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The Effect of Treatment with Triethylaluminium on the Hydrogenation and Hydrodesulfurization Activity of Molybdenum, Cobalt, and Nickel Sulfide Catalysts

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The activities for hydrogenation of hex-1-ene (1 atm, 573 K) and hydrodesulfurization (hds) of thiophene (1 atm, 673 K) of alumina-supported molybdenum, cobalt, and nickel sulfide catalysts, and a sulfided Co–Mo/γ-Al_2O_3 catalyst have been measured before and after treatment of the catalyst with triethylaluminium ($AlEt_3$). The triethylaluminium treatment (a) increased the hex-1-ene hydrogenation activity of the individual sulfides; (b) decreased the hex-1-ene hydrogenation activity of the sulfided Co–Mo/γ-Al_2O_3; (c) increased the thiophene hds activity of sulfided Mo/γ-Al_2O_3; (d) decreased the thiophene hds activity of the other catalysts and loss of promoting effect of Co on sulfided Mo in the sulfided Co–Mo/γ-Al_2O_3 catalyst. The hydrogenation activities of the catalysts decreased after they had been used for hds. The $AlEt_3$ treatment of the catalysts also caused changes in their electron spin resonance spectra which are attributed to reduction of oxidic Mo(V) to oxidic Mo(III) and sulfided Co(II) to sulfided Co(I). The work provides additional evidence that the active species is a Mo(IV) sulfide promoted by Co(II).

INTRODUCTION

Metal sulfides with catalytic properties for hydrogenation and hydrodesulfurization are those of the first-row transition metals and various heavier metals such as molybdenum and tungsten (*1*). Reactions catalyzed by metal sulfides include hydrogenation of unsaturated and aromatic hydrocarbons, dehydrogenation and isomerization of hydrocarbons, and hydrogenolysis of, for example, C–S bonds as in hydrodesulfurization (*2*). The metal sulfides are generally less active than metals and oxides. However, the development of more active sulfide catalysts might provide alternative catalysts to metals and oxides where, for example, catalyst poisoning by sulfur is a problem, and they might also provide catalysts with selectivities different from those of metals and oxides. When metal oxides and sulfides are used as catalysts in a hydrogen atmosphere active sites are created by surface reduction and there is loss of oxygen and sulfur as H_2O and H_2S.

According to a recent report (*3*) a Ni/Al_2O_3 catalyst may be activated for benzene hydrogenation by reduction with trimethylaluminium. The $AlMe_3$-treated catalyst was more active than one reduced in hydrogen apparently because of more extensive reduction and greater dispersion of the active species. A patent (*4*) claims that the olefin hydrogenation activity of alumina-supported metal sulfides may similarly be greatly enhanced by treatment with triethylaluminium. This observation was interesting in connection with activity–structure relations for sulfide catalysts and as possibly providing a method of preparing highly active sulfide catalysts; we have, therefore, investigated the effect of $AlEt_3$ on the activities of cobalt, nickel, and molybdenum sulfides in the hydrogenation of hex-1-ene and the hydrodesulfurization (hds) of thiophene.

The electron spin resonance (ESR) spec-

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tra of the catalysts were recorded in order to determine whether treatment with triethylaluminium caused the formation or disappearance of paramagnetic species which could be associated with changes in catalytic properties.

EXPERIMENTAL

Catalysts. Alumina-supported sulfides of molybdenum, cobalt, and nickel were prepared by impregnating γ-alumina (Ketjen, hds-base, 35–60 mesh, BET surface area = 204 m^2/g, water pore volume = 0.91 cm^3/g) by the pore-filling method with aqueous solutions of ammonium heptamolybdate, cobalt acetate, and nickel nitrate, followed by drying, heat treatment (623–673 K, 3 h, N_2), and sulfiding (10% v/v H_2S in H_2, 50 cm^3/min, 623 K, 15 h; H_2, 673 K, 1 h) in the catalytic reactor. A mixed (Co + Mo) sulfide catalyst was prepared by sulfiding a technical Co–Mo–O/γ-Al_2O_3 catalyst (Ketjen, 35–60 mesh). The concentration of the active metals in the oxide forms of the catalysts were: Mo/Al_2O_3, Mo 7.3; Co/Al_2O_3, Co 3.2; Ni/Al_2O_3, Ni 5.0; Co–Mo/Al_2O_3, Co 3.0, Mo 8.0 wt%. Mo, Co, and Ni catalysts were prepared using Ketjen γ-Al_2O_3 support and subjected to the same thermal treatment as the Ketjen Co–Mo catalyst. Our catalysts and the Ketjen catalyst were subjected to the same pretreatment and sulfiding procedure.

