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Infrared and Optical Spectroscopic Study of Co–Mo–Al_2O_3 Catalysts[1]

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The oxide form of the Co–Mo–Al_2O_3 system and its interaction with CO, H_2O, thiophene, and pyridine have been studied by ir and electronic spectroscopy. From changes induced in the spectrum of Co^{2+} on adsorption of the above molecules, it is inferred that, even though a major fraction of cobalt is tetrahedrally coordinated to oxygen, a significant portion occurs on the surface with a trigonal (C_{3v}) coordination and adsorbs these molecules. The presence of molybdenum oxide is necessary for the formation of such trigonal Co^{2+} ions since, in its absence, the optical spectrum does not reveal the presence of trigonal Co^{2+}. Infrared spectroscopy was used to study the nature of the hydroxyl groups on Co–Al_2O_3, Mo–Al_2O_3, and Co–Mo–Al_2O_3. Cobalt was found to exert a major control on the mode of interaction of molybdenum species with the surface hydroxyls of alumina. In the presence of cobalt, reaction of selective OH groups with molybdenum-containing species occurs, leading to the presence of molybdenum in specific sites (probably in parallel rows) on the alumina surface. From the ir spectrum of adsorbed pyridine, it is found that both Brønsted and Lewis acid sites occur on the oxide surface. On sulfidation, Brønsted sites disappear. At least some of the Lewis sites constitute coordinatively unsaturated Co^{2+} and Al^{3+} ions.

I. INTRODUCTION

Even though the Co–Mo–Al_2O_3 catalyst system used in hydrodesulfurization reactions has been investigated by a variety of techniques, no convincing picture of the nature and promoting role of cobalt has yet emerged. For example, is the promoting effect of cobalt purely structural in character or does it also intervene in the reaction process? More specifically, do some of the cobalt ions occur on the surface and are, hence, accessible to reactant molecules? Or, are they all *exclusively* situated in subsurface layers and, hence, inaccessible, as postulated, for example, by the monolayer model of Schuit and Gates (*1*)? In the latter case, cobalt will be purely a structural promoter. Otherwise, the possibility that part of cobalt also serves as adsorption and reaction centers during the hydrodesulfurization reaction cannot be ruled out. A clarification of this question is essential for an understanding of the promoting effect of cobalt. In the present investigation, various probe molecules like H_2O, CO, pyridine, thiophene, and 1-butene have been adsorbed on the surface and the resultant changes in the energy levels, if any, of surface cobalt ions have been followed by near ir and electronic spectroscopy. Only those cobalt ions on the surface which act as adsorption sites are expected

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to undergo changes in their electronic spectra on adsorption of these molecules. It is proposed to demonstrate that not only do coordinatively unsaturated cobalt ions occur in the surface layer but also that they chemisorb the above-mentioned probe molecules and undergo characteristic changes in their spectral properties.

The surface of alumina is known to contain basic, neutral, and acidic hydroxyl groups (*2*). How are these groups affected when Mo, either alone or along with Co, is deposited on alumina? Infrared spectroscopy is ideally suited for such an investigation. Even though Kiviat and Petrakis (*3*) have reported the formation of pyridinium ions on the surface of $Mo-Al_2O_3$ and $Co-Mo-Al_2O_3$, no ir spectroscopic study of the nature of the hydroxyl groups on these catalysts and their perturbation in the presence of adsorbed molecules has so far been reported. Results of the present study indicate that cobalt and molybdenum species have mutual influence not only on the state of each other but also on the relative concentrations of the various hydroxyl groups (of alumina) when present simultaneously on the alumina support.

II. EXPERIMENTAL

The high purity (>99.9%) alumina (from pure boehmite) support had a BET surface area of 180 m^2/g and contained about 650 ppm of Na and less than 10 and 20 ppm of Fe and Si, respectively. This alumina was impregnated with an aqueous solution of cobalt nitrate to obtain the CoAl sample (2.8% CoO by wt). The Mo–alumina (MoAl) sample (12% MoO_3 by wt) was prepared by impregnation from an aqueous solution of ammonium paramolybdate. The Co–Mo–alumina (CoMoAl: 2.5% CoO and 11.5% MoO_3 by wt, respectively) was prepared similarly by a simultaneous impregnation of cobalt and molybdenum from an aqueous solution containing a mixture of cobalt nitrate and ammonium paramolybdate. All the samples were dried at 383 K for 24 hr and were calcined in air at 823 K for 24 hr prior to use. A commercial sample of similar composition (Harshaw) was also used for purposes of comparison.

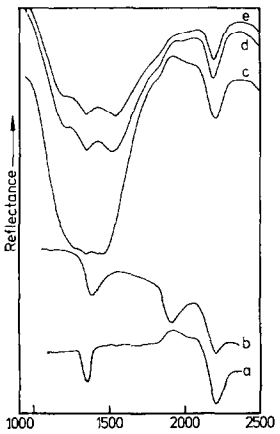


FIG. 1. Diffuse reflectance spectra of samples Al, MoAl, CoAl, CoMoAl, and Harshaw (a, b, c, d, and e, respectively) in the region 1000 to 2500 nm. The curves have been shifted in the ordinate direction for better exposition.

The vaccum cell used in ir spectroscopic investigations has been described before (*4*). The spectra were scanned with a Perkin–Elmer ir spectrometer Model 225. All spectra were scanned at ambient temperatures. Samples were examined in the form of thin, compressed (2×10^7 Pa), self-supporting wafers. Due to the heating of the sample in the ir beam, its temperature during a typical scan is estimated to be around 353 K. Attenuation of the reference beam was used to enhance the quality of the spectra. The spectral resolution was about 2–3 cm^{-1} in all experiments.

The diffuse reflectance electronic spectra of the samples were measured with a Beckman ratio recording spectrophotometer (Model DK-2 A). The sample, in the form of a powder, was contained in special quartz sample cells which could be attached to a conventional high vacuum system and pretreated at temperatures up to 873 K under different ambient conditions. The samples were then isolated from the vacuum system

and, without being exposed to air, were transferred to the spectrophotometer; their spectra were recorded at room temperatures. Unless otherwise mentioned, all samples were studied only in the oxide state. Anhydrous $BaSO_4$ was used as the reference.

III. RESULTS AND DISCUSSION

1. *Nature of Cobalt*

(*a*) *Tetrahedral* Co^{2+}. Figures 1 and 2 show the electronic spectra of the various samples in the region 400 to 2500 nm in the oxide state after evacuation at 773 K for 2 hr. Pure alumina exhibits a small absorption band at 1350 nm. It is also responsible for the strong adsorption in the region around 2200 and 2700 nm (the latter not shown in Figs. 1 and 2), respectively. In samples containing cobalt (CoAl, CoMoAl, and Harshaw, respectively) there are two intense triplets around 1375 and 575 nm, respectively. These bands are due to cobalt surrounded tetrahedrally by oxygen ions (*5*). Molybdenum, when present (as in samples of MoAl, CoMoAl, and Harshaw, respectively), is responsible for the strong absorption below 400 nm.

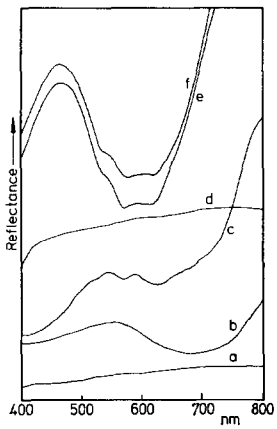


FIG. 2. Diffuse reflectance spectra of samples Al, Co_3O_3, CoAl, MoAl, CoMoAl, and Harshaw (a, b, c, d, e, and f, respectively) in the region 400 to 800 nm. The curves have been shifted in the ordinate direction for better exposition.

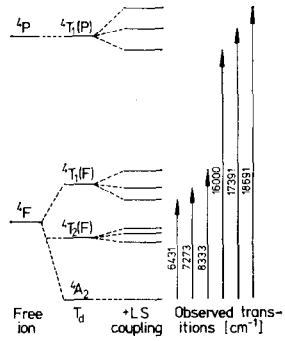


FIG. 3. Schematic diagram of the electronic transitions and band assignments for Co^{2+} in the CoMoAl sample. (Wavenumbers of transitions observed in present study.)

Lipsch and Schuit (*6*) had also observed a similar strong absorption due to molybdenum in this range and had assigned it to a monolayer of molybdenum oxide.

In a crystal field environment of T_d symmetry, the ground-state energy level ^4F of Co^{2+} is split into three levels, $^4A_2$, $^4T_2$, and $^4T_1(F)$, respectively. Electronic transitions among these and the next higher level $^4T_1(P)$ are shown schematically in Fig. 3. The diagram (*5*) also illustrates the split induced in the energy levels due to spin–orbit (or LS) coupling. The bands due to cobalt (in the sample CoMoAl) observed in Figs. 1 and 2 are assigned to the various transitions shown in Fig. 3. The band due to the transition ($^4T_2 \leftarrow {}^4A_2$) occurs around 2200 nm, but, since there is also a strong band in this region due to alumina, it is difficult to assign the frequency of transition accurately. The spectrum of the Harshaw sample (curve e in Fig. 1 and curve f in Fig. 2) is quite similar to that of CoMoAl. We may, hence, conclude that the cobalt ions in both these samples are in very similar environments and that at least a significant fraction of them possesses a T_d symmetry with respect to oxygen ions. Based on our results, it is difficult to rule out completely the presence of Co^{2+} in octahedral environments since the intensity of the corresponding bands will be an order of

TABLE 1

Crystal Field Parameters for Co^{2+} in Tetrahedral Symmetry[a]

Compound	ν_2	ν_3	$10\,D_q$	B	Reference
Co/ZnS	6,640	14,300	3,855	622	(*5*)
$Co(NO_3)^{2-}$	8,860	18,600	4,660	755	(*25*)
$Co(N_3)_4^{2-}$	6,750	14,900	3,920	658	(*26*)
CoMoAl	7,017	16,949	4,059	786	Present study
Harshaw	6,780	16,949	3,903	801	Present study

[a] Values are expressed per centimeter.

magnitude lower and hence will be masked by the intense bands of the tetrahedral Co^{2+} (*7*).

In order to describe semiquantitatively the electronic energy levels of tetrahedral Co^{2+} in both these samples, values of their crystal field stabilization energy, $10D_q$, and Racah's parameter B were computed (*8*). Evaluation of the Tanabe–Sugano matrices for tetrahedral Co^{2+} leads to the following equations for ν_2 and ν_3 [the frequencies are expressed per centimeter for the transitions $^4T_1(F) \leftarrow {}^4A_2$ and $^4T_1(P) \leftarrow {}^4A_2$, respectively]:

$$\nu_2 = 15D_q + 7.5B - Q,$$

$$\nu_3 = 15D_q + 7.5B + Q.$$

where $Q = \frac{1}{2}[(-6D_q + 15B)^2 + 64(D_q)^2]^{\frac{1}{2}}$. By substituting the observed values of ν_2 and ν_3 from the spectra and solving the equations simultaneously, values of $10D_q$ and B may be obtained. For computational purposes, the ν_2 and ν_3 transition frequencies were assumed to correspond with the centers of gravity of the triplet bands (*9*). In Table 1, values of $10D_q$ and B so derived along with ν_2 and ν_3 values are compared with those of known, well-defined complexes of cobalt possessing T_d symmetry. Within the limitations of the theory (*10*) the agreement seems to be satisfactory and confirms our conclusion that the predominant fraction of cobalt is indeed tetrahedrally surrounded by oxide ions. Whether these four oxide ions are in turn coordinated only to aluminium (as in $CoAl_2O_4$), or only to molybdenum (as in $CoMoO_4$), or to both aluminium and molybdenum [as in $Al_2(MoO_4)_3$] is not clear from our results. In our opinion, the published studies of this system by ESCA (*11*), reflectance spectroscopy (*5*, *12*), and ESR (*13*, *14*) also fail to provide an unambiguous answer to the above question. These spectroscopic techniques measure atomic properties and are not sufficiently sensitive to yield information about the presence, if any, of short-range order (on the order of, say, 1 nm) in the amorphous samples. X-Ray scattering techniques might, probably, be more useful.

Before describing the changes in the absorption spectrum of cobalt on adsorption of various probe molecules it is worthwhile to point out the influence of molybdenum on the site symmetry around Co^{2+}. In Figs. 1 and 2 the absorption curves for Co^{2+} in CoAl are seen to be quite different from those in CoMoAl (compare Figs. 1c and 2c with 1d and 2e, respectively). In