

Effect of gallium ions and of preparation methods on the structural properties of cobalt-molybdenum-alumina catalysts

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may in fact determine the conformations of particular residues through significant dipole-dipole interactions. The purpose of presenting the results of Table III here is merely to demonstrate that the approximate method is a valid one. Evaluation of the actual role played by long-range electrostatic effects in such processes as protein folding remains to be performed.

The computational time savings using the dipole method for the long-range interactions in a protein the size of pancreatic trypsin inhibitor is about 2.5. Thus, it also results in substantial reductions in computational times.

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References and Notes

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Effect of Gallium Ions and of Preparation Methods on the Structural Properties of Cobalt-Molybdenum-Alumina Catalysts

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Small amounts of gallium ions were added to γ -alumina and their influence on the structural properties of the system Co-(Mo)/ γ -Al₂O₃ was studied. It is shown that, due to the presence of Ga³⁺ ions, a "surface" spinel CoAl₂O₄ is formed with a larger amount of Co²⁺ in tetrahedral sites as compared to the spinel formed on gallium-free alumina. A decrease of the segregated Co₃O₄ is also observed. A possible effect of gallium ions on molybdenum is discussed. It is also reported that different preparation methods (single or double impregnation) lead to the formation of different surface species. Cobalt aluminate, molybdate monolayer, and Co₃O₄, depending on the Co content, are formed on doubly impregnated specimens. Cobalt aluminate and cobalt molybdate are the main species formed on singly impregnated specimens. Finally brief consideration is given to how the Co and Mo species, present in the oxide form, change in the sulfided form.

1. Introduction

In previous studies of supported oxide systems on alumina, it was shown that a "surface spinel" (MnAl₂O₄,¹ CoAl₂O₄,² NiAl₂O₄,³ CuAl₂O₄,^{4a,b}) was formed, either alone or in addition to an oxide phase. Additions of trace amounts of Zn²⁺, Ga³⁺, and Ge⁴⁺ ions⁵ modify the surface properties of alumina, thus affecting the structural features of supported transition metal ions. The presence of these ions, all having a preference for the tetrahedral site, favors a normal cation distribution in the surface spinel NiAl₂O₄.⁵ Since the type of symmetry adopted by supported cobalt and molybdenum directly influences their reactivity, it was of interest to investigate the influence of Ga³⁺ ions in the

hydrodesulfurization (HDS) of Co-Mo-alumina catalysts. Within this framework we have also examined how the order of addition of transition metal ion promoters affects the structural properties of the Co-Mo/Ga₂O₃- γ -Al₂O₃ system in the oxide form, and how the Co and Mo surface species present in the oxide forms are related to those developed in the sulfided catalysts.

2. Experimental Section

2.1. Catalyst Preparation. The gallium-containing γ -alumina support (A γ Ga) was prepared by impregnating γ -Al₂O₃⁶ with gallium nitrate. The soaked mass, dried at 120 °C, was heated at 500 °C for 15 h. Two nominal Ga contents (atoms per 100 Al atoms) were prepared: 0.6 and 4 (designated as A γ Ga0.6 and A γ Ga4).

Different portions of the A γ Ga0.6 and A γ Ga4 supports were impregnated with a solution of cobalt nitrate of

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TABLE I: Gallium-Containing Specimens and Their Properties

Samples	Co content, ^a wt %	Curie constant, C, erg G ⁻² mol ⁻¹ K	Magnetic moment, μ_B	Weiss temp $-\theta$, K	Co ²⁺ _{tet} , %
A γ GaCo(0.6:1)	1.12	3.11	4.99	20	42
A γ GaCo(0.6:2)	2.29	2.95	4.86	28	59
A γ GaCo(0.6:3)	3.15	2.96	4.87	35	58
A γ GaCo(0.6:4)	4.32	2.96	4.87	38	58
A γ GaCo(0.6:5)	5.29	2.95	4.86	46	(59) ^b
A-A γ GaMoCo(0.6:5:1)	1.42	3.60	5.35	30	0
A-A γ GaMoCo(0.6:5:2)	2.11	2.97	4.90	25	57
A-A γ GaMoCo(0.6:5:3)	3.31	2.97	4.90	30	57
A-A γ GaMoCo(0.6:5:4)	4.19	3.05	4.94	30	48
A-A γ GaMoCo(0.6:5:5)	4.96	3.05	4.94	36	(48) ^b
B-A γ GaMoCo(0.6:5:1)	1.17	2.86	4.80	22	68
B-A γ GaMoCo(0.6:5:2)	2.30	3.00	4.90	25	54
B-A γ GaMoCo(0.6:5:3)	3.07	3.28	5.12	23	24
B-A γ GaMoCo(0.6:5:4)	4.21	3.20	5.08	25	32
B-A γ GaMoCo(0.6:5:5)	4.80	3.28	5.12	23	24

^a Analytical, see text. ^b Due to the presence of Co₃O₄, the value is less accurate.

