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Characterization of oxide Co-Mo/γ-Al_2O_3 hydrodesulphurization catalysts prepared by different methods

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Three series of oxidic Co–Mo/γ-Al_2O_3 catalysts with different cobalt content and prepared by three different methods have been studied by X-ray diffraction, diffuse reflectance spectroscopy and magnetic techniques. The results show that the formation of Co and Mo surface species is affected by the method of catalyst preparation and that Mo enhances the dispersion of the cobalt species. The presence of Co_3O_4 was clearly detected in cobalt-rich samples prepared by a two-step method, especially when Mo was incorporated by equilibrium adsorption. It also seems that in catalysts prepared by "wet" consecutive impregnation Co favours the formation of a Mo multilayer on the surface of Al_2O_3. However, in catalysts prepared by simultaneous impregnation the segregation of Co_3O_4 and the formation of a Mo multilayer occurs less extensively.

1. Introduction

The catalysts more commonly used in hydrodesulphurization (HDS) processes consist of oxides of Co and Mo supported on Al_2O_3 [1, 2]. They have been the subject of many research studies and have been characterized by a wide variety of techniques, which have been recently reviewed [3].

It is well known that different surface and bulk phases can be present on these complex catalysts. Their formation and distribution depends on several factors such as chemical composition, calcination temperature, support characteristics and method of preparation. Despite all these studies, it can be seen in the literature that the presence of some species is still a subject of controversy. Many of the diagreements seem to be due to differences in the method of preparation of the catalysts and also to the limitations of the characterization techniques used [3]. Although it is generally acknowleged that the method of catalyst preparation can affect the catalyst structure, it has hardly been investigated [3–8] and the importance and details of catalyst preparation methods have been generally understated in the study of these catalysts.

In the present paper we have made an attempt to characterize the surface structural differences of three series of Co–Mo/γ-Al_2O_3 catalysts in the oxide form, prepared by three of the methods more usually employed, namely, simultaneous impregnation, consecutive impregnation and equilibrium adsorption. We report the results of X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and magnetic measurements.

2. Experimental method

2.1. Materials and preparation of catalysts

The γ-Al_2O_3 used was Girdler T-126, with a specific surface area of 188 $m^2\ g^{-1}$ and a pore volume of 0.39 $m\ g^{-1}$; $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$(p.a.) was

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obtained from Panreac and $Co(NO_3)_2 \cdot 6H_2O$(p.a.) from Riedel.

Three different series of samples were prepared:

Series A: Samples were obtained by simultaneous impregnation of γ-Al_2O_3 with an aqueous solution containing both ammonium paramolybdate and cobalt nitrate. The Mo and Co contents in the solution were chosen to yield the required Mo and Co loading in the final catalysts. The excess solvent was evaporated at 350 K and 27 kNm^{-2} in a rotary evaporator and the samples were then heated in flowing air at 650 K for 2.5 h and, finally, at 820 K for 4.5 h.

Series B: Alumina was first impregnated with Mo solution, followed by drying, decomposition and calcination as described above for Series A. The sample thus obtained was designated B-0. Different portions of this sample were then impregnated with the Co solution and, finally, dried and calcined after the Mo impregnation.

Series G: Alumina was first equilibrated with an aqueous solution of Mo at room temperature until the amount of Mo incorporated was of the same order as that produced by the other two methods, and then filtered, dried and calcined as described for Series A. Different portions of the sample designated G-0 were subsequently impregnated with an aqueous solution of cobalt nitrate following the same procedure as in Series A and B, i.e. evaporating to dryness, in order to obtain the final catalysts with the required Co loading, then dried and calcined.

For comparison, some other reference samples of Co/γ-Al_2O_3 (Samples H-1 and H-2) and Co_3O_4 were prepared. Samples H were obtained in a similar manner to Samples A. Bulk Co_3O_4 was prepared by the calcination of $CoCO_3$ (D'Hemio, p.a.) at 770 K.

2.2. Chemical analysis and physical characterization

Chemical analysis of the catalysts was carried out by atomic absorption using a Perkin-Elmer 360 spectrophotometer. The composition of all catalysts, their BET surface areas and colours and effective magnetic moments are reported in Table I.

Diffuse reflectance spectra (DRS) were recorded in the range 210 to 1200 nm (about 50 000 to 8 000 cm^{-1}) using a Beckman DU spectrophotometer and the same alumina as reference.

Magnetic measurements were carried out at

TABLE I Composition and properties of catalysts

Catalyst	MoO_3 * (%)	CoO* (%)	Atomic Co† (%)	Colour	Surface area ($m^2 g^{-1}$)	μ_{eff} (BM)‡
A-38	9.3	0.87	0.59	Light blue	183	5.01
A-7	9.3	2.0	1.36	Light blue	161	4.83
A-3	8.9	3.1	2.11	Blue	173	4.66
A-9	8.5	3.8	2.59	Blue	170	4.55
A-8	8.7	4.8	3.27	Blue-grey	170	4.46
B-0	8.5	0.0	0.0	White	189	–
B-10	8.6	1.1	0.75	Light blue	181	4.96
B-12	8.6	2.1	1.43	Blue	194	4.84
B-11	8.6	2.2	1.50	Blue	185	4.74
B-13	8.5	2.8	1.91	Blue	197	4.52
B-14	8.5	3.9	2.65	Blue-black	189	4.45
B-15	8.6	4.7	3.20	Black-blue	177	4.28
G-0	8.3	0.0	–	White	183	–
G-2	8.3	1.26	0.86	Light blue	183	4.71
G-3	8.3	2.00	1.36	Blue-grey	186	4.57
G-4	8.3	3.20	2.18	Blue-black	186	4.33
G-5	8.3	3.92	2.67	Black	178	4.23
H-1	0.0	1.0	0.68	Light blue	–	4.54
H-2	0.0	5.0	3.40	Black	–	2.86

