O vapor at room temperature, 97 and 75% of the protons present on the pure γ-alumina and reduced molybdena–alumina catalysts, respectively, now appeared in the NMR signal. This was a

TABLE 1

NMR Data Taken at Various Degrees of Dehydroxylation for the Alumina and Molybdena–Alumina Catalysts

Sample	Pretreatment temp. (°C)	Linewidth[a] (G)	Second moment (G^2)	OH/cm² × 10^{-14} (NMR)	OH/cm² × 10^{-14} (by D_2)[b]	Fraction observed
γ-Alumina	150	4.4	2.89	8.3	9.7	86
	200	4.5	2.77	7.2	8.3	87
	300	3.3	1.43	4.3	6.4	67
	400	2.6	0.80	2.9	4.9	59
	500	3.1	0.96	2.3	3.6	64
Molybdena–Alumina						
Oxidized	150	3.4	1.87	3.4	3.8	90
	200	3.1	1.30	2.0	2.9	68
	300	2.56	0.83	1.0	1.8	56
e/Mo = 0.8	150	3.7	2.19	3.6	5.7	64
	200	3.1	1.66	2.3	4.0	58
	300	2.7	1.21	1.6	3.1	53
	400	2.45	0.96	0.9	2.5	37
	500	1.9	0.5	0.7	2.0	35
e/Mo = 1.0	150	3.7	2.4	3.8	5.0	76
	200	3.3	1.85	2.3	4.4	52
	300	2.7	1.2	2.0	3.5	57
	400	2.0	0.6	1.2	2.9	41
	500	1.9	—	0.6	2.4	26
e/Mo = 1.3	150	3.6	2.2	3.5	5.0	70
	200	3.2	1.7	2.8	4.4	65
	300	2.3	0.9	1.7	3.5	50
	400	2.2	0.7	1.0	2.9	35
	500	2.0	—	0.5	2.4	22

[a] Corrected for modulation amplitude.

[b] Measured by D_2 exchange (*4*).

considerable increase over the initial values of 64 and 21%.

The theoretical second moments for a fully hydroxylated alumina surface were calculated for the (100), (110), and (111) planes of alumina, based upon the Knözinger–Ratnasamy model (*5*). The results of these calculations are presented in Table 3. The values given show the individual contributions to the theoretical second moment arising from either ^{1}H–^{27}Al or ^{1}H–^{1}H dipolar interactions for each of the five types of hydroxyl group proposed by the model. In this treatment, each crystal face was treated separately.

Characterization of H_R

Using the Sprengle pump, H_R could be measured directly and these values are found to agree with those calculated from mass balances in reduction–reoxidation cycles (*9*, *12*). This comparison is made in Table 4.

The Sprengle pump was also used to measure the amount of hydrogen removed as H_R as the temperature was increased in a stepwise maner. For this series of measurements, the catalyst was reduced at 508°C such that *e*/Mo = 1.4. Then, the sample was isolated and quenched to room temperature. The small amount of gas-phase H_2 remaining in the reactor was removed and measured volumetrically. The temperature was then raised in increments and the sample was pumped until no further hydrogen was evolved. The data are presented in Fig.

TABLE 2

Adsorption of D_2O (99.2%) on Dehydroxylated Catalysts

Experiment	Hydrogen content/cm² × 10^{-14}		
	Exchange	NMR	% H observed
Alumina			
13-hr evacuation at 500°C	3.6	2.3	64
16-hr adsorption of D_2O at 150°C; evac. for 5 min	3.6	2.6	72
16-hr adsorption of D_2O at room temp; evac. for 5 min	3.6	3.5	97
Molybdena–alumina			
13-hr evacuation at 500°C	2.4	0.5	21
16-hr adsorption of D_2O at 150°C; evac. for 5 min	2.4	1.0	42
16-hr adsorption of D_2O at room temp; evac. for 5 min	2.4	~1.8	~75

2. The range of temperatures over which the desorption occurred suggested that a distribution of site strengths exists. After evacuation at 400°C, only about 30% of the total H_R had been removed, and only after evacuation at the reduction temperature was the value calculated from the reoxidation data approached (5.01 vs 5.14 cm³/g).