TABLE II: Gallium-Containing Specimens and Their Properties

Samples	Co content, ^a wt %	Curie constant, C, erg G ⁻² mol ⁻¹ K	Magnetic moment, μ_B	Weiss temp $-\theta$, K	Co ²⁺ _{tet} , %
A γ GaCo(4:1)	1.10				
A γ GaCo(4:2)	2.10	3.08	4.99	22	45
A γ GaCo(4:3)	3.05	3.06	4.95	35	47
A γ GaCo(4:4)	4.12	3.03	4.93	40	49
A γ GaCo(4:5)	5.20	2.95	4.86	43	(59) ^b
A-A γ GaMoCo(4:5:1)	0.95	3.39	5.21	22	12
A-A γ GaMoCo(4:5:2)	1.91	3.14	5.01	24	39
A-A γ GaMoCo(4:5:3)	3.12	2.98	4.89	28	(57) ^b
A-A γ GaMoCo(4:5:4)	4.44	2.48	4.48	30	c
A-A γ GaMoCo(4:5:5)	5.00	2.54	4.53	30	c
B-A γ GaMoCo(4:5:1)	0.97	2.95	4.88	10	59
B-A γ GaMoCo(4:5:2)	1.72	3.21	5.07	25	31
B-A γ GaMoCo(4:5:3)	2.77	3.20	5.07	26	32
B-A γ GaMoCo(4:5:4)	3.52	3.26	5.13	36	26
B-A γ GaMoCo(4:5:5)	4.50	3.20	5.08	31	32
CoMoO ₄ (green)	26.8	3.53	5.32	11	0
CoMoO ₄ (violet)	26.8	3.42	5.24	13	8

^a Analytical, see text. ^b Due to the presence of Co₃O₄, the value is less accurate. ^c Value not calculated due to the large amount of Co₃O₄ present.

known concentration. The material was then dried at 120 °C, ground, and fired at 600 °C for 24 h in air. Cobalt- and gallium-containing catalysts are designated as A γ GaCo(0.6:*x*) and A γ GaCo(4:*x*) with *x* (nominal Co content in atoms per 100 Al atoms) equal to 1, 2, 3, 4, or 5.

The Co-Mo-Ga-containing catalysts were prepared by two different methods.

Method A. The supports A γ Ga0.6 and A γ Ga4 were impregnated with an ammonium heptamolybdate solution to obtain a Mo content of 5 atom % with respect to 100 Al atoms. The paste was dried at 120 °C, ground, and fired at 500 °C for 5 h. The catalysts so obtained are designated as A γ GaMo(0.6:5) and A γ GaMo(4:5).

Cobalt was subsequently added to different portions of A γ GaMo(0.6:5) and A γ GaMo(4:5) by impregnation with a cobalt nitrate solution followed by drying at 120 °C, grinding, and firing in air at 600 °C for 24 h. The catalysts are designated as A-A γ GaMoCo(0.6:5:*x*) and A-A γ GaMoCo(4:5:*x*) with *x* = 1, 2, 3, 4, or 5 atoms of Co per 100 Al atoms.

Method B. The supports A γ Ga0.6 and A γ Ga4 were impregnated with an ammonium heptamolybdate solution in the same amount as in method A followed only by drying at 120 °C. Different portions of this material were again impregnated with a solution of cobalt nitrate. The mass was then dried at 120 °C, ground, and fired at 600

°C for 24 h in air. The catalysts so obtained are designated as B-A γ GaMoCo(0.6:5:*x*) and B-A γ GaMoCo(4:5:*x*) where *x* has the same values as before.

Sulfurization. Portions of A γ GaCo(0.6:*x*), A-A γ GaMoCo(0.6:5:*x*), and B-A γ GaMoCo(0.6:5:*x*) catalysts were sulfided in a silica reactor at 400 °C, for 2 h, in a flow of H₂ (90 cm³/min) and H₂S (10 cm³/min).

2.2. Physical Characterization and Chemical Analysis. Optical reflectance spectra were recorded on a Beckman DK 1 instrument, in the range 2500–210 nm at room temperature, using γ -Al₂O₃ as a reference. To check the influence of grain size on the reflectance spectra, some specimens were ground for 5 and 20 h in a mechanical mortar. The same spectrum was obtained in both cases. Therefore all spectra were recorded for samples ground for 5 h.

Magnetic susceptibility measurements were carried out by the Gouy method⁷ in the temperature range 100–295 K. The specimens were contained in a sealed silica tube.