*Grams of MoO_3 (or CoO) per 100 g Al_2O_3.
† Atoms of Co per 100 atoms of aluminium.
‡At 300 K.

room temperature using a Stanton MC-5 Gouy balance provided with a Newport C electromagnet.

X-ray diffraction (XRD) diagrams were recorded using a Philips PW 1730 instrument.

3. Results

3.1. X-ray diffraction diagrams

Catalysts with low Co content did not show any diffraction lines other than those corresponding to γ-Al_2O_3.

Fig. 1 shows the X-ray diffraction diagrams of the Co-rich samples in each catalyst series, together with those of the original γ-Al_2O_3 and Co_3O_4. Catalyst H-2 clearly exhibits, in addition to the diffractions of pure alumina, several small lines that coincide with those of Co_3O_4, e.g. the lines corresponding to $d = 0.155$, 0.165 and 0.286 nm. On the contrary, Samples A-8, B-15 and G-5 show apparently unchanged diagrams if compared with those of γ-Al_2O_3. However, a careful examination reveals some differences: (i) an increase in the intensity of the line at $d = 0.286$ nm, particularly of Samples B-15 and G-5 which were prepared by a two-step procedure; (ii) a sharpening of the line at $d = 0.244$ nm; and (iii) a shoulder in the high-spacing side of the (400) peak. These differences, in addition to the black colour exhibited by these samples, strongly suggest the presence of small amounts of Co_3O_4 in these samples, in agreement with the X-ray results reported in the literature [9].

3.2. Diffuse reflectance spectra

Figs 2 to 5 show the DRS between 200 and 1200 nm of the catalyst Series A, B, G and H (reference samples: Co/Al_2O_3, Co_3O_4), respectively. The spectra have been vertically displaced for clarity. No difference was found in the bands exhibited by the three series of samples, but some differences in the evolution of the spectra with increasing cobalt content could be observed.

In the 225 to 340 nm region, which corresponds to charge transfer transitions $O^{2-} \rightarrow Mo^{6+}$ in octahedral and/or tetrahedral co-ordination, Series A shows ill-defined bands around 235 and 280 to 300 nm, while in Series B and G broad bands at 235 and 280 to 300 nm are clearly detected. In Series B and G a broadening in the high-wavelength side of the band about 280 nm with increasing cobalt content can be detected. This seems to be a result of the overlapping of the initial band at 280 nm and a new one at 300 nm, which develops when the cobalt content increases. Also, in these catalysts the relative intensity of the broad band at 280 to 300 nm with respect to the 235 nm band increases with the cobalt content, particularly in Series G, while in Series A no change could be detected.

In the high-wavelength side of the spectrum the catalysts with a low Co content in the three series of catalysts exhibit very similar features to those of Sample H-1 with a broad triple band at 525, 580 and 625 nm. On increasing the cobalt content, the three series of catalysts develop a shoulder at about 720 nm and an increase in absorbance in the 350 to 550 nm region. However, each series shows a different behaviour with regard to the increase in the intensity of the 720 nm band with the cobalt content. This variation has been plotted in Fig. 6. The increase is gradual for Samples A, but more pronounced for Series B and even more for Series G. For comparison, the intensities of the same band for Mo-free samples have also been plotted in Fig. 6. It is worth noting that on samples containing only cobalt the intensity of the shoulder at 720 nm is very large when compared to corresponding samples containing molybdenum with a similar cobalt content.

3.3. Magnetic results

Effective magnetic moments, μ_{eff}, calculated from the magnetic susceptibilities corrected for the diamagnetic contributions of all components and for ferromagnetism are given in Table I. The effective magnetic moments decrease with increasing cobalt content and Fig. 7 shows that it appears to follow a different trend, which depends on the preparation method.

4. Discussion

4.1. X-ray analysis

The incorporation of Co into Al_2O_3 can be achieved leading to different surface or bulk compounds, e.g. CoO, Co_3O_4, $CoAl_2O_4$, etc. Its identification by XRD is limited to particle sizes larger than 4 nm [3], as smaller particles do not give diffraction lines distinguishable from the wide bands of Al_2O_3. The presence of CoO would be evident by a peak at $d = 0.2130$ nm in the XRD diagram, corresponding to the (200) plane of this NaCl-type oxide, but this peak is absent for all the Co-rich samples in Fig. 1; although CoO can be present, its percentage should decrease on