Attempts to readsorb H_R at the reduction temperature showed that adsorption times the order of 20 hr were necessary to readsorb H_R quantitatively (*4*), which is in marked contrast with the 3 hr necessary to form it during the initial reduction, or the 90 min necessary to remove it by direct evacuation through a liquid-nitrogen trap. Since normal adsorption processes are almost invariably exothermic, this behavior is unusual, i.e., desorption having an activation energy higher than adsorption (by the heat of adsorption) might be expected to be the slower process.

The proton magnetic resonance of the hydroxyl groups contained on the catalyst surface before and after the removal of H_R is shown in Fig. 3. The integrated intensity of the NMR line decreased as H_R was removed; no other resonance lines were observed although others may have been buried under the envelope of the hydroxyl signal or broadened beyond detectability. Nevertheless, Fig. 3 provides strong evidence to link H_R with the surface hydroxyls. The data of Table 5 complete the link; the relationship shows that for each H_R molecule removed, one hydroxyl is lost from the NMR signla. This was in agreement with previously published infrared results (*4*).

DISCUSSION

One objective of research in catalysis is to establish a model for the working catalyst which can be used to provide a framework for the discussion of catalytic results. In the present case this has involved understanding the surface chemistry of the alumina support and the epitaxial molybdena layer formed on it was well as that of the

TABLE 3

A Summary of the Theoretical Second Moment Calculations for a Completely Hydroxylated Alumina Surface, Using the Notation Prescribed by Knötzinger and Ratnasamy (*5*)

Crystal face	Layer	^1H–^{27}Al contribution to $\langle H^2 \rangle$					^1H–^1H contribution	$\langle H^2 \rangle$,G²
		Ia	Ib	IIa	IIb	III		
(111)	A	0.6904	—	0.7901	—	—	4.642	7.690
	B	—	—	—	0.6839	0.8831		
(110)	C	0.5720	—	—	0.6349	—	1.828	3.342
	D	—	0.3074	—	—	—		
(100)	—	—	0.2928	—	—	—	3.401	3.694

TABLE 4

Comparison of Calculated and Measured Values of Hydrogen Reversibly Held

e/Mo	Final pressure (Torr)	H_R (cm^3/g, NTP)	
		Measured	Calculated[a]
1.3	3.4	1.82	1.88
1.3	27	2.79	2.53
1.3	95	3.59	3.20
1.5	160	4.66	4.45
1.5	300	3.99	4.00

[a] References (*9*, *12*).

reduced catalyst. Indeed the approach which has been taken is to deduce the structure of the latter from a knowledge of the former and the changes which occurred on reduction. The present results indicate that certain modifications should be made in existing monolayer models. The data of Table 1 confirmed (*4*) that surface hydroxyl groups are eliminated as the molybdena layer grows onto the surface, i.e., hexavalent molybdena species replace the terminal OH. They also show indirectly that the molybdena must be clustered into islands or patches on the support surface leaving other portions free. The rationale for this will be developed below.

The loading of the present catalyst (~5 × 10^{20} Mo^{+6}/g) was sufficient to cover a major portion of the first epitaxial layer, but to remove only about one-third of the total (~34 × 10^{20}/g) number of surface hydroxyl groups expected to be present when the alumina is immersed in H_2O (assuming each Mo^{+6} group can replace 2 OH (*16*). This can be understood when it is recalled that the addition of two layers are required to terminate the spinel lattice; thus, on some planes hydroxyl groups are bound to the top two underlying layers. The data suggest that the molybdena overgrowth occurred in several layers on a part of the support surface rather than being spread uniformly over the entire surface. Before presenting the evidence for this, however, the NMR data from the surface hydroxyl groups of the alumina support must first be considered and understood.