X-ray analysis was carried out with Co radiation, using a Debye-Scherrer camera (114 nm diameter) or a diffractometer (Philips).

Chemical analysis for cobalt was performed by atomic absorption techniques (Varian Techtron AA5); concentrated H₂SO₄ was used to dissolve the specimens.³ The catalysts and some of their properties are listed in Tables I and II.

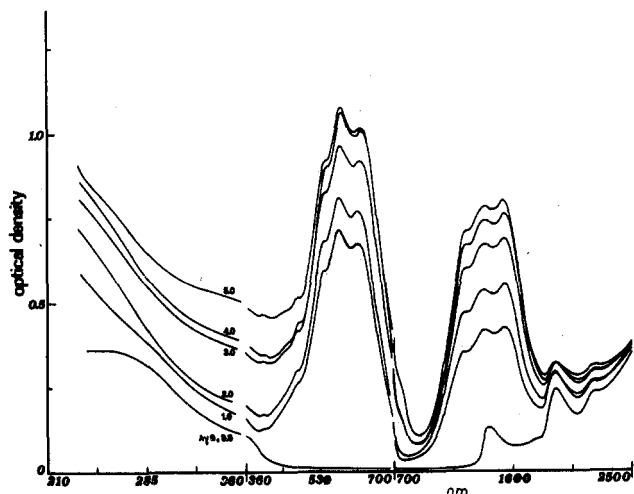


Figure 1. Reflectance spectra of $A\gamma\text{GaCo}(0.6:x)$ specimens with $x = 0-5$.

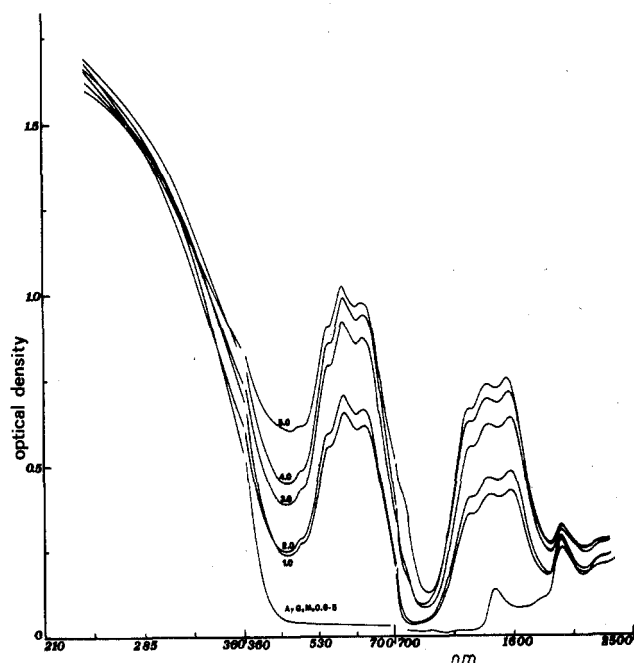


Figure 2. Reflectance spectra of $A-A\gamma\text{GaMoCo}(0.6:5:x)$ specimens with $x = 0-5$.

3. Experimental Results

3.1. *Reflectance Spectra.* Reflectance spectra were recorded for all samples. As the pattern of their spectra is essentially the same only representative series are reported. Figures 1 and 2 show the reflectance spectra of the $A\gamma\text{GaCo}(0.6:x)$ and $A-A\gamma\text{GaMoCo}(0.6:5:x)$ series, respectively. Detailed analysis of the reflectance spectra of Co^{2+} in different environments and of the assignment of optical transitions was discussed elsewhere.² Inspection of Figures 1 and 2 leads to the following conclusions:

(a) The spectra of the $A\gamma\text{GaCo}$ and $A\gamma\text{GaMoCo}$ specimens are dominated by bands due to Co^{2+} ions in tetrahedral symmetry² and their general pattern is qualitatively similar to that of the spinel $\text{Co}_x\text{Mg}_{1-x}\text{Al}_2\text{O}_4$ and of $\text{Co}^{2+}/\gamma\text{-Al}_2\text{O}_3$.²

(b) With increasing cobalt content the intensity of the absorption band at 578 nm is lower in the series $A\gamma\text{Co}_x$ (with $x \leq 3$ atom % since Co_3O_4 is present at higher x)² than in the $A\gamma\text{GaCo}(0.6:x)$ series, Figure 3, as well as for the $A\gamma\text{GaCo}(4:x)$ series.