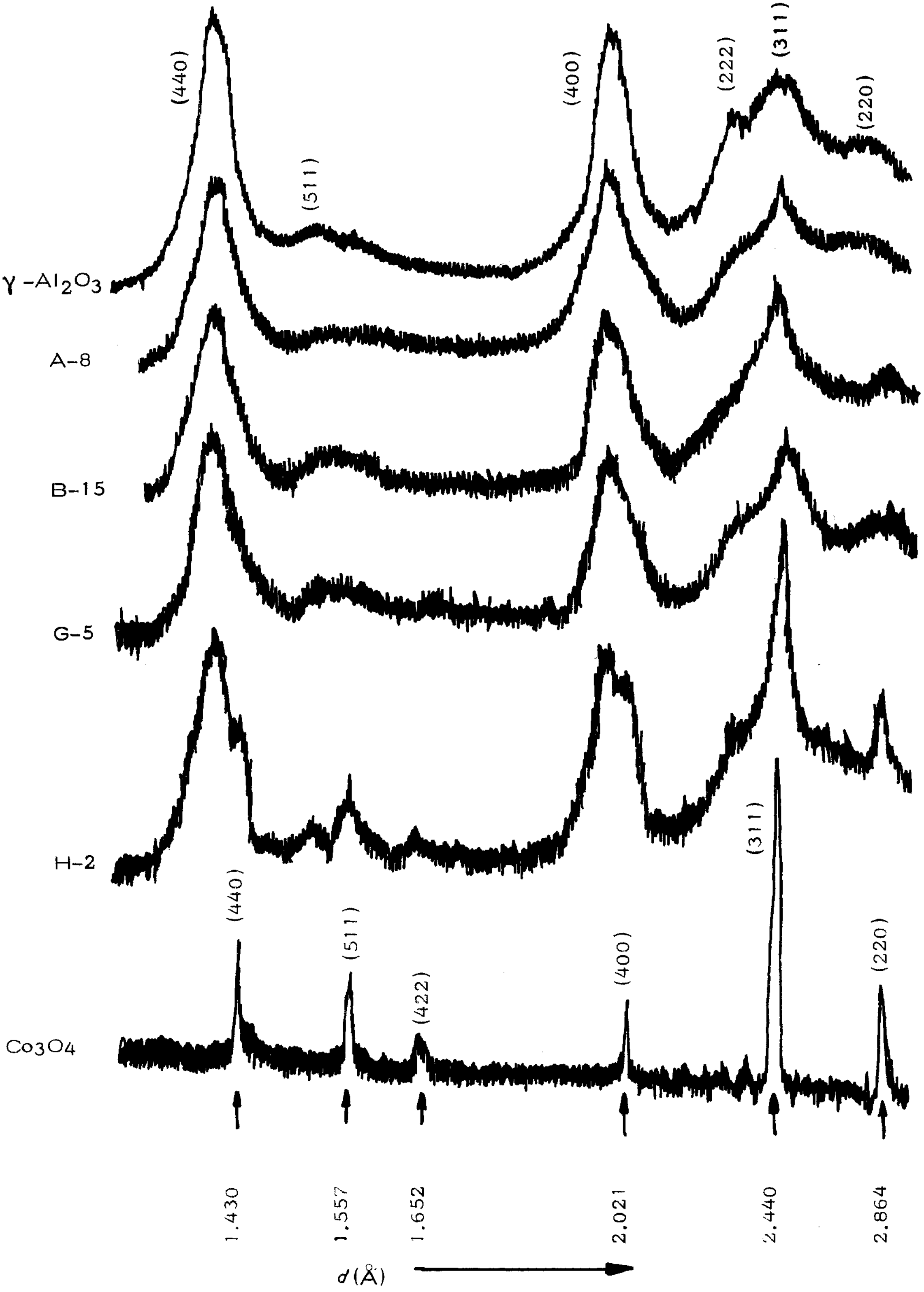

Figure 1 X-ray diffraction diagrams of γ-Al_2O_3, Co_3O_4 and the Co-rich catalysts in each series.