The data (Table 1) show that not all the hydroxyl groups present on the support or raw catalyst are detectable by NMR. The removal of an OH group from the surface of alumina during dehydroxylation reduces

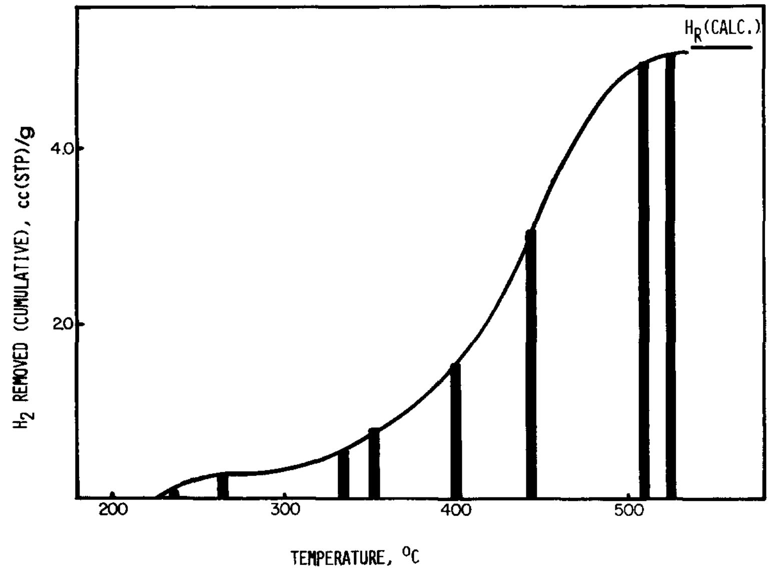


FIG. 2. The H_2 removed (cumulative) versus evacuation temperature as measured with a Sprengle pump.

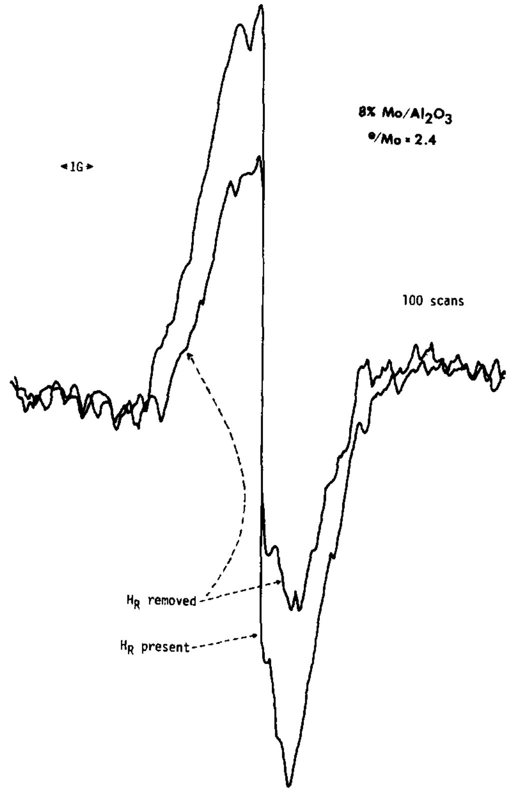


FIG. 3. The NMR line observed by an extensively reduced molybdena–alumina catalyst showing the effect of the removal of H$_R$.

the axial symmetry of the underlying ^{27}Al cation. This in turn will decrease its longitudinal relaxation time (T_1) by allowing relaxation to occur via the interaction of the electric quadrupole moment with the asymmetric field (*19*). In principle any nucleus interacting very strongly with these ^{27}Al cations may subsequently have its T_2 reduced (linewidth increased) such that the resonance signal from the second nucleus is broadened sufficiently to prevent its detection. If the second nucleus is an ^{1}H located on a neighboring hydroxyl group, rehydroxylation of the surface with OD groups should remove the above-mentioned effect and the percentage of the OH groups observable by NMR should increase. This was observed; the data are summarized in Table 2.

Evidence that dehydroxylation of the alumina surface gave rise to new relaxation processes was obtained in a brief NMR study of benzene molecules on the surfaces of aluminas dehydroxylated to various extents. The longitudinal relaxation time, T_1, was measured at −138°C for 0.5 monolayer after evacuation of the alumina at 150° and then at 500°C. In the first instance, where the surface was nearly completely hydroxylated, T_1 was 0.3 sec, while on the surface formed at 500°C it was 0.04 sec, i.e., lower by a factor of 8. Similar results for H$_2$ adsorbed at −195°C have been reported for H$_2$ (*6*). In all cases, corresponding increases in linewidth were obtained as T_1 decreased. Both T_1 and T_2 also decreased with increasing coverage. Whatever the explanation, the facts are that as the strength of the interaction increased (as with decreasing coverage), T_1 and T_2 decreased together. If the linewidth is already fairly broad, as with the surface hydroxyl groups,