Recalling that the band at 578 nm is the most intense band for $\text{Co}^{2+}_{\text{tet}}$, one is led to the conclusion that the

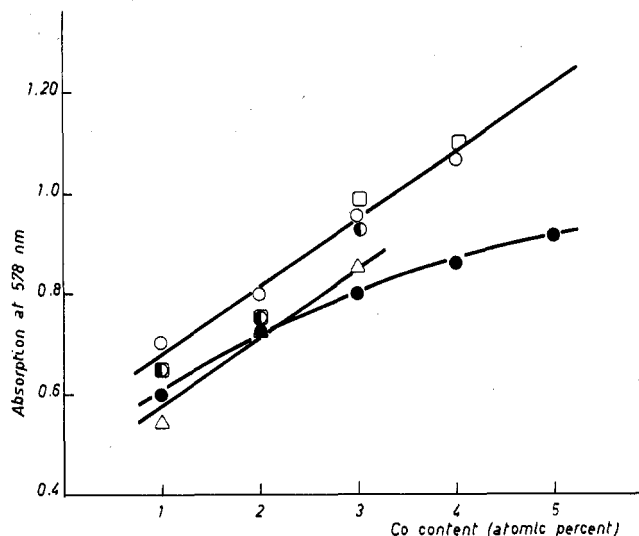


Figure 3. Intensity of the absorption band at 578 nm vs. cobalt content (atom percent): (Δ) $A\gamma\text{Co}_x$; (\circ) $A\gamma\text{GaCo}(0.6:x)$; (\bullet) $B-A\gamma\text{GaMoCo}(0.6:5:x)$; (\square) $A\gamma\text{GaCo}(4:x)$; (\bullet) $A-A\gamma\text{GaMoCo}(0.6:5:x)$.

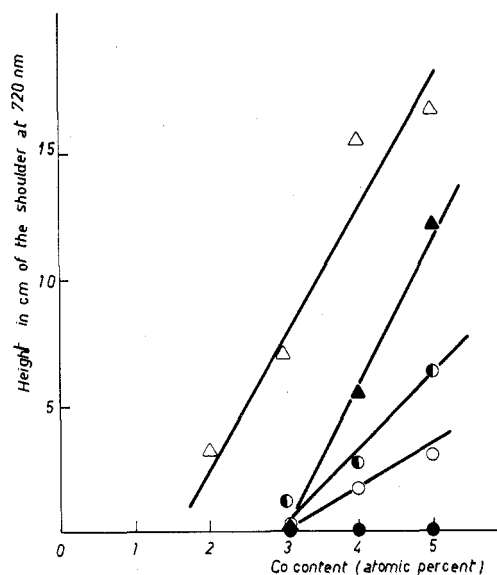


Figure 4. Intensity of the shoulder at 720 nm (Co_3O_4) vs. cobalt content (atom percent): (Δ) $A\gamma\text{Co}_x$; (\circ) $A\gamma\text{GaCo}(0.6:x)$; (\blacktriangle) $A\gamma\text{MoCo}(5:x)$; (\bullet) $A-A\gamma\text{GaMoCo}(0.6:5:x)$; (\bullet) $B-A\gamma\text{GaMoCo}(0.6:5:x)$.

amount of $\text{Co}^{2+}_{\text{tet}}$ is higher in Ga-containing specimens.

(c) Moreover, inspection of Figure 3 shows that the intensity of the band at 578 nm increases linearly with the Co content for $A\gamma\text{GaCo}(0.6:x)$ as well as for $A\gamma\text{GaCo}(4:x)$ and $A-A\gamma\text{GaMoCo}(0.6:5:x)$, while this is not the case for $B-A\gamma\text{GaMoCo}$, for which the curves become concave toward the abscissa at high Co content. This can be attributed to the presence of a new type of Co^{2+} with different symmetry. Since the extinction coefficient for octahedral Co^{2+} ions is smaller than for tetrahedral ions, the new type of Co^{2+} absorption can be attributed to ions in octahedral symmetry, probably in a new phase (the x-ray section clarifies this point).

(d) It is now useful to analyze the intensity of the shoulder at 720 nm, due to Co_3O_4 ² for different series of specimens. Figure 4 shows the change in intensity, reported as the height of the shoulder in cm, with increasing cobalt content for the series $A\gamma\text{GaCo}(0.6:x)$ and A - and B - $A\gamma\text{GaMoCo}(0.6:5:x)$; the figure also includes data for $A\gamma\text{Co}_x$ and $A\gamma\text{MoCo}(5:x)$.²

The gallium-free $A\gamma\text{Co}_x$ and $A\gamma\text{MoCo}(5:x)$ have a larger amount of Co_3O_4 , as compared to the gallium-containing

specimens $A\gamma\text{GaCo}(0.6:x)$ and $A-A\gamma\text{GaMoCo}(0.6:5:x)$ (with $x = 1-5$). Note that the samples of series $B-A\gamma\text{GaMoCo}$ do not show the presence of Co_3O_4 .