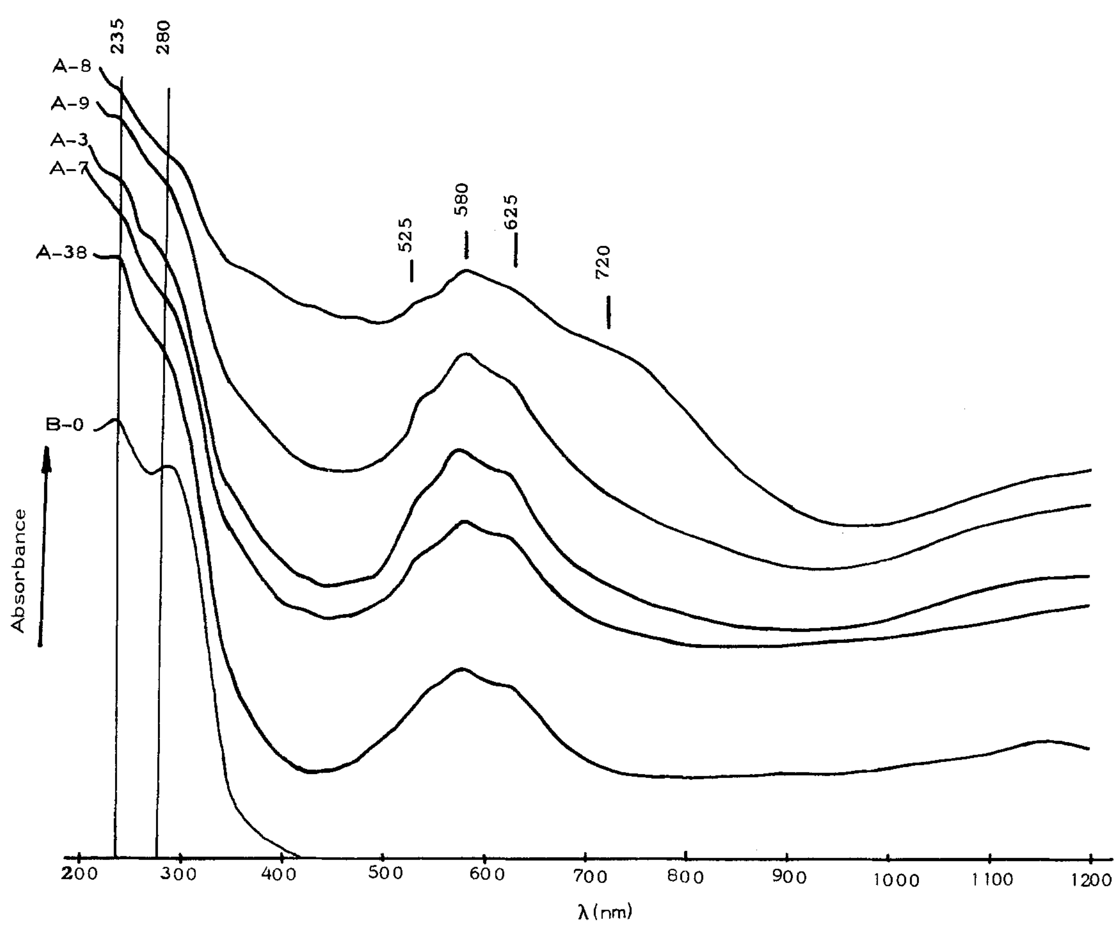

Figure 2 Diffuse reflectance spectra of Series A samples; simultaneous impregnation method.

increasing Co content, as an increase would lead to larger μ_{eff} due to the O_h, high-spin symmetry of the Co(II) species in this oxide (see below). On the other hand, the presence or absence of $CoAl_2O_4$ is not clear at all from the XRD results only, as its peaks coincide with those of Co_3O_4, and due to the similar arrangement of anions (spinel structure) many reflections become indistinguishable. However, the presence of $CoAl_2O_4$ in the Co-rich samples is not indicated by the magnetic results, as too low values of μ_{eff} are actually reached due to tetrahedral Co(II) species; data in the literature indicate that, on the contrary, it predominates in samples with low Co content [3, 9].

4.2. Diffuse reflectance spectra

4.2.1. *Molybdenum species*

According to the literature, absorption bands in the 260 to 280 nm region are atributed to tetrahedral Mo^{6+}, Mo(T); in the 290 to 330 nm region to octahedral Mo^{6+}, Mo(O); and the band at 225 to 240 nm is assigned to both Mo(T) and Mo(O) [10–13].

On the basis of these assignments, all catalysts contain predominantly Mo(T), particularly at low Co contents. However, this Mo(T) species should not be the only one present in the catalysts, since the increasing broadening observed in Series B and C, as Co content increases, indicate some asymmetry around the Mo ions. This fact suggests, therefore, that some Mo(O), probably distorted, could also be present in the catalysts prepared by a two-step procedure, namely, Series B and G. Nevertheless, the percentage of Mo(O) species in catalysts with low Co content, if it exists, should be small and apparently increases as the Co content increases. Indeed, a relative increase