TABLE 5

Calculation of the Number of OH Groups Lost When H$_R$ is Removed as Molecular Hydrogen

e/Mo	H$_R$[a]		Decrease in integrated intensity[b]	
	(cm^3/g)	H$_2$/cm^2 × 10^{-14c}	OH/cm^2 × 10^{-14c}	OH/H$_R$ (±0.2)
1.0	5.01	0.75	0.9	1.2
1.3	7.05	1.03	0.8	0.8
1.3	2.49	0.36	0.3	0.8
2.4	2.51	0.36	0.46	1.3

[a] Direct measurement.

[b] By NMR.

[c] Surface area = 185 m^2/g (N$_2$ BET). From Refs. (*9*, *12*).

the additional broadening due to dehydroxylation will render the signal undetectable.

In the present work, the percentage of the OH groups observable by NMR (with respect to those known to be present by exchange measurements (*4*)) increased from 64 to 72% on γ-alumina and from 22 to 42% on a reduced molybdena–alumina catalyst (*e*/Mo = 1.3) when D_2O was added and evacuated at 150°C. The adsorption of D_2O at room temperature led to the observation of nearly all the hydroxyls on the alumina and about 75% of those on the reduced catalyst. These results suggest that the exposed ^{27}Al cations are responsible for the protons "lost" in the NMR measurements on alumina, and for the most part on molybdena–alumina. In this latter case, however, a substantial fraction of the OH groups remain unobservable by NMR even after D_2O addition at room temperature. Presumably this is because some of them are interacting with unpaired electrons on reduced molybdenum centers. Indeed, when viewed in this light it is surprising that the signal intensity is as large as observed. Consider that at least 10% (probably closer to 50%) of the 5×10^{20} Mo/g on the catalyst are present as Mo^{+5} when it has been reduced by 1.0 or 1.3 *e*/Mo. The signal from any OH group within 10 Å of such a center should be broadened beyond detection. Thus, were the Mo^{+5} and OH uniformly distributed over the surface, no signal should be obtained from 158 m^2/g. The surface area of the reduced catalyst was 185 m^2/g; therefore, no signal should have been obtained from 85% of protons present. Thus, the data suggest clustering of OH groups into areas not covered by molybdena, which implies that two or more layers are present on the molybdena-covered portion. These ideas are reinforced when it is recalled that any center carrying an unpaired electron, e.g., Mo^{5+} or Mo^{4+}, should function in the same way.

A plot of experimentally measured values of the second moment of the NMR signal versus the hydroxyl concentration (measured by NMR) is presented in Fig. 4. All the molybdena–alumina catalysts, regardless of extent of reduction, exhibited the same behavior, i.e., the introduction of paramagentic centers by reduction had no observable effect upon the second moment.

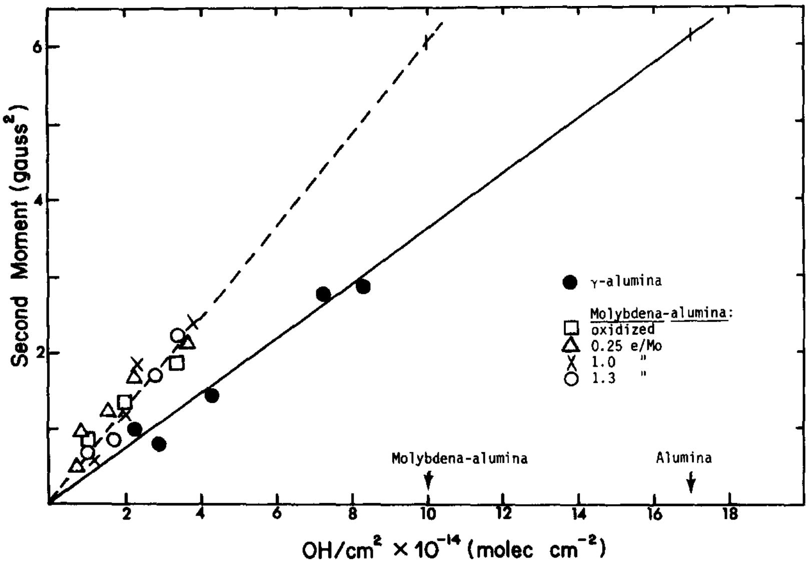
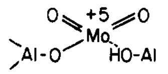


FIG. 4. A plot of the observed second moment versus hydroxyl concentration (measured by NMR). The arrows indicate completely hydroxylated surfaces.