In conclusion, the reflectance spectra show that the presence of Ga^{3+} ions hinders the formation of Co_3O_4 . Moreover it favors a more normal CoAl_2O_4 spinel, i.e., a larger amount of Co^{2+} in tetrahedral sites, except for the B series in which formation of CoMoO_4 is favored (see x-ray section).

3.2. X-Ray Measurements. The phase identification via x-ray spectra for supported catalysts presents difficulties. However, the analysis of the results, as far as the presence of the surface spinel CoAl_2O_4 and/or Co_3O_4 is concerned, can be made along lines similar to those discussed elsewhere^{2,3} by comparing the intensities of different reflections, and, in more detail, the intensity profiles. The x-ray findings parallel the spectroscopic results.

It is useful to examine in more detail the x-ray spectra of $A\gamma\text{GaMoCo}$ catalysts according the method of preparation.

Method A. The x-ray pattern of $A-A\gamma\text{GaMoCo}(0.6:5:x)$ and $A-A\gamma\text{GaMoCo}(4:5:x)$ catalysts indicates only the formation of the surface spinel CoAl_2O_4 .

Method B. The formation of CoAl_2O_4 as a surface spinel is confirmed. Moreover, additional lines are visible for $\text{Co} \geq 2$ atom % and their intensity increases with cobalt content. These lines are attributable to CoMoO_4 phases; the lines at d spacing = 6.25, 3.50, 3.12, and 2.09 Å to the green CoMoO_4 ⁸ and the line at d spacing = 3.36 Å to the violet CoMoO_4 , called the "B" phase by Ricol^{9,10} and β phase by Sleight and Chamberland.¹¹ In particular, in the specimens with 0.6 atom % Ga both phases are present, while in specimens with 4 atom % Ga only the violet phase is present. Since this phase can be transformed into the green phase by grinding,^{10,12} we ground $B-A\gamma\text{GaMoCo}(4:5:x)$ for several hours. As a consequence, the line characteristic of the violet phase disappeared and the lines characteristic of the green phase appeared. Both CoMoO_4 phases were prepared to check the x-ray spectra.

Sulfided Catalysts. Sulfided $A\gamma\text{GaCo}(0.6:x)$ and $A-A\gamma\text{GaMoCo}(0.6:5:x)$ show spinel phase lines sharper than the corresponding oxidized specimens, without any additional lines. By way of contrast, the sulfided $B-A\gamma\text{GaMoCo}$ for $\text{Co} > 2$ show, besides sharper spinel phase lines, new lines at $d = 5.67, 2.98, 1.91,$ and 1.75 Å, attributable to Co_9S_8 (ASTM index). No lines attributable to MoS_2 appear; note that the lines of CoMoO_4 disappeared.

3.3. Magnetic Measurements. Tables I and II report the Curie constant C , the Weiss temperature θ , and the magnetic moment μ calculated from the Curie-Weiss law $\chi = C/(T - \theta)$, where χ is the magnetic susceptibility per mole of cobalt (actual analytical content) after correction for the diamagnetic contribution of all components.

Figure 5 reports the variation of C with cobalt content for some representative specimens and includes the data for $A\gamma\text{Co}_x$ and $A\gamma\text{MoCo}(5:x)$ ² for comparison.

From inspection of Figure 5 and Tables I and II it appears that the C values follow different trends according to whether gallium ions are present or absent and to the preparation method.

In principle, the C value is dependent on two distinct facts: (a) the presence of different phases, such as Co_3O_4 ($C \approx 1$),¹³ CoAl_2O_4 ($C_{\text{oct}} = 3.50$ ¹⁴ and $C_{\text{tet}} = 2.57$),¹⁵ or CoMoO_4 ($C = 3.54$); (b) the distribution of Co^{2+} ions among A (tetrahedral) and B (octahedral) sites of the surface spinel CoAl_2O_4 ; a higher C value corresponds to a higher $\text{Co}^{2+}_{\text{oct}}/\text{Co}^{2+}_{\text{tet}}$ ratio.