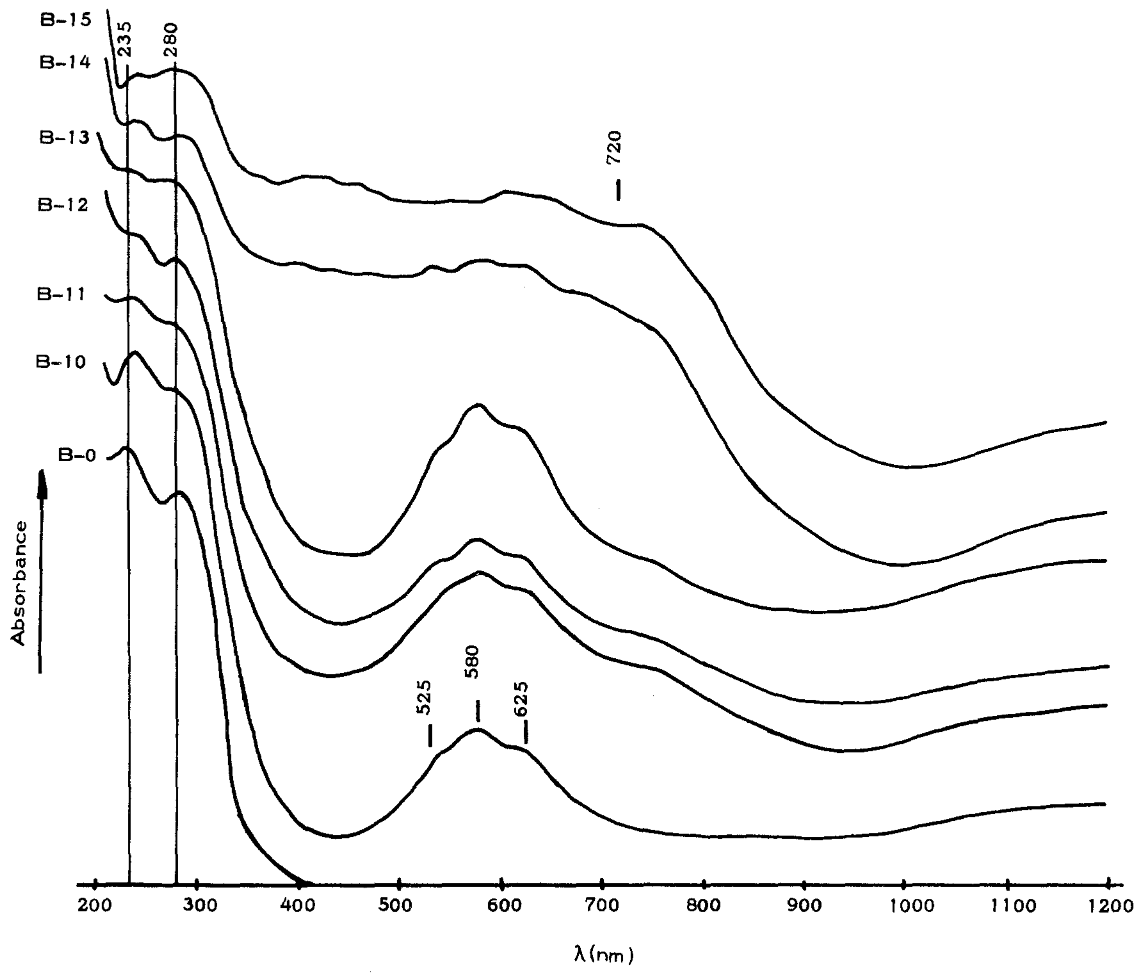

Figure 3 Diffuse reflectance spectra of Series B samples; consecutive impregnation method.

in the intensity of the band about 300 nm (with respect to the 235 nm band) is evident in Figs 3 and 4.

Thus, in Co–Mo/γ-Al_2O_3 catalysts prepared by consecutive impregnations, Mo being incorporated first, it seems that Co has some influence on the co-ordinative environment of Mo, enhancing the arrangement of some of the Mo ions in a distorted octahedral co-ordination, possibly in a polymeric form, according to the band assignment made for the 270 to 295 nm range in molybdenum supported catalysts [14], which has been ascribed to the formation of Mo–O–Mo bridges. This effect of Co in promoting the distortion of Mo(T) and the formation of polymeric entities was not detected by infra-red spectroscopy in a previous work [15], but it has been shown by Raman spectroscopy in various studies [6, 14, 16, 17].

In Co–Mo/γ-Al_2O_3 catalysts prepared by the pore-filling method, a similar broadening effect of the band around 312 nm was reported and was interpreted as assuming that Co interacts with the oxymolybdenum species, probably by forming Co–O–Mo bonds. The band broadening was attributed to an increase in the number of octahedral oxymolybdenum species.

4.2.2. Cobalt species

Oxidic Co^{+2} species in a tetrahedral co-ordination, Co(T), show a characteristic triplet of bands at 1250, 1350 and 1560 nm, and another triplet at 624, 590 and 550 nm [9, 11, 18, 19]. According to this assignment, Co in Sample H-1 should be tetrahedrally co-ordinated, as a surface $CoAl_2O_4$ spinel [4, 9]. However, Sample H-2 shows a very different spectrum. It is dominated by two broad