Treatment with triethylaluminium. A solution of $AlEt_3$ (ca. 1 cm^3, 20% in hexane) was injected into the reactor through a septum cap onto the sulfided catalyst (0.25 g as oxide) under N_2 at room temperature (ca. 293 K). Excess of $AlEt_3$ was drained off after 0.5 h contact and the catalyst was further stripped under N_2 (4 h, 673 K).

Apparatus. A conventional fixed-bed glass microreactor was used. The equipment had facilities for allowing nitrogen, hydrogen, or the sulfiding gas mixture to flow over the catalyst and for pulse and flow experiment at 1 atm and up to 773 K. Temperature control was ±1.0 K.

Hydrogenation of hex-1-ene. Pulses (5 μl) of hex-1-ene (Puriss, Koch-Light) were injected through a septum cap into hydrogen (40 cm^3/min, 1 atm) flowing over the catalysts (0.25 g) at 573 K. The product, a mixture of hexane and hex-1-ene, was analyzed with a flame ionization type GLC (Perkin Elmer F 33, 4.7 m column of bis-2-methoxyethyladipate on Chromosorb P, 30%) fitted with a gas sampling valve and connected to a chart-recorder via a computing integrator (Model 308, Laboratory Data Control).

Hydrodesulfurization of thiophene. Thiophene (8 vol%) introduced into flowing hydrogen (40 cm^3/min, 1 atm) via a saturator immersed in a water bath at 300 K with temperature control ±0.01 K, was passed over the catalysts (0.25 g as oxide) at 673 K. Total product analysis was carried out as in the hex-1-ene hydrogenation experiments.

ESR measurements. The ESR spectra were obtained at room temperature (ca. 293 K) on a Varian E-3 X-band spectrometer operating at 9.507 GHz. ESR measurements were restricted to room temperature where paramagnetic cobalt(II) will not give a spectrum owing to fast spin-lattice relaxation. The magnetic field was modulated at 100 kHz and the first derivative of the spectrum was recorded. α,α-Diphenyl β-picrylhydrazyl was used for calibration of *g* values. In order to avoid contact of catalyst samples with air all operations (thermal treatment of the catalysts under nitrogen, sulfiding, treatment with triethylaluminum, and with thiophene with conditions and procedures the same as in the catalytic experiments) were conducted in a specially designed microreactor which could also be used as an ESR tube. The microreactor was similar to the one used by Konings *et al.* (5) but it had additional facilities for injecting $AlEt_3$ through a septum cap onto the sample. The reactor-cum-ESR tube was filled with the sample (0.25 g of catalyst in the oxide form) to a height equal to the depth of the resonant cavity.

RESULTS AND DISCUSSION

Neither fresh nor $AlEt_3$-treated γ-Al_2O_3 (the catalyst support) was active in hex-1-ene hydrogenation. Also there was no hydrogenation when hex-1-ene was injected into helium flowing over the untreated and $AlEt_3$-treated catalysts. Thus the catalysts are not a source of hydrogen.

Catalytic Properties and the Effect of Triethylaluminium

Conversion and product distribution are given in Table 1 for hex-1-ene hydrogenation in pulse experiments (first pulse) and for thiophene hds in flow experiments (steady state, attained after ca. 2 h). The data were reproducible to within ±2% and the estimated error was within ±5%. The catalytic behavior of the sulfides and the effect of $AlEt_3$ treatment may be summarized as follows:

(a) Conversion of hex-1-ene to hexane over alumina-supported molybdenum, cobalt, and nickel sulfides was indeed greatly enhanced by treatment of the sulfide catalysts with $AlEt_3$, a result in accordance with the patent claim (*4*). The order of increasing effect as shown by the ratios of the hydrogenation after and before treatment with $AlEt_3$ was Mo–S $\ll$ Ni–S $<$ Co–S. Here *M*–S (*M* = Mo, Co, or Ni) represents a sulfided and reduced oxide catalyst and this notation will be used for all the sulfided samples in the following text. However, the hydrogenation activity of the Co–Mo–S/γ-Al_2O_3 was decreased by treatment with $AlEt_3$. $AlEt_3$ probably destroys the high dispersion in MoS_2 crystallites (*6*) and also it is likely that reduction of Mo ions and/or blocking of active sites takes place.

(b) The activating effect of $AlEt_3$ found in the hydrogenation experiments did not persist after the catalysts were exposed to thiophene. The order of decrease in activity (as deduced from the ratio of the activities after and before exposure to thiophene) was as follows: for the untreated catalysts, Ni–S $<$ Mo–S $<$ Co–S; for the $AlEt_3$-treated catalysts, Ni–S $<$ Mo–S $<$ Co–S. In each case the loss in activity for the untreated catalyst is slower than the $AlEt_3$-treated ones. We conclude that any new or additional hydrogenation sites created by treatment of the

TABLE 1

Hydrogenation of Hex-1-ene and Hydrosulfurization of Thiophene over Molybdenum, Cobalt, and Nickel Sulfide Catalysts before and after Treatment with Triethylaluminium

Catalyst	Hex-1-ene hydrogenation[a] 10^2 (conversion to hexane)		Thiophene hds[b,c]			
	Before hds	After hds	10^2 (conversion to C_4-hydrocarbons)	$10^2(B/\Sigma C_4)$	B2/B1	T-B2/C-B2
Mo–S/Al_2O_3	29.0	7.72	4.67	7.07	2.38	1.09
+ $AlEt_3$	98.3	12.2	9.15	12.2	3.00	1.85
Co–S/Al_2O_3	6.63	1.18	2.55	1.56	1.47	2.19
+ $AlEt_3$	89.0	0.95	1.64	1.20	1.42	1.38
Ni–S/Al_2O_3	1.49	1.66	2.69	1.12	2.33	2.38
+ $AlEt_3$	16.3	2.63	1.39	1.40	2.11	2.44
Co–Mo–S/Al_2O_3	58.9	14.1	19.9	12.0	3.19	2.16
+ $AlEt_3$	30.0	11.1	11.6	9.09	3.18	2.00

[a] Pulse experiments, 573 K.

[b] Flow experiments, 673 K, >2 h on stream.

[c] Hydrocarbons: butane (B), but-1-ene (B1), total but-2-ene (B2), *trans* but-2-ene (T-B2), and *cis* but-2-ene (C-B2).

individual sulfides with $AlEt_3$ are strongly and almost completely poisoned as a result of exposure to thiophene in the hds reaction. The Co–Mo–S catalyst whose hydrogenation activity decreases due to $AlEt_3$ treatment, unlike the single metal sulfides, also becomes deactivated as a result of exposure to thiophene. The activity of $AlEt_3$-treated Co–Mo–S seems to remain lower than that of the untreated catalyst even after the catalysts have been exposed to thiophene vapor.

We reach the same conclusion from considering the proportion of butane in the products of thiophene hds. The ratio butane/C_4-hydrocarbons (or butane/butene) has often been considered as a measure of the hydrogenation selectivity during hds (assuming that the butane is formed by hydrogenation of butene produced in thiophene hds). Our results show that the effect of $AlEt_3$ on the butane/C_4 ratio is similar to its effect on hex-1-ene hydrogenation after hds. The relative extents of hydrogenation before and after $AlEt_3$ treatment of the catalysts are similar both for hex-1-ene hydrogenation and butane formation. For catalysts exposed to thiophene $AlEt_3$ does not greatly increase the extent of hydrogenation and for the Co–S and Co–Mo–S catalysts actually decreases the hydrogenation. Therefore, the activating effect of $AlEt_3$ did not persist after the catalysts had been exposed to thiophene; any new sites created by $AlEt_3$ were poisoned.

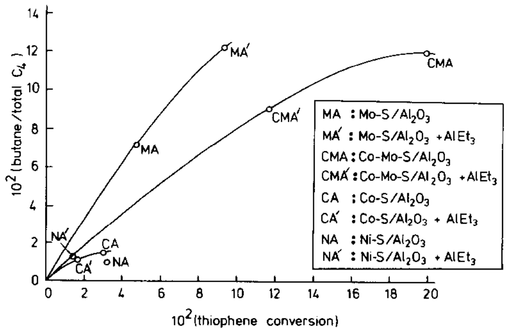

FIG. 1. Effect of cobalt on butane formation during hydrodesulfurization (673 K, 1 atm) of thiophene over metal sulfide catalysts.

(c) Conversion of thiophene (i.e., the hds activity) was increased almost twofold by $AlEt_3$ treatment of the Mo–S/γ-Al_2O_3 catalyst but the hds activity of the other catalysts, including the Co–Mo–S/γ-Al_2O_3 catalyst, was actually decreased by $AlEt_3$. The isomerization of the catalysts (ratio of but-2-ene to but-1-ene and *trans* but-2-ene to *cis* but-2-ene) was hardly affected by the $AlEt_3$ treatment.

The Effect of Cobalt on the Catalytic Properties

The proportion of butane in the products at a given thiophene conversion has been regarded as an indication of the selectivity of the catalyst for hydrogenation. The relationship is usually expressed as a plot of butane/total-C_4 vs thiophene conversion and we show a plot of our results in Fig. 1. Our results provide a comparison of catalysts with similar compositions. We see that the line for the cobalt catalysts is below that for the Mo-only catalysts. Thus the effect of cobalt is to suppress butane formation and promote thiophene conversion. The cobalt-containing catalysts are the more selective toward desulfurization. This is in agreement with the results reported and reviewed (*7*) by previous workers. Figure 1 also brings out the different effect of $AlEt_3$ on the Mo and Co–Mo catalysts. Whereas $AlEt_3$ promotes desulfurization and butane formation over Mo–S/Al_2O_3, $AlEt_3$ decreases both over Co–Mo–S/Al_2O_3. The decrease of desulfurization is greater than the decrease of butane formation. Thus $AlEt_3$ renders the Co–Mo–S/Al_2O_3 catalyst less selective toward desulfurization.

ESR Spectra

Spectra and *g*-values (determined at the turning point) are shown in Figs. 2 and 3.

The MoO_3/Al_2O_3 catalysts which were calcined under nitrogen at 673 K (Fig. 2a) gave two signals: $g = 1.93$ (strong) and $g = 2.00$ (very weak). When the catalyst was

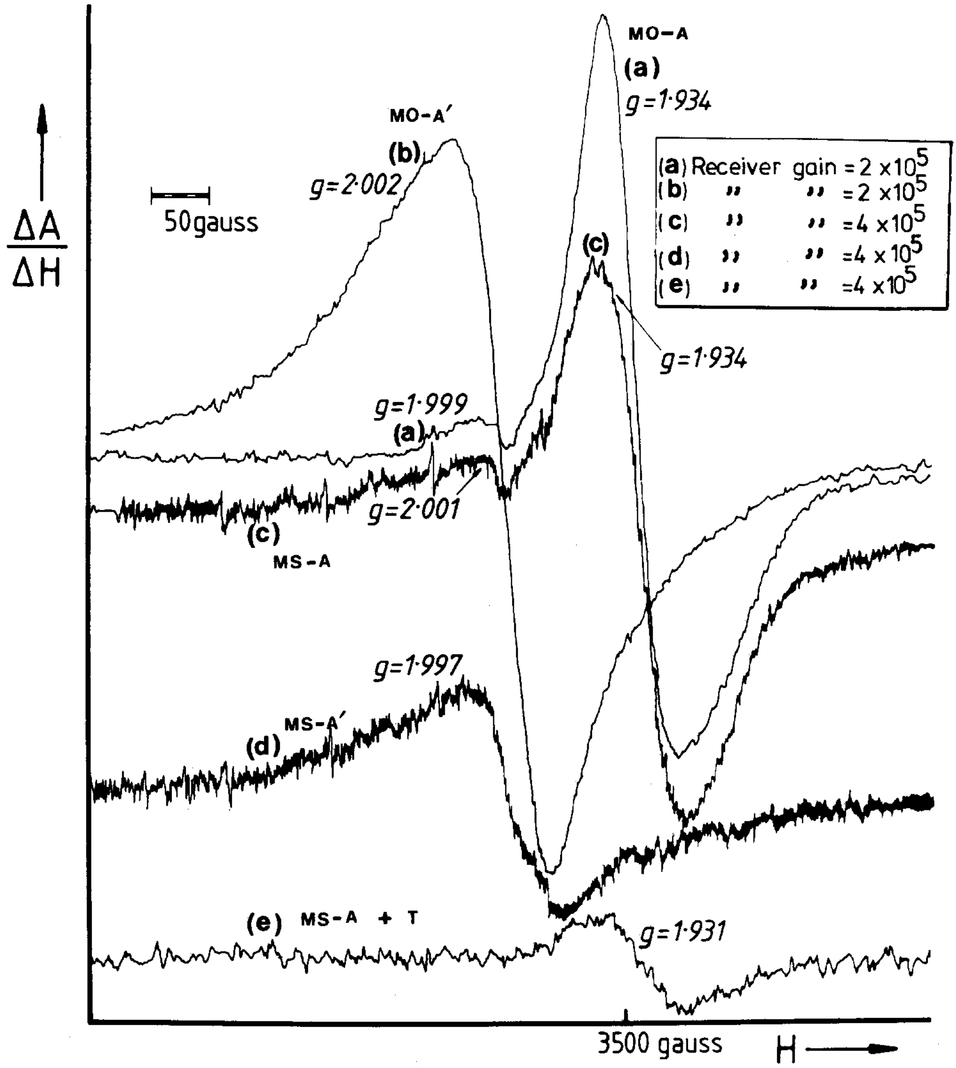

FIG. 2. Room temperature X-band ESR spectra: (a) Mo–O/Al_2O_3; (b) Mo–O/Al_2O_3 + $AlEt_3$; (c) Mo–S/Al_2O_3; (d) Mo–S/Al_2O_3 + $AlEt_3$; (e) Mo–S/Al_2O_3 used for hds of thiophene for 20 min.

treated with $AlEt_3$ the $g = 1.93$ signal disappeared and the $g = 2.00$ signal became much stronger (Fig. 2b). Both signals disappeared when the catalyst was exposed to or heated in air. We assign both signals to reduced oxomolybdenum species. The $g = 1.93$ signal has been observed before (*8*) and assigned to Mo(V) in tetrahedral coordination by oxide ions. The fact that the $g = 2.00$ signal becomes very intense after the $AlEt_3$ treatment suggests that it arises from a further stage of reduction, possibly a Mo(III)-oxo species. The higher *g*-value is consistent with Mo(III) (*9*).

The spectrum of Co–Mo–S/γ-Al_2O_3 (i.e., sulfided Co–Mo–O/γ-Al_2O_3) showed (Fig. 3a) a very intense signal at $g = 1.94$ and a very weak signal at $g = 2.00$. The $g = 1.94$ signal, which we assign as before to a tetrahedral oxoMo(V) species, is more intense than the corresponding signal in the MoO_3/Al_2O_3 and Mo–S/Al_2O_3 catalysts. Thus one effect of cobalt is to increase the concentration of oxomolybdenum(V) [either by pro-

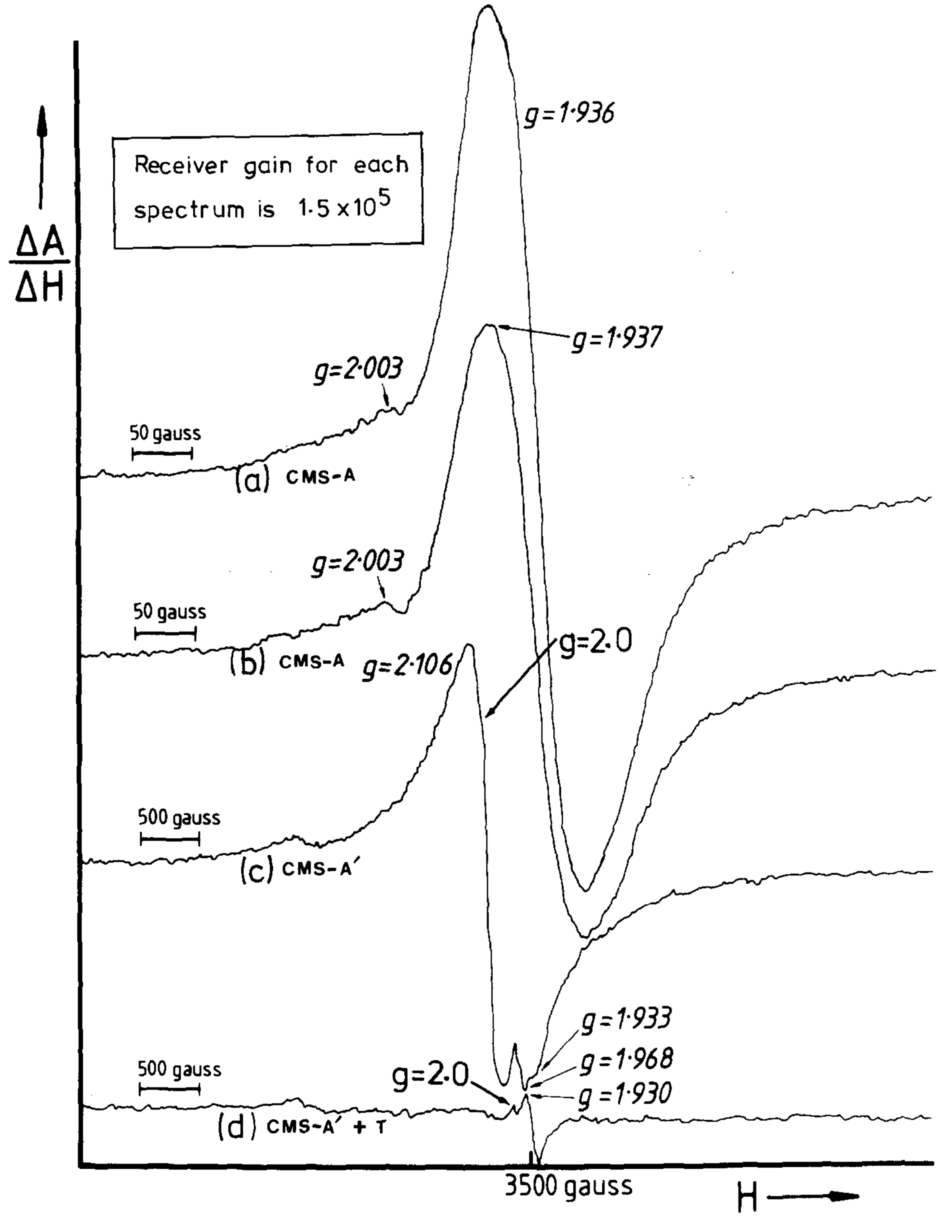

FIG. 3. Room temperature X-band ESR spectra: (a) Co–Mo–S/Al_2O_3 obtained after sulfidation of Co–Mo–O/Al_2O_3 for 0.5 h; (b) Co–Mo–S/Al_2O_3 obtained after sulfidation of Co–Mo–O/Al_2O_3 for 15 h; (c) Co–Mo–S/Al_2O_3(Co–Mo–O, sulfided for 15 h) + $AlEt_3$; (d) after the use of (c) for hds of thiophene for 20 min.

moting formation of Mo(V) by reduction of Mo(VI) or by stabilizing Mo(V) against reduction to MoS_2]. No ESR signal was obtained from CoO/γ-Al_2O_3 and Co–S/γ-Al_2O_3.

We now describe the effect of the $AlEt_3$ treatment on the ESR spectra of the various catalysts. Treatment of MoO_3/Al_2O_3 with $AlEt_3$ caused the intensity of the $g = 2.00$ signal greatly to increase and the $g = 1.93$ signal to disappear (Figs. 2a and b). If the $g = 2.00$ signal is correctly assigned to Mo(III), then $AlEt_3$ reduces oxoMo(V) [and presumably oxoMo(VI)] to oxoMo(III) [and possibly also to oxoMo(IV) which would not be detected by ESR].

When Mo–S/Al_2O_3 was treated with $AlEt_3$ the $g = 1.93$ signal disappeared and a signal at $g = 2.00$ appeared (Figs. 2c and d). The $g = 2.00$ signal was less intense than for MoO_3/Al_2O_3 treated with $AlEt_3$. There now arises a problem of assignment since we are concerned with the sulfided catalysts which may still, of course, contain some oxomolybdenum species. The signal with $g = 1.995$ observed for bulk and supported MoS_2 catalysts has been assigned (*5*) to a surface Mo(III)–S species. It is unlikely that Mo(III)–S and Mo(III)–O species would have precisely the same *g*-values and therefore we consider that the $g = 2.00$ signal arises from a Mo(III)–O species.

Treatment of Co–Mo–S/Al_2O_3 with $AlEt_3$ gave a spectrum (Fig. 3c) with a split signal with *g*-values of 1.93 [assigned to Mo(V), as before] and 2.11. The spectrum is similar in appearance and *g*-value to the spectrum observed (Fig. 7 in Ref. (*10*)] ($g = 2.16$) when a sulfided Co–Mo/Al_2O_3 catalyst was reduced with hydrogen. The $g = 2.16$ signal was assigned to a low spin Co(III)–S or Co(I)–S species. Since our $g = 2.11$ signal was produced by reaction with $AlEt_3$ (a reducing agent) we consider that it is due to Co(I)–S. This is confirmed from our experiment with $AlEt_3$-treated Co–S/γ-Al_2O_3 which showed an ESR signal with $g = 2.11$ (see Fig. 4) while $AlEt_3$-treated Co–O/γ-Al_2O_3 did not show any signal. Since $AlEt_3$ treatment of the Mo/Al_2O_3 catalysts produces a $g = 2.11$ Mo(III) signal we might have expected such a signal for the $AlEt_3$-treated Co–Mo/$AlEt_3$ catalysts. We observe a slight shoulder at $g = 2.00$ but were unable to resolve it from the intense $g = 2.11$ signal.

We now describe the effect of exposure to thiophene on the spectra of the sulfided catalysts. For Mo–S/Al_2O_3 thiophene caused the $g = 1.93$ signal, although still observed, to decrease in intensity (Fig. 2e). Thiophene had no effect on the spectrum of Mo–S/Al_2O_3 treated with $AlEt_3$; the strong signal at $g = 2.00$ remained. However, the cobalt-containing samples behaved in an opposite manner. The spectrum of Co–Mo–S/Al_2O_3 was not affected by thiophene (the $g = 1.94$ peak remained), but for $AlEt_3$-treated Co–Mo–S/Al_2O_3 thiophene caused disappearance of the $g = 2.11$ signal and weak $g = 1.93$ and $g = 2.00$ signals remained. Thus thiophene had little, if any, effect on the Mo(III)–O [or possibly Mo(III)–S] species ($g = 2.00$), caused the signal ($g = 2.11$) of the Co(I)–S species to disappear and caused a decrease of the Mo(V)–O signal ($g = 1.93$) in those catalysts which did not contain cobalt. The intensity of the Mo(V)–O signal is hardly changed by thiophene when in the cobalt-containing catalysts. So cobalt stabilizes the Mo(V)–O species even during the hds reaction. Exposure of $AlEt_3$-treated Co–S/γ-Al_2O_3 to thiophene vapor (at 673 K) resulted in the disappearance of the $g = 2.11$ peak as has been observed in the case of $AlEt_3$-treated Co–Mo–S/γ-Al_2O_3.

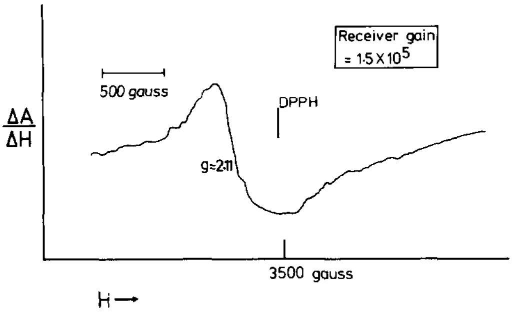

FIG. 4. Room temperature X-band ESR spectrum of $AlEt_3$-treated Co–S/Al_2O_3.

We now attempt to relate changes in the catalytic properties and in the ESR spectra of the catalysts.

The most active hex-1-ene hydrogenation catalyst (98% conversion) was Mo–S/Al_2O_3 treated with $AlEt_3$. This was also the only sulfided catalyst with a strong $g = 2.00$ signal. However, we cannot attribute all of the hydrogenation activity to the species [Mo(III)–O or Mo(III)–S] giving rise to this signal since the Co–Mo–S/Al_2O_3 catalyst for which the $g = 2.00$ signal was very weak was also a good hydrogenation catalyst (59% conversion of hex-1-ene). Thus formation of the $g = 2.00$ species may enhance the hydrogenation activity but this species is not the sole source of hydrogenation activity. Also the presence of the $g = 1.93$ signal does not correlate with the high hydrogenation activity. Therefore, it may be suggested that the olefin hydrogenation activity is not associated solely with a paramagnetic Mo species (Mo^{5+} or Mo^{3+}). This result is in agreement with the work of Voorhoeve and Stuiver (*11*) who showed that the cyclohexene hydrogenation activity of WS_2 does not correlate with a W^{3+} ESR signal (which, in fact, correlated with benzene hydrogenation activity). So it is likely that olefin hydrogenation is associated primarily with diamagnetic centers such as exposed Mo^{4+} in the edge plane of MoS_2 crystallites in the sulfided catalysts (just as for W^{4+} in WS_2). We reach the same conclusion by considering the effect of thiophene on the hydrogenation activity. After exposure to thiophene all of the catalysts, whether treated with $AlEt_3$ or not, had roughly the same hydrogenation activity (10–14%). Thus any new hydrogenation sites created by $AlEt_3$ are strongly poisoned by thiophene. Also any increase of olefin hydrogenation activity associated with the reduced cobalt species ($g = 2.11$) was strongly poisoned by thiophene. The appearance of the $g = 2.11$ signal for Co–Mo–S/Al_2O_3 + $AlEt_3$ was accompanied by a decrease of hydrogenation activity suggesting that the Co(I)–S is not a major hydrogenation catalyst.

With regard to desulfurization, $AlEt_3$ caused an increase of activity of the Mo–S/Al_2O_3 catalyst and a decrease for the Co-promoted catalyst. The increase of activity was accompanied by an increase of Mo(III) ($g = 2.00$) and a decrease of Mo(V) ($g = 1.93$). The Co–Mo–S/Al_2O_3 catalyst had the highest hds activity and the strongest Mo(V) signal ($g = 1.94$). Although some earlier work (*5*, *12–14*) has demonstrated an apparent correlation between Mo(V) and hds activity there is disagreement about the role of Mo(V) (if any) in hds. The $AlEt_3$-treated Mo–S/Al_2O_3 catalyst, which did not show a Mo(V) signal, is active in hds and so the presence of Mo(V) is not required for activity. We would regard Mo(V) as a precursor of the active species. An outstanding result was the loss of the effect of Co(II) as a promoter in Co–Mo–S/Al_2O_3 catalyst when it was treated with $AlEt_3$. This is evidently a consequence of reduction of Co(II) to Co(I) ($g = 2.11$) and probably also Mo(V) directly to Mo(III) (decrease of $g = 1.94$ and increase of $g = 2.11$). If, as is generally accepted, a Mo(IV) sulfide (bulk or monolayer) is the active Mo species in hds then any direct reduction of Mo(V) to Mo(III) would be deleterious. Our results support the view that the active species is a Mo(IV) sulfide promoted by Co(II).

CONCLUSIONS

Our object was to determine if, and to what extent, sulfide catalysts could be activated by treatment with triethylaluminium. In the hydrogenation of hex-1-ene, triethylaluminium increased the activity of Mo–S/Al_2O_3, Co–S/Al_2O_3, and Ni–S/Al_2O_3 (i.e., sulfided MoO_3, CoO and NiO on γ-alumina) but caused a decrease of activity of a Co–Mo–S/Al_2O_3 (i.e., sulfided CoO–MoO_3/γ-Al_2O_3) catalyst. In hydrodesulfurization of thiophene, triethylaluminium increased the activity of Mo–S/Al_2O_3 but caused a decrease of activity of the other catalysts and loss of the promoting effect of Co(II) in the Co–Mo–S/Al_2O_3 catalyst. From changes in the ESR spectra of the catalysts, it appeared that triethylaluminium reduced molybdenum in the catalyst to Mo(III)–O or Mo(III)–S species and formation of these species could account for increased hydrogenation activity of the Mo–S/Al_2O_3 catalyst, but olefin hydrogenation activity was not associated solely with a paramagnetic Mo species. Formation of Co(I) species through reduction of Co(II) by triethylaluminium is one possible reason for the loss of activity in these catalysts in both hydrogenation and hds. The increase of hds activity of the Mo–S/Al_2O_3 catalyst after treatment with $AlEt_3$ may be associated with increased MoS_2 as a result of reduction of Mo(V) and possibly also formation of a Mo(III)–S species. Our results generally support the view that the active species in hds catalysts is a Mo(IV) sulfide promoted by Co(II). Treatment of a Co–Mo/Al_2O_3 catalyst with $AlEt_3$ reduced Co(II) to Co(I) and also Mo(V) to Mo(III) instead of Mo(IV) and so was detrimental rather than beneficial.

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