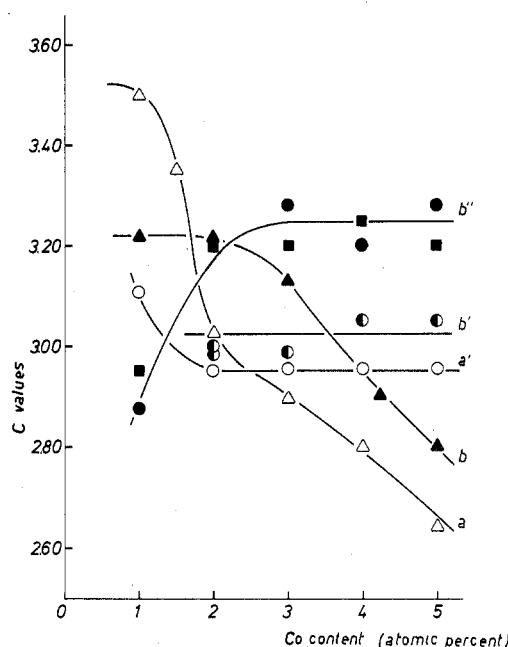


Figure 5. Curie constant, C , vs. cobalt content (atom percent): (Δ) $A\gamma\text{Co}_x$; (\circ) $A\gamma\text{GaCo}(0.6:x)$; (\blacktriangle) $A\gamma\text{MoCo}(5:x)$; (\bullet) $A-A\gamma\text{GaMoCo}(0.6:5:x)$; (\bullet) $B-A\gamma\text{GaMoCo}(0.6:5:x)$; (\square) $B-A\gamma\text{GaMoCo}(4:5:x)$.

It is then appropriate to examine the magnetic results in order to establish whether the variations in C correspond to the presence of these different phases or to a variation of the $\text{Co}^{2+}_{\text{oct}}/\text{Co}^{2+}_{\text{tet}}$ ratio in the surface spinel CoAl_2O_4 . (a) Since only CoAl_2O_4 is present at low cobalt content ($\text{Co} \leq 2$, see above), the C values depend on Co^{2+} ion distribution among A and B sites of the surface spinel CoAl_2O_4 . Thus, comparison of $A\gamma\text{Co}_x$ with $A\gamma\text{GaCo}(0.6:x)$ (curve a and a' of Figure 5) indicates that the presence of Ga^{3+} ions favors a more normal spinel; in fact, a smaller C values means a higher $\text{Co}^{2+}_{\text{tet}}$ content. (b) At higher cobalt content ($\text{Co} \geq 2$), the C values strongly decrease for the sample of series $A\gamma\text{Co}_x$ (curve a) and $A\gamma\text{MoCo}(5:x)$ (curve b), due to the presence of the phase Co_3O_4 , while it remains constant (curve a' and b') for samples of series $A\gamma\text{GaCo}(0.6:x)$ and $A-A\gamma\text{GaMoCo}(0.6:5:x)$. In this last case, they reflect the distribution of Co^{2+} ions among A and B sites of spinel CoAl_2O_4 , this being the major Co species present. (c) As for the specimens of series $B-A\gamma\text{GaMoCo}$, the magnetic data (curve b'', Figure 5) shows an increase of C up to $C = 2$. This is due to the building up of the CoMoO_4 phase in which Co^{2+} ions occupy octahedral sites.

Estimate of the Degree of Inversion from Magnetic Data. An estimate of the cobalt ions distributed in octahedral and tetrahedral sites can be made for those samples in which the Co^{2+} ions can be assumed to be present as the surface spinel CoAl_2O_4 ; for this purpose we will then neglect the samples containing amounts of Co_3O_4 . For the $B-A\gamma\text{GaMoCo}$ catalyst, containing the surface spinel CoAl_2O_4 and CoMoO_4 , it is also possible to estimate the amount of tetrahedral and octahedral cobalt ions. However, we can assume that the tetrahedral cobalt is present completely as the surface spinel CoAl_2O_4 , for the octahedral cobalt we cannot determine how much is present as CoAl_2O_4 and how much as CoMoO_4 . From the experimental values of the Curie constant, C_{expt} , and taking into account these restrictions, it is possible to use the law of additivity for computing the fraction of Co^{2+} ions in octahedral and tetrahedral sites.^{3,5} The results obtained using $C_{\text{oct}} = 3.50$ ¹⁴ and $C_{\text{tet}} = 2.57$ ¹⁵ are reported in Tables I and II.

It is necessary to emphasize that the percent values given for $\text{Co}^{2+}_{\text{tet}}$ are only estimates, because of the choice of C_{oct} and C_{tet} , but the relative effect should be real.

Discussion

The presence and amounts of Co_3O_4 , CoMoO_4 , and CoAl_2O_4 are not determined solely by the chemical composition but also by the method of preparation, namely, A and B. Furthermore, the results show that the surface spinel CoAl_2O_4 is always present and its cation distribution is affected by the presence of foreign ions (i.e., in this case, Ga^{3+} ions). Moreover, segregation of the Co_3O_4 phase depends on several factors, such as the cobalt content, the method of preparation, and the presence of Ga^{3+} ions.