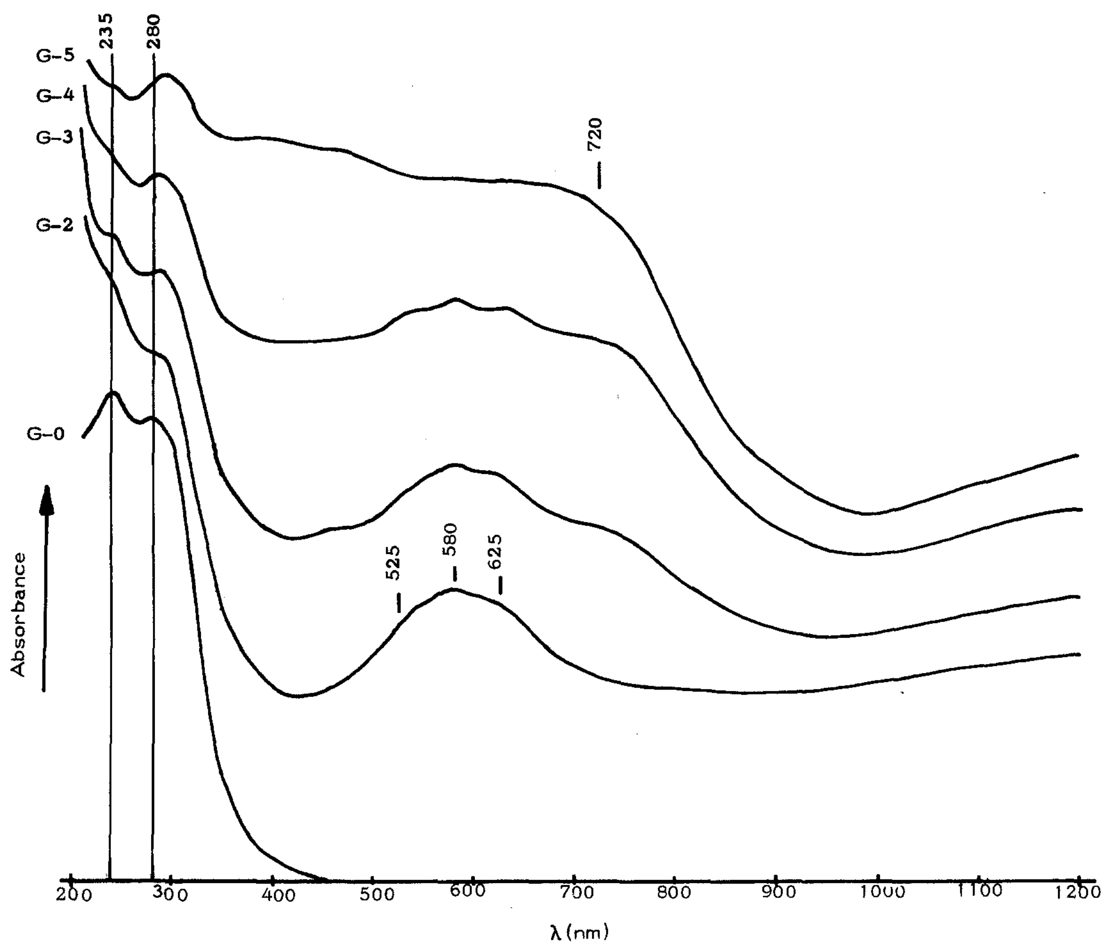

Figure 4 Diffuse reflectance spectra of Series G samples; equilibrium adsorption method.

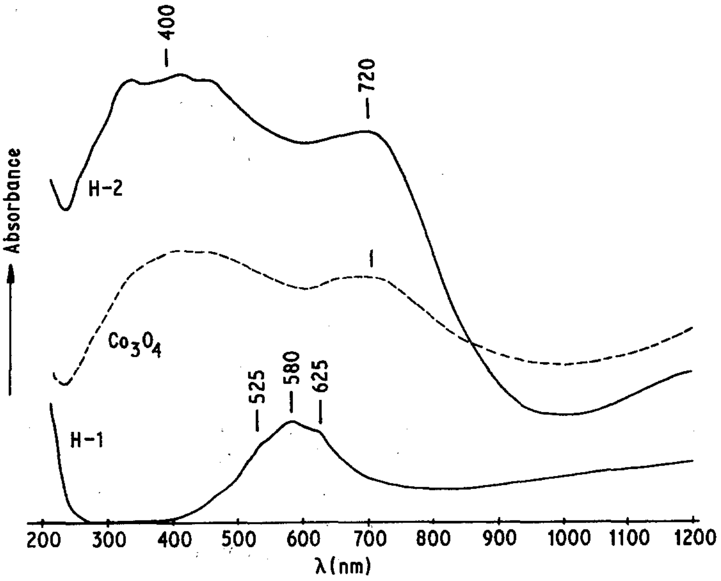

Figure 5 Diffuse reflectance spectra of Series H samples (———) and of Co_3O_4, diluted in γ-Al_2O_3 (- - - -).

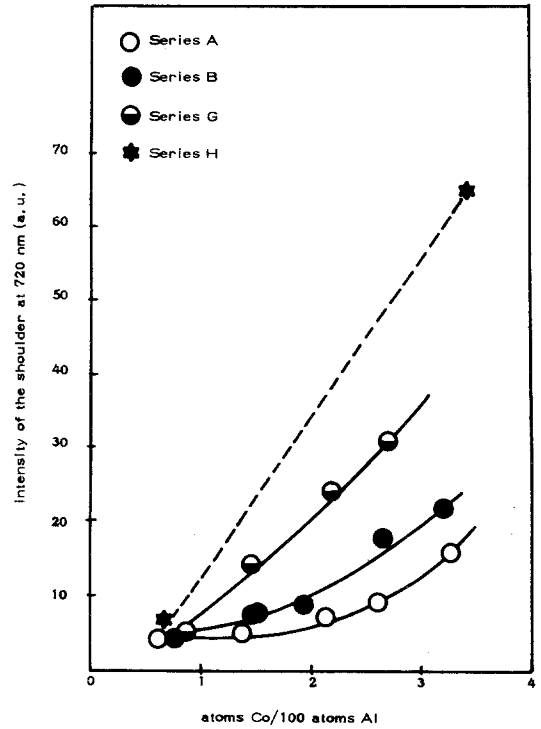

Figure 6 Variation in the intensity of the shoulder, identified as due to Co_3O_4, at 720 nm with the Co content.

bands at about 400 and 720 nm, that overlap in the region around 550 nm. In this region, both Co(T) and Co(O) have absorption bands and then the presence of any of these Co species cannot be completely excluded. From the similarity of the spectrum of Sample H-2 with that of Co_3O_4, it can be concluded that Co_3O_4 is present in Sample H-2, in agreement with our X-ray results (see above) and with the findings of other authors [9, 11].