This figure also shows that for the point at which saturation of the surfaces with hydroxyls (indicated for each sample by the arrows in Fig. 4), the same second moment was observed for both the pure and modified alumina catalysts, viz., ~6 G^2. Although the molybdena content was adequate to about cover the entire alumina surface with the first-layer overgrowth, these data indicate that roughly half the exposed surface consists of alumina. This again implies a patch model of the surface whereby the paramolybdate ions introduced remain essentially intact until they are calcinated, and after calcination they cover portions of the surface corresponding roughly to half the available area.

The addition of the molybdena phase to alumina has been shown to have a pronounced effect upon the surface acidity (*9, 18*), in seeming disagreement with the observation that typical alumina hydroxyls are being detected by NMR. However, the enhanced acidity would very likely be attributable to just those hydroxyls which cannot be observed, viz., those located near centers of paramagnetism. Furthermore, hydroxyl groups located on the molybdena layer would exhibit a smaller second moment, due to the relatively weak ^1H–$^{93,95}Mo$ dipolar interaction, but this difference would not be observed in the overall measurement if these were present in small proportion. Moreover, the portion of H_I which has been described (*4*) as



should not appear in the resonance signal and may account for some or all of the missing portion. Thus, the observable hydroxyl groups are probably not "near the action" in terms of surface catalysis.

The reversibly chemisorbed hydrogen, H_R, characterized herein, is of considerable interest. The salient questions are concerned with its nature. What kind of bonding can hold hydrogen on the surface of the catalyst at temperatures up to 600°C? Is it dissociated into equivalent or inequivalent species? And on what kind of sites? The volumetric data show that H_R desorbs as H_2 (not H_2O) over a range of temperatures, but that it can be removed quantitatively only at the reduction temperature, i.e., the temperature at which it was formed. Once removed, it readsorbs very slowly (*4*). This is unusual, since the activation energy for desorption is ordinarily much higher than that for adsorption.

The NMR data given above indicated that one hydroxyl group was removed for about every H_R molecule desorbed from the surface. This suggested that it was heterolytically cleaved upon adsorption to form a hydroxyl group and some other type of species unobservable by NMR; this could be a hydride similar to that observed on ZnO (*17*). Several attempts to observe an infrared band corresponding to a hydride-type species have failed, but this was not conclusive. However, these studies did show that the removal of a molecule of H_R caused the equivalent of one hydroxyl group to disappear from the OH region of the spectrum (*4*). The failure to observe a metal–hydrogen stretch in the infrared does not preclude the existence of such a species, since the band could be dipole broadened or broadened due to a wide distribution of site strengths; such a distribution was suggested by the isothermal desorption data.

The inability of NMR to observe certain types of hydroxyl groups because of fast relaxation effected by paramagnetic centers or the ^{27}Al-quadrupole could account for the missing half of H_R. However, based upon the agreement between the NMR and infrared data, we think it probable that the species H_R is heterolytically cleaved upon adsorption to form only one hydroxyl group per molecule of H_R adsorbed. Furthermore, until other evidence becomes available, the nature of the second species formed must remain the subject of speculation.

In light of this discussion, the relationship of H_R to hydrogenation catalysis remains an intriguing mystery; any consideration of hydrogenation must start with the mechanism by which hydrogen is dissociated and held by the surface. The sluggishness of the readsorption process precludes the identification of H_R as the chemisorbed species required to hydrogenate ethylene around room temperature. It may, on the other hand, function in processes such as hydrodesulfurization which occur under more stringent conditions. Thus, the question remains whether the species responsible for low-temperature hydrogenation is a portion of H_R having a very low activation energy and heat, or whether H_R represents a separate phenomenon.

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