We discuss in order the following topics: (1) the effect of gallium ions on the cobalt and molybdenum; (2) the state of the surface according to the method of preparation; (3) the sulfided specimens.

Influence of Gallium Ions on Cobalt and Molybdenum. In principle, in a spinel the M^{2+} ions can occupy tetrahedral (A) and/or octahedral (B) sites and the relative $\text{M}^{2+}_{\text{oct}}/\text{M}^{2+}_{\text{tet}}$ ratio depends on several parameters.¹⁶ In addition, recent studies⁵ on the structural and magnetic properties of Ni^{2+} ions supported on alumina showed that a small addition of Zn^{2+} , Ga^{3+} , or Ge^{4+} , all having a preference for tetrahedral sites, shifts the cation distribution in the surface spinel NiAl_2O_4 toward a more normal one.

The observed behavior was explained by invoking the polarization of anions toward tetrahedral sites. With this in mind, one would expect that the addition of cobalt ions to gallium-containing alumina, $\text{A}\gamma\text{GaCo}$ specimens, leads to a more normal CoAl_2O_4 spinel. The experimental observation matches this picture fully.

Especially in the specimens with high cobalt content, the experimental data (Figure 4) show that Co_3O_4 segregation is strongly decreased in the Ga-containing specimens ($\text{A}\gamma\text{GaCo}$ as compared to $\text{A}\gamma\text{Cox}$). In order to rationalize this point, we recall that segregation of oxides in supported systems is mainly affected by two factors:^{4a} (a) the stability of ions in the 2+ oxidation state; and (b) the diffusion pathways in the alumina lattice. It has been shown¹⁷ that for cations at tetrahedral sites the possible pathways in a spinel lattice always include a saddle position of octahedral symmetry. Now, if the crystal field around the octahedral sites is decreased when Ga^{3+} ions are added,⁵ one would expect a higher rate of diffusion of Co^{2+} ions. As a consequence, a greater amount of spinel is formed while the segregation of Co_3O_4 decreases.

The presence of Ga^{3+} may also influence the attachment of molybdate ions on the alumina surface. Molybdate monolayer formation has been extensively discussed by several authors.^{2,18-21} In our case it may be recalled that OH groups bonded to aluminum ions are about 100 times more basic than those bonded to gallium ions.²² Consequently, one would expect that molybdenum acid would react preferentially with aluminum octahedral OH giving molybdate ions attached to the surface. For a topotactic process, the molybdenum ions would occupy tetrahedral sites by extending the spinel structure immediately above the plane.^{20,21} As compared to $\text{A}\gamma\text{Mo}$, the $\text{A}\gamma\text{GaMo}$ specimens will have a somewhat larger amount of Mo^{6+} in tetrahedral sites and this fact may be relevant for catalytic reactions.

Influence of the Method of Preparation. Method A. This method consists of three successive impregnations and three calcinations according to the sequence Ga, Mo, and Co.

The first addition of Ga modifies the properties of the alumina surface.⁵ The second impregnation and calcination allows the Mo to react with the modified surface of the alumina giving a monolayer of molybdate ions attached to the alumina surface, in registry with the structure.^{2,18-21} In our case no separate phase of MoO_3 can be identified since the molybdenum content is fairly low. The cobalt, added with the third impregnation, now finds the structure of the external layers of alumina altered by the presence of Ga^{3+} and molybdate ions.

It may be noted that the presence of Ga^{3+} ions still allows the cobalt ions to react with alumina and favors a more normal spinel.

Finally, it should be emphasized that there is not a tendency to form the compound CoMoO_4 , since all the molybdenum has already reacted with the alumina surface.

Method B. Since B- $\text{A}\gamma\text{GaMoCo}$ catalysts were prepared by three impregnations but only two calcinations, the cobalt and molybdenum, react simultaneously (not in succession, as described for method A) with the alumina surface, and with each other. In fact, three reactions at 600 °C are able to occur simultaneously: (1) the reaction between Co- and Ga-containing alumina will give the cobalt aluminate, CoAl_2O_4 , and Co_3O_4 at high Co content; (2) the reaction between molybdenum and alumina will form molybdate ions attached to the alumina surface; (3) the reaction between molybdenum and cobalt¹² forms the CoMoO_4 phase.

The first reaction is dependent on the diffusion of cobalt ions into the external layers of alumina. The large surface area of alumina assists the process, by increasing the contact area between reagents.

The second reaction, considered as an acid-base reaction, should be dependent on the strength of the relative acids and bases involved and on the dispersion of molybdenum.

As far as the third reaction, the results obtained by Haber and Ziolkowski¹² for the system $\text{Co}_3\text{O}_4\text{-MoO}_3$ at 500 °C clearly indicate that the CoMoO_4 formation is rapid and dependent on the diffusion of molybdenum ions into Co_3O_4 grains. Thus, the species expected to arise as a function of Co content when the three reactions occur simultaneously can be accounted for as follows.

At low cobalt content, only the first and the second reactions occur. Apparently, the third process (CoMoO_4 formation) is also very rapid at 600 °C¹² although the strong interaction between cobalt and alumina tends to decompose the CoMoO_4 when this compound is heated with pure alumina.²³

Only at higher cobalt content does the formation of cobalt molybdate also occur, as a process taking place on the Co-rich external layers in competition with the diffusion of cobalt into the alumina. The experimental results match this picture fully. The x-ray data have shown that the formation of the CoMoO_4 phase starts to occur for a cobalt content ≥ 2 and its amount increases with increasing cobalt content. The reflectance spectra and magnetic measurements parallel the x-ray data showing that the cobalt ions, at higher cobalt content, go into octahedral sites as expected if CoMoO_4 is formed.

Sulfided Catalysts. As already reported, the effect of sulfiding is confined to the surface layers.² The process can be pictured as an exchange of surface OH^- to SH^- with a concomitant reduction of Mo^{6+} to lower oxidation states.^{2,24-27}

To throw light on the Co and Mo species which can be formed during the sulfurization, one has to take into account the species present in the oxide state.

According to literature data^{2,21,25,28} and to our results, the CoAl_2O_4 cannot be sulfided, but only their surface OH^- can be transformed into SH^- . However, if cobalt is present as separate phases (Co_3O_4 or CoMoO_4) it will undergo the Co_9S_8 transformation.^{2,21,28} Concerning molybdenum, it is currently reported that the sulfiding process of the Mo monolayer leads to an "oxysulfo" species rather than to a sulfided one.^{2,24,25} This conclusion is based on the lack of observation of MoS_2 . However, it must be pointed out that the sulfiding of B-A γ GaMoCo specimens, in which CoMoO_4 is present, produces only Co_9S_8 , the conditions being suitable for the formation of Co_9S_8 and MoS_2 . Indeed the sulfiding of pure and silica supported (Co-Mo/SiO₂) CoMoO_4 leads to the formation of cobalt and molybdenum sulfides.²⁹ Therefore, it can be argued that the growth of MoS_2 crystallites on alumina supported specimens probably occurs in two dimensions, failing x-ray detection. Another possibility could be that the crystallites are three-dimensional, but very small. Indeed, XPS studies show that MoS_2 is probably present.^{27,30}

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Analysis of Torsional Spectra of Molecules with Two Internal C_{3v} Rotors. 7.[†] Far-Infrared and Low-Frequency Raman Spectra of the Gaseous Dimethylphosphine

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The Raman spectrum of gaseous dimethylphosphine at a resolution of 1 cm^{-1} has been recorded between 100 and 400 cm^{-1} . The far-infrared spectrum has been recorded over the same frequency range with a resolution of 0.5 cm^{-1} . Considerable torsional data are reported and used to characterize the torsional potential function based on a semirigid model. The average effective V_3 was found to be $701 \pm 3\text{ cm}^{-1}$ (2.01 kcal/mol). The cosine-cosine coupling term, V_{33} , was found to be $240 \pm 8\text{ cm}^{-1}$ (0.68 kcal/mol) and the sine-sine term, V'_{33} , has a value of $-55 \pm 2\text{ cm}^{-1}$ (-0.16 kcal/mol). These data are compared to the corresponding quantities obtained from microwave data. Comparisons are also given to similar quantities obtained for other molecules.

Introduction

The vibrational spectrum of dimethylphosphine has been previously reported.^{1,2} Beachell and Katlafsky¹ reported the infrared spectrum of the gas and the Raman spectrum of the liquid and tentatively assigned the Raman lines at 236 and 318 cm^{-1} as the torsional motions. However, neither of these lines appeared in either the infrared or Raman spectra reported by Durlig and

Saunders² and these authors concluded that these two bands arose from impurities in the earlier sample. Durlig and Saunders² reported bands in the far-infrared spectra of solid $(\text{CH}_3)_2\text{PH}$ and $(\text{CD}_3)_2\text{PH}$ at 180 and 140 cm^{-1} , respectively, and assigned these bands to the CH_3 and CD_3 torsional modes. It was assumed that the frequencies for both torsional modes were essentially degenerate for both molecules and the threefold periodic barriers were calculated to be 2.14 and 2.30 kcal/mol for the CH_3 and CD_3 rotors, respectively. The barrier calculation was necessarily simplified because a proper characterization of the potential function for two interacting threefold rotors requires considerable experimental data.³⁻⁶ The availability of a

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