On comparing the spectrum of Sample H-1 and catalysts with low Co content, it is evident that the dominant Co species on these Co-poor samples is Co(T). On these samples, there is no evidence of the presence of Co(O), although it cannot be excluded, since if tetrahedral Co^{2+} ions occur together with octahedral ones, the stronger bands of the former will cover the weaker bands of the later [9, 10].

On increasing the Co content, the three series of samples developed an increasing shoulder around 720 nm and an increasing absorption in the region 300 to 500 nm, which has been attributed to Co_3O_4 [9, 11]. This assignment is supported by the spectrum of Co_3O_4 shown in Fig. 5. The increase of the shoulder at 720 nm is different for each series of catalysts. The results in Fig. 6 indicate that the amount of Co_3O_4 increases with increasing Co content, being larger in the series of catalysts prepared by consectutive impregnation methods, particularly in Series G. It is interesting to notice that Co–Mo/γ-Al_2O_3 samples have less Co_3O_4 than Co/γ-Al_2O_3 samples with a similar Co content and it may be concluded that Mo inhibits, to some extent, the formation of Co_3O_4. A similar conclusion has been reached by other authors [9, 11, 20]. On the other hand, Fig. 6 indicates that the formation of Co_3O_4 is highly dependent on the way Mo and Co has been incorporated.

4.3. Magnetic results

Effective magnetic moments reported for tetrahedral $Co^{2+}(^4A_2)$ are in the range 4.2 to 4.7 BM [4, 10] and for octahedral Co^{2+} (high spin $^4T_{1g}$) in the range 4.7 to 5.3 BM [4, 10]. Thus, the μ_{eff} value of Sample H-1, 4.54 BM, indicates that cobalt is mainly tetrahedral in a surface $CoAl_2O_4$

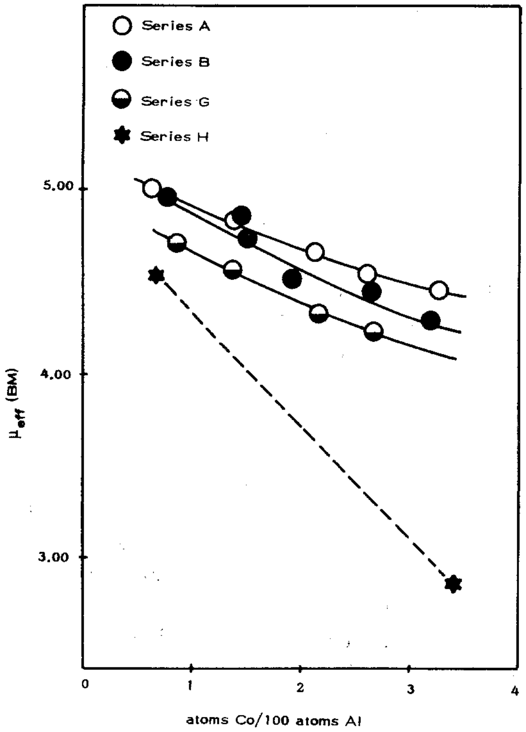

Figure 7 Variation in the effective magnetic moment, μ_{eff} (BM), with the Co content.

spinel, in agreement with the DRS results. The catalyst samples containing Mo with a similar Co content have a higher magnetic moment (about 4.9 BM), which is attributed to the larger occupance of octahedral sites in Al_2O_3 by Co^{2+} due to competition for tetrahedral sites by Mo. As the concentration of Co in the catalyst increases, a marked decrease in the magnetic moment is observed. According to the literature [4, 9, 10], this is due to two different phenomena: (i) an increase in the proportion of tetrahedral Co^{2+} in the surface $CoAl_2O_4$ spinel, and (ii) an increase of low-spin octahedral Co^{3+} species ($^1A_{1g}$) by oxidation, during calcination, of Co^{2+} (preferently occupying octahedral sites) and the formation of Co_3O_4, as shown by the DRS results. The presence of Co_3O_4 is clearly evident in Sample H-2, since the magnetic moment measured is relatively close to the value 1.8 BM reported for Co_3O_4. Furthermore, the DRS of this sample showed characteristic features of Co_3O_4.

It is interesting that the corresponding Co–Mo/γ-Al_2O_3 samples have a larger magnetic moment, hence, a small proportion of Co_3O_4. A similar effect has previously been reported [9, 11]. On comparing the three catalysts series, the variation of the magnetic moments with the Co content follows, in general, a similar tendency to that observed for the intensity of the band at 720 nm, plotted in Fig. 6. Samples containing only Co and Series G and B have smaller magnetic moments than Series A because in the latter one the proportion of Co in the Co_3O_4 form is smaller. In catalysts with a low Co content, as the formation of Co_3O_4 is not likely to occur, the differences in the magnetic moment are small and can be attributed to a different $Co^{2+}_{tet}/Co^{2+}_{oct}$ ratio in the $CoAl_2O_4$ species.

4.4. Effect of the method of preparation on the nature of Co and Mo species at the surfaces of the catalysts

The conclusions made from the DRS results are in close agreement with those from magnetic measurements, as Figs 6 and 7 reveal; both DRS and the magnetic results show that in catalysts with a low Co content the dominant Co species is a surface $CoAl_2O_4$ spinel (Co^{2+} in the alumina lattice located near or immediately below the alumina surface), thus giving rise to the typical blue colour. It is also shown that on increasing the Co loading an increase in the formation of Co_3O_4 takes place, as the change of catalyst colour from light blue to deeper blue and to black reveals. The formation of the Co_3O_4 species occurred mostly however when Mo was absent, because Mo has an enhancing effect on the dispersion of Co [20], due to the strong interaction taking place between Mo and Co [8, 11, 20].

In the case of Co–Mo catalysts where Mo is first incorporated on the Al_2O_3 (Series B and G), the diffusion of Co ions to the external layers of Al_2O_3 to form "surface" $CoAl_2O_4$ is hindered by a monolayer of molybdate which blocks the access to the support. Also, the interaction between Co and Mo is not favoured because the molybdates are strongly anchored to the alumina by calcination. Consequently the superficial coating of Co can be oxidized to form Co_3O_4 at moderate Co loadings. However, on simultaneous impregnation there is the possibility that both the support and the adsorbed molybdates can interact with Co more easily. In this case the formation of $CoAl_2O_4$ and, also, of interacting Co–Mo species are favoured. Both effects, but particularly the interacting Co–Mo species, result in a better dispersion of Co and, hence, the segregation of Co_3O_4 does not occur until the Co is present in high concentrations in the simultaneous impregnation catalyst series.

Moreover, the way Mo is incorporated also seems to be important. A higher segregation of Co_3O_4 occurs in those catalysts where Mo was incorporated by equilibrium adsorption (Series G); it could be due to a higher coverage of the alumina surface by a Mo "interrupted monolayer" when this method of preparation is used. Consequently, less free alumina surface should be accesible to Co ions and then they should segregate as Co_3O_4 at lower Co loadings.

No marked differences can be detected by X-ray diffraction with regard to the behaviour of the different series of samples containing Mo, but DRS shows that the oxidation process $Co^{2+} \rightarrow Co^{3+}$, with the simultaneous migration to octahedral holes, is less favoured on simultaneous impregnation. Then, Mo avoids the formation of Co_3O_4 microdomains large enough to be detected by X-ray diffraction, although the presence of Co^{3+} and Co^{2+} ions in octahedral and tetrahedral environments (as they occur in Co_3O_4) is clearly indicated by DRS and magnetic measurements.

It is also interesting to observe that the preparation method of catalysts seems to influence the Mo arrangement, since, in the simultaneous impregnation methods most of the species appear tetrahedrally co-ordinated as a Mo monolayer. However, in the Co-rich catalysts prepared by consecutive impregnations, the DRS results showed that a fraction of the Mo is present in an octahedral-like environment such as a distorted polymolybdate monolayer or multilayer of Mo, similar to an incipient bulk MoO_3 structure [20]. Thus, high Co loading in catalysts prepared by a two-step "wet" impregnation method favoured the segregation of Co_3O_4, but it seems that it also promoted the formation of a small proportion of polymolybdates or aggregates of Mo similar to MoO_3. The results of O_2 chemisorption on reduced Mo/Al_2O_3 and $Co-Mo/Al_2O_3$ catalysts showed that the decrease in the equivalent molybdenum area of the $Co-Mo/Al_2O_3$ samples with respect to the corresponding Mo/Al_2O_3 samples was small [21]. This decrease in O_2 chemisorption could be attributed to a partial coverage of Mo by Co as a bilayer on the surface of the catalyst [20], or to the formation of a Mo multilayer.

Taking into account that Co could not be detected in the solution from catalyst extraction with ammonia, whereas in the same solution approximately 80 wt% of the Mo in the catalyst could be solubilized [22], it is unlikely that a high fraction of Mo and Co can be present as a "Co–Mo bilayer". On the other hand, it is then more probable that Co enhances the formation of a polymolybdate rather than a bulk-like MoO_3 species, otherwise the decrease in chemisorbed O_2 should be more pronounced. We may speculate that the formation mechanism of these polymolybdates is *not* a redistribution of Mo on the surface, but rather a bridging of close MoO_4^{2-} species induced through the Co species placed on the alumina surface in the surroundings (not on top) of MoO_4^{2-} species. This configuration, probably two-dimensional, cannot be precise and should be taken as tentative. This hypothesis would be consistent with the findings obtained by i.r. spectroscopy [15] from which it was concluded that Co impregnated on a calcined Mo/Al_2O_3 catalyst did not apparently modify the previous anchoring of Mo in alumina.

Thus, in our catalyst (moderate loadings), prepared by the consecutive "wet" impregnation and equilibrium adsorption methods, most of the Mo is present as a monolayer of Mo^{6+} with a small fraction, presumably, in polymeric form. However, in catalysts prepared by the simultaneous "wet" impregnation no appreciable (by using DRS) amount of polymeric or bulk-like MoO_3 should be formed.

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