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ISOTHERMAL GRAVIMETRY AND MAGNETIC PROPERTIES OF $CoO–MoO_3–\gamma Al_2O_3$ CATALYSTS

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ABSTRACT

Isothermal gravimetry and magnetic susceptibility of MoO_3, $Mo–Al_2O_3$, $Co–Al_2O_3$ and $Co–Mo–Al_2O_3$ with/without Na^+ ions have been studied in order to investigate the reducibility of the systems in H_2, H_2–hydrocarbons and H_2–hydrocarbon–thiophene. These studies have evidenced the formation of metallic cobalt during reduction of cobalt–moly catalysts containing Na^+ ions in the Al_2O_3 support. This metallic cobalt accelerates the reduction of supported MoO_3. However, in the absence of sodium, cobalt exerts an inhibitory influence on the reduction of $Mo–Al_2O_3$. The inhibition is caused mainly due to retention of the water evolved during the process by well-dispersed Co^{2+} ions which are incapable of undergoing reduction. The presence of sulfur also helps in suppressing the reduction to cobalt metal.

INTRODUCTION

In recent years, extensive studies have been reported on the nature of the cobalt and molybdenum species in hydrodesulfurisation catalysts[1-6]. However, the influence of the structural features of the support on the formation of such species has not been thoroughly studied. In the present communication, isothermal thermogravimetric analysis of a number of cobalt–moly catalysts ($Co–Mo–Al_2O_3$) prepared by varying modes of impregnation of the Co and Mo salts on γ-alumina with or without Na^+ ions, have been carried out in order to study the reducibility (in hydrogen) of the systems.

Magnetic susceptibility measurements have also been used to study the presence of metallic cobalt in the $Co–Mo–Al_2O_3$ catalysts under reduction conditions only in the presence of sodium. For this purpose, samples of $Co–Mo–Al_2O_3$ catalysts with and without sodium have been reduced at various temperatures in H_2, $H–_2$ hydrocarbon, H_2–hydrocarbon–thiophene atmospheres.

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It has already been reported[6] that cobalt, present in the subsurface layers of γ-alumina prevents the phase transformation and sintering of the support. This process would have otherwise been accelerated by MoO_3, especially during the calcination of the oxide prior to sulfidation. Now, the influence of the sodium ions of the support on the nature of the active cobalt species formed on the oxide precursor is established on the basis of reducibility of the system.

EXPERIMENTAL

Sample A was prepared by calcining Boehmite at 550°C for 24 h in air and was found to be pure γ-alumina. Sample B was obtained from A and contained 260 ppm of sodium ions by weight. Samples C and D were prepared by impregnation of ammonium paramolybdate on samples A and B, respectively. These samples contained 12.5% of MoO_3 by weight. Samples E and F were obtained by impregnating cobalt nitrate on A and B, respectively and contained 2% CoO, by weight. In the preparation of samples G and H both the ammonium paramolybdate and cobalt nitrate solutions were impregnated simultaneously on the supports A and B, respectively. These samples consisted of 2.0% CoO and 12.5% MoO_3 by weight. In the preparation of sample I, the support B was impregnated with the cobalt nitrate solution. The ammonium paramolybdate solution was then impregnated on the resulting material. This mode of impregnation was reversed while preparing sample J. Samples I and J contained 12.5 and 2.0% by weight of MoO_3 and CoO, respectively.

Samples B–J were dried at 110°C (24 h) and calcined in air at 550°C for 6 h before use. Sample K (pure MoO_3) was obtained by decomposition of ammonium paramolybdate at 500°C in air for 16 h. Sample L was pure Co_3O_4 prepared by calcining cobaltous carbonate at 500°C in air for 12 h.

A Fisher TG apparatus (1 mg per mV full scale deflection) was used to study the isothermal reduction. The procedure used was as follows: Approximately 30 mg of the sample was loaded in the TG bucket. Then dry He–N_2 mixture (150 ml (STP)/min) was passed into the apparatus and the sample was subjected to heating and maintained at 110°C till no further weight loss was marked. The sample was again heated within the temperature range 490–550°C and maintained constant at this temperature for about 2 h. The He–N_2 mixture was then disconnected and H_2 passed in (150 ml/STP/min). The weight-changes of the sample were noted after the 5th min of H_2 entry.

Magnetic susceptibilities of powdered samples were determined at 305 K on a Andhra Scientific, India, Electro magnet with Gouy Balance System calibrated with nickel chloride solutions[7]

RESULTS

The reduction studies could not be carried out below 490°C because water formed in the reduction was readsorbed on the surface of the sample resulting in lack of the reproducibility of the data. Therefore, the range 490–550 °C was selected for the reduction experiments. The equation used for determining the reducibility was as follows:

$$\alpha \text{ (reducibility)} = \frac{W_1 - W_t}{\Delta W}$$

where W_1 is the initial weight

W_t is the weight at time t

and ΔW is the calculated weight-loss for a particular reduction course

ΔW was the calculated weight-loss for the following processes of reduction:

(1) For Mo–Al_2O_3 and Mo–Al_2O_3–Na: $MoO_3 + H_2 \rightarrow MoO_2 + H_2O \quad (\alpha_1)$

(2) For Co–Al_2O_3 and Co–Al_2O_3–Na: $Co_3O_4 + 4H_2 \rightarrow 3Co + 4H_2O \quad (\alpha_2)$

(3) For Co–Mo–Al_2O_3 and Co–Mo–Al_2O_3–Na: $Co_3O_4 \cdot MoO_3 + 5H_2 \rightarrow 3Co + MoO_2 + 5H_2O (\alpha_3)$

Where α_1, α_2 and α_3 are the corresponding reducibilities.

Reduction of Mo–Al_2O_3 and Mo–Al_2O_3–Na

The results of isothermal gravimetry of the Mo–Al_2O_3 with/without Na^+ ions are shown in the Fig. 2A. At the reduction temperature, blank experiments were first carried out to see whether Al_2O_3 or Al_2O_3–Na undergoes any weight loss when the carrier gas was changed for He–N_2 to H_2. However, the weight loss observed was very small and was used as a 'correction factor' in all the cases.

MoO_3 was reduced at 490, 510, 530, 550 °C, respectively and α_1 values were calculated. The plot of α_1 vs. t is shown in Fig. 1. It was observed that the reduction of MoO_3 continued even after 4 h.

Mo–Al_2O_3 and Mo–Al_2O_3–Na samples were reduced at the above temperatures and are shown in Fig. 2. The following observations were noted:

(1) Period of complete reduction of these two samples is more than that of MoO_3.

(2) Initial rate of reduction of Mo–Al_2O_3 and Mo–Al_2O_3–Na is more than that of MoO_3 whereas the final level of reduction is much higher for MoO_3.

(3) The final level of reduction of Mo–Al_2O_3 is inhibited by Al_2O_3 in agreement with the observations of Sondag et al.[8].

Reduction of Co–Al_2O_3 and Co–Al_2O_3–Na

These results are shown in Fig. 2B. The Co present in these samples are in the form of Co_3O_4 and it was seen that Co_3O_4 underwent complete reduction to the metallic state in about 12 min. The reducibility of Co–Al_2O_3–Na was found to be

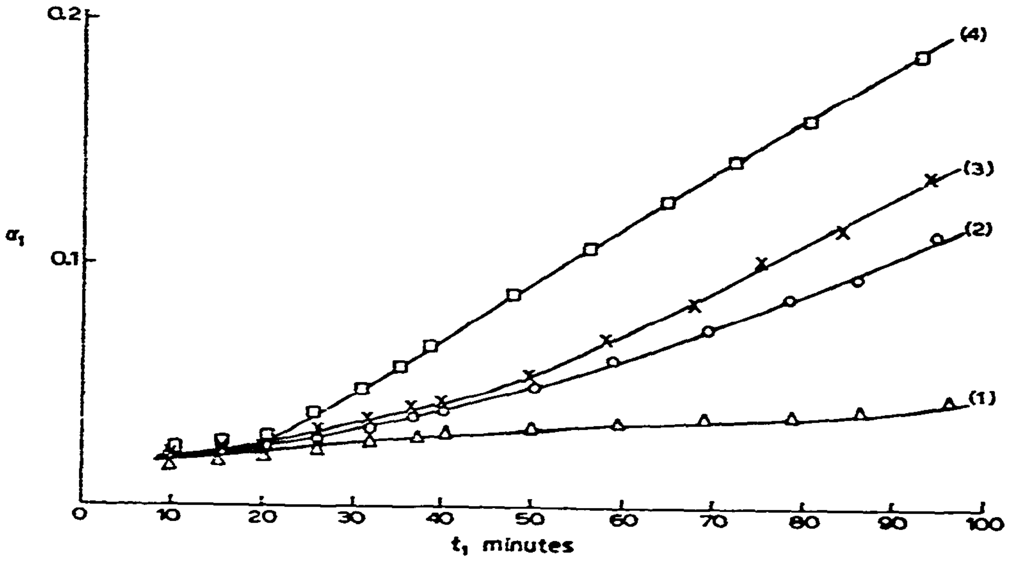

Fig. 1. Isothermal reduction of MoO_3 at 490, 510, 530 and 550 °C (1, 2, 3 and 4, respectively).

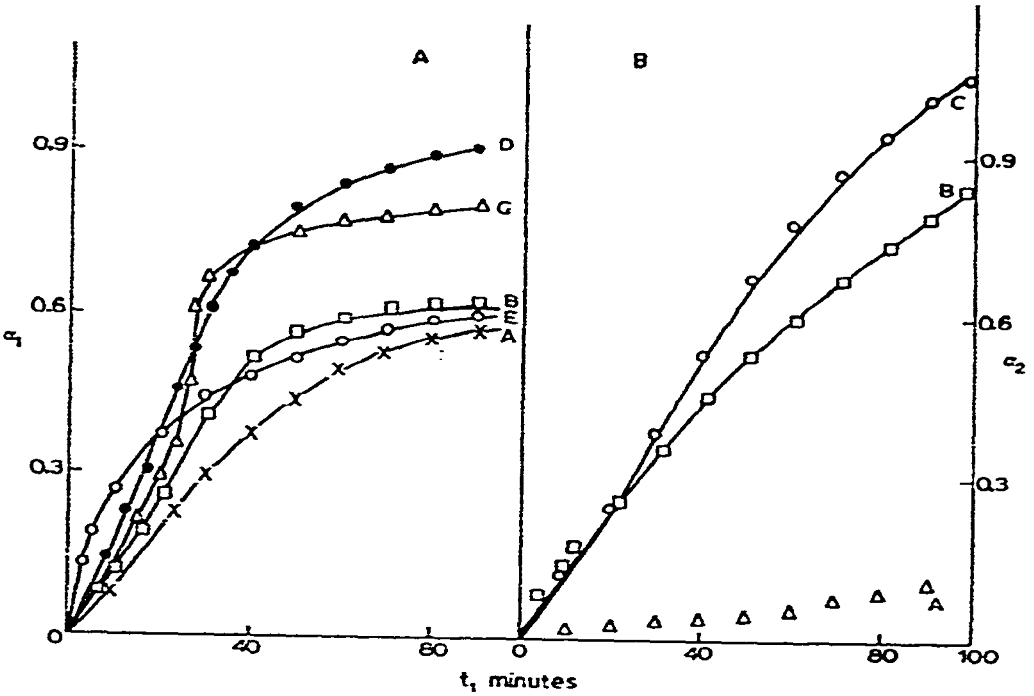

Fig. 2. (A) Isothermal reduction of Mo–Al_2O_3 at 490, 510, 530 and 550 °C (A, B, C and D, respectively) and Mo–Al_2O_3–Na at 490 °C (E) (B). Isothermal reduction of sintered Co–Al_2O_3, Co–Al_2O_3 and Co–Al_2O_3–Na at 490 °C (A, B and C, respectively).

higher than that of Co–Al_2O_3. The following may be the reasons for such type of behaviour:

When the Na^+ ions are absent in the support cobalt possibly goes into the Al^{3+} vacancies of the alumina in the position where it is not likely to be reduced to the metallic state during reduction. However, when Na^+ ions are present, sodium enters these sites preferentially depriving the cobalt species and thus most of the cobalt is converted into easily reducible oxides (more probably Co_3O_4) which, in turn, are converted into Co metal in H_2. Hence this might be the reason for the observed difference in reducibility of these two systems.

Reduction of Co–Mo–Al_3O_3 and Co–Mo–Al_2O_3–Na

The reducibility curves of these systems are shown in Fig. 3. The samples Co–Mo–Al_2O_3 and Co–Mo–Al_2O_3–Na prepared by simultaneous impregnation of the cobalt nitrate and ammonium paramolybdate solution exhibit different reducibility at identical conditions. The higher reducibility of the second one compared to the

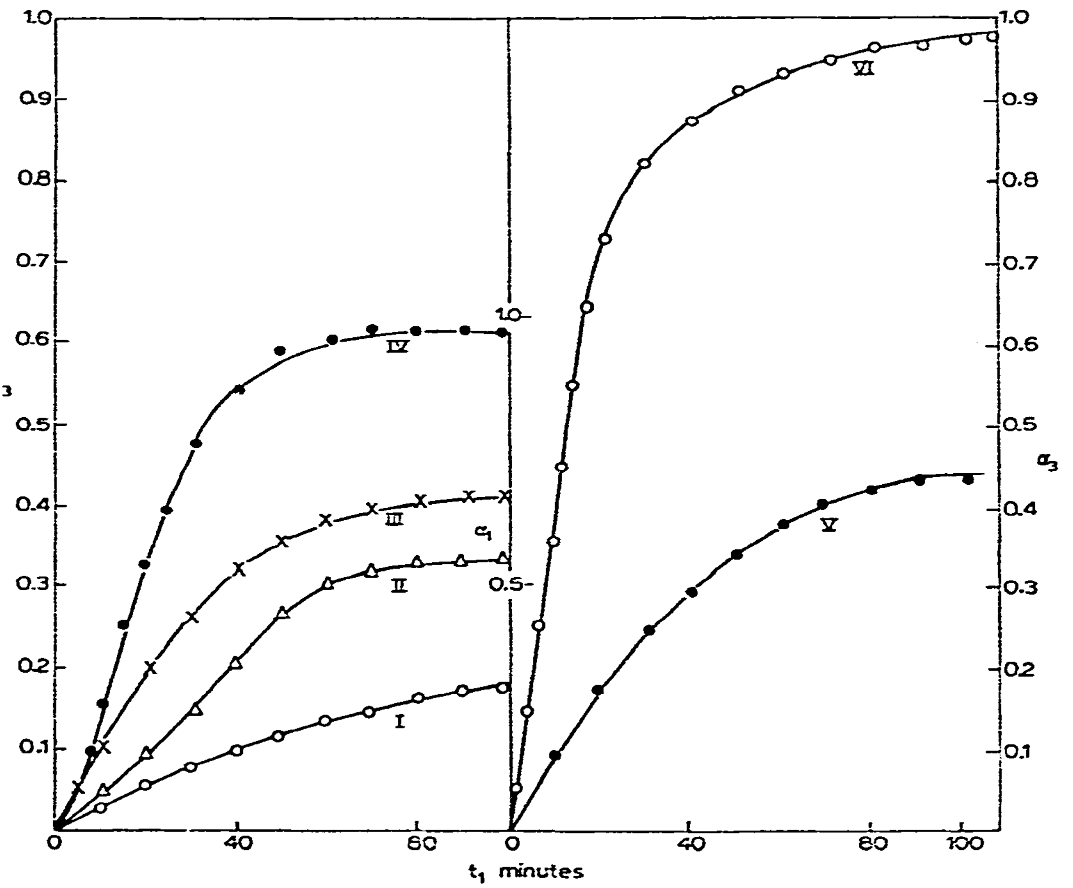

Fig. 3. Isothermal reduction of Co–Mo–Al_2O_3(S), Mo–Al_2O_3, Mo–Al_2O_3–Na, Co–Mo–Al_2O_3–Na(S), Co–Mo–Al_2O_3–Na and Mo–Co–Al_2O_3–Na at 490°C (I, II, III, IV, V and VI respectively).

first substantiates the earlier prediction that Co_3O_4 is formed in the presence of Na^+ ions and reduced to the metal in hydrogen. The reduction of MoO_3 phase seems to be accelerated by the presence of this metallic cobalt. However, comparison of the reduction characteristics of Mo–Al_2O_3 with Co–Mo–Al_2O_3 and Mo–Al_2O_3–Na with Co–Mo–Al_2O_3–Na at 490°C yields the following conclusion. In the absence of Na^+ ions, the reduction of MoO_3 is inhibited by cobalt whereas in the presence of Na^+ ions, it is accelerated.

Effects of sample weight on the reducibility of MoO_3, Mo–Al_2O_3 and Co–Mo–Al_2O_3

The results of the influence of sample-weight on the reducibility are shown in Fig. 4. It is apparent that the rate of reduction is inversely dependent on the sample mass. It indicates that the reverse reaction, i.e., reaction of water with reduced MoO_3 controls the overall rate of reduction in all the cases. Vasilev et al.[9] has also reported that the water evolved during the reaction inhibited further reduction of MoO_3.

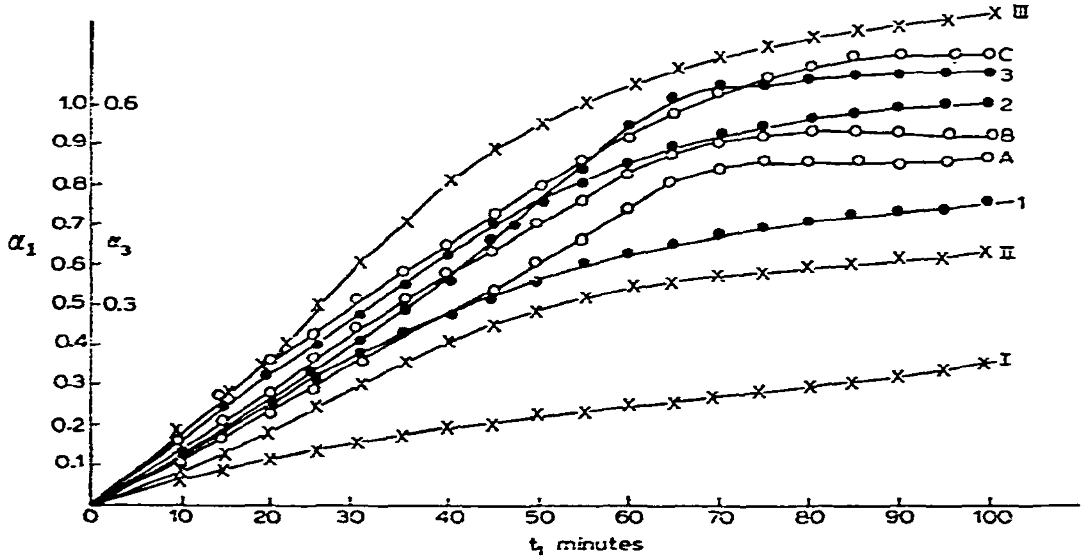

Fig. 4. Influence of Sample weight (9, 18, 36 mg) on the reducibility of MoO_3 (I, II and III, respectively), Mo–Al_2O_3 (A, B and C, respectively) and Co–Mo–Al_2O_3(S) (1, 2 and 3, respectively).

Surface acidity of Co–Mo–Al_2O_3 catalysts

The acid strength distribution of the surface sites in the various samples[10] is shown in Table 1. The notable features of this study are the following. In the absence of Na^+, the Co–Mo–Al_2O_3 catalyst is more acidic than Mo–Al_2O_3. When Na^+ is present, however, they have similar acidic properties. In other words, the interaction between the cobalt and molybdenum moieties to generate strong acid sites is inhibited by the Na^+ concentration of the alumina support. Thus, it is reasonable that the stronger acid sites in the Co–Mo–Al_2O_3 retain the water evolved during reduction strongly with the consequent inhibition of the process. However, this inhibitory

TABLE 1

SURFACE ACID STRENGTH DISTRIBUTION IN THE Co-Mo-Al_2O_3 SYSTEMS

Differences in n-butylamine titer values[a] for indicators of various p*K*a values.

Sample	$5 > pKa > 3.3$	$3.3 > pKa > 2$	$2 > pKa > -3$	$-3 > pKa > -5.6$	$pKa < -5.6$
A. Al_2O_3	0.8	0	0	3.4	0
B. Al_2O_3-Na	0	0	0	0.9	0
C. Mo-Al_2O_3	3.4	0	0	5.0	5.0
D. Mo-Al_2O_3-Na	1.5	0	0	3.6	6.0
E. Co-Al_2O_3	0.1	0	0	6.6	0
F. Co-Al_2O_3-Na	0.8	0	0	6.2	0
G. CoMo-Al_2O_3	1.0	0	5.0	1.6	9.4
H. CoMo-Al_2O_3-Na	2.2	0	0	2.4	6.5
I. Co-Mo-Al_2O_3-Na	1.0	0	0.8	3.0	7.0
J. Mo-Co-Al_2O_3-Na	0.7	0	0	3.9	5.0
K. MoO_3	18.1	0	22.1	20.1	64.2

[a] Number of n-butylamine molecules consumed by 1000 $A^{\circ 2}$ of the surface of the samples; the values are reproducible to about ±0.8.

influence of cobalt is removed when such types of acid sites are absent as in the case of CoMo–Al_2O_3–Na.

Magnetic susceptibility of Co–Mo–Al_2O_3 catalysts

The magnetic moments μ_{eff} of Co–Mo–Al_2O_3 and Co–Mo–Al_2O_3–Na under various conditions of pretreatment are shown in Table 2. Samples Mo–Al_2O_3 and Mo–Al_2O_3–Na both in the fresh state and after the pretreatment show negligible gram susceptibility (χ_g) and hence are not discussed further. Plots of χ_g against reciprocal field ($1/H$) are shown in Fig. 5. Dependence of χ_g on H was found only in the case of the Co–Mo–Al_2O_3–Na system indicating thereby ferromagnetism in the sample.

TABLE 2

MAGNETIC MOMENTS OF Co–Mo–Al_2O_3 AND Co–Mo–Al_2O_3–Na UNDER VARIOUS CONDITIONS

S No.	*Pretreament*	*μ_{eff}, B. M.*	
		Co–Mo–Al_2O_3	*Co–Mo–Al_2O_3–Na*
1.	Fresh	4.9	5.6
2.	Reduction in H_2 at 380°C for 3 h	5.0	6.3
3.	Reduction in H_2 at 500°C for 3 h	5.1	7.1
4.	Reduction in H_2+hydrocarbon flow (10:1) (iso-octane) at atm. press; LHSV = 3) at 380°C for 3 h	4.9	5.9
5.	1% S as thiophene was added to the feed of (4).		5.6
6.	As in (4) above; but carried at 500°C		6.9
7.	1% S as thiophene was added to the feed of (6)		5.0

For the fresh catalysts, μ_{eff} for Co–Mo–Al_2O_3–Na (5.6B.M.) was found to be higher than that for Co–Mo–Al_2O_3 (4.9 B.M.). On reduction in H_2 or in H_2–hydrocarbon at 380°C the value of μ_{eff} for Co–Mo–Al_2O_3 remains almost the same. However, for the sample with Na^+, μ_{eff} value increases from 5.6 for the fresh catalyst to 7.1 B.M. on reduction in H_2 at 500°C followed by ferromagnetic contribution. At a reduction temperature of 380°C the catalyst does not exhibit ferromagnetic behaviour indicating thereby incomplete reduction whereas at 500°C, the presence of metallic cobalt is revealed. The increase in μ_{eff} values for Co–Mo–Al_2O_3–Na reduced at 380°C is due to the reduction of Co^{2+} ions but the absence of ferromagnetic contribution indicates that the reduction is not complete and the reduced species, e.g., Co is sufficiently well dispersed in the diamagnetic MoO_3–Al_2O_3, thereby not developing a condensed ferromagnetic phase.

Reduction of these samples in the H_2-hydrocarbon mixture yields interesting results. At 380°C, the μ_{eff} value (5.9 B.M.) is intermediate between those of fresh

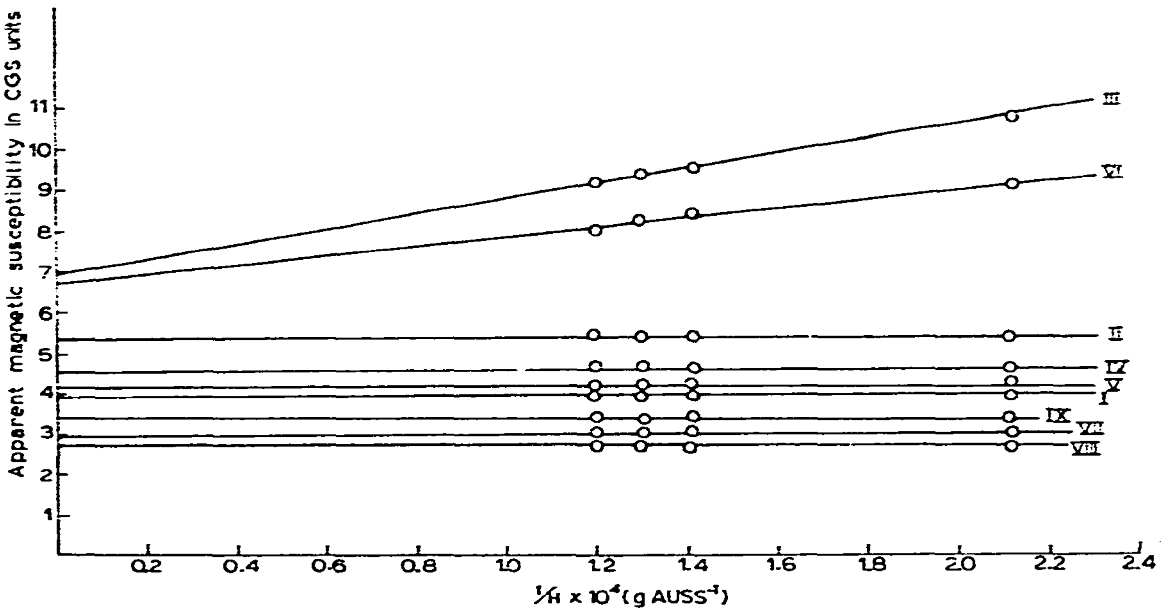

Fig. 5. Variation of apparent magnetic susceptibility (x_g) with the reciprocal of the magnetic field ($1/H$) for various samples. (I) Co–Mo–Al_2O_3–Na (fresh catalyst); (II) Co–Mo–Al_2O_3–Na reduced in a flow of H_2 at 380°C for 3 h; (III) Co–Mo–Al_2O_3–Na reduced in a flow of H_2 at 500°C for 3 h; (IV) Co–Mo–Al_2O_3–Na reduced in a flow of H_2+iso-octene at 380°C for 3 h; (V) Co–Mo–Al_2O_3–Na reduced in a flow of H_2+iso-octene+thiophene at 380°C for 3 h; (VI) Co–Mo–Al_2O_3–Na reduced in a flow of H_2+iso-octene at 500°C for 3 h; (VII) Co–Mo–Al_2O_3–Na reduced in a flow of H_2+iso-octene+thiophene at 500°C for 3 h; (VIII) Co–Mo–Al_2O_3, fresh catalyst; (IX) Co–Mo–Al_2O_3 reduced in a flow of H_2 at 500°C for 3 h.

(5.6 B.M.) and H_2-reduced (6.3) samples. A similar behaviour is also marked at 500°C. However, when 1% sulphur is present in the feed the reducibility of cobalt is markedly affected. At 380°C, μ_{eff} (5.6 B.M.) is similar to that of the fresh catalyst. At 500°C, μ_{eff} decreases to 5.0 B.M. which is attributed to the formation of the sulphides of cobalt in the presence of H_2S at 500°C. These sulphides are reported to have a low magnetic susceptibility. For example, the molar magnetic susceptibility of CoS at 20°C is only 225×10^{-6} cgs units whereas those of CoO, Co_2O_3 and Co_3O_4 are 4900, 4560 and 7380×10^{-6} cgs units, respectively[11].

DISCUSSIONS

The reduction of MoO_3 in H_2 might be due to the formation of oxygen vacancies (created by the removal of oxygen atoms by hydrogen) which correspond to the nuclei-formation stage and their further growth by diffusion and agglomeration constitutes the nuclei-growth stage.

When MoO_3 is deposited on Al_2O_3 support, the forces of interaction between the MoO_6 octahedra are reduced due to the greater dispersion and interaction with the support. Hence, the rate of reduction (i.e., rates of nuclei formation) are accelerated. But due to the strong retention of the evolved water molecules by the adjoining Al_2O_3 surface positions, reduction is arrested earlier and the maximum level of reduction attained is lower than in pure MoO_3.

Cobalt, when supported on Al_2O_3 may be present in at least two different structural positions[13]. (1) as Co^{2+} in Al^{3+} vacancies on the Al_2O_3 surface, the δ phase; or (2) as Co_3O_4, β phase. In the former position, it is not reduced by H_2[13], whereas in the latter form, it is easily reducible to Co°. All the Co–Al_2O_3 and Co–Mo–Al_2O_3 samples consist of both forms and the relative proportions are highly influenced by the Na^+ content of Al_2O_3 as well as other preparative variables. The proportion of the β phase increases when Na^+ ions are present on the support ($\alpha_{Co-Al_2O_3-Na} > \alpha_{Co-Al_2O_3}$). These Na^+ ions capture the Al^{3+} vacancies, thus depriving the Co^{2+} ions of adsorption sites. The effect of cobalt on the reducibility of Mo–Al_2O_3 is influenced by the relative proportions of δ and β phase cobalt on the Al_2O_3 surface. When sodium ions are absent, the former, due to structural interaction with Al_2O_3 and MoO_3 phases, remains unreduced under the reduction conditions and attenuates the reduction of MoO_3 (dispersed) by accelerating the retention of the water formed during reduction. When Na^+ ions are present, cobalt, mostly present as Co_3O_4 is reduced to the metallic cobalt and enhances the reduction of the MoO_3 phase. This is again substantiated by the fact that the reducibility of Mo–Co–Al_2O_3–Na is higher than that of Co–Mo–Al_2O_3–Na. The formation of Co_3O_4 is more probable when cobalt is impregnated 'on top' of MoO_3 than directly on the Al_2O_3 surface. In the latter case, more cobalt ions are expected to interact directly with the alumina surface and hence arrest reduction in H_2.

The relatively high μ_{eff} value for the Co–Mo–Al_3O_3–Na indicates that in the presence of pre-impregnated Na^+ ions on the alumina surface, more cobalt ions occupy positions in which they are octahedrally surrounded by oxide ions. Such positions are: (1) Co^{2+} ions in the octahedral Al^{3+} vacancies in the Al_2O_3 support; (2) Co^{2+} ions in Co and Co_3O_4; and (3) Co^{2+} ions in $CoMoO_4$.

An interesting observation is the identical value of μ_{eff} for the fresh Co–Mo–Al_2O_3–Na and for the sample reduced at 380°C in a flow of H_2–hydrocarbon–thiophene. This identity may be accounted for two reasons: (1) the Co^{2+} ions in the fresh catalysts are neither reduced to lower valent state nor sulphided to CoS; or (2) The increase in μ_{eff} caused by reduction of part of the Co^{2+} ions to CoO is exactly compensated by the decrease due to the formation of the sulphide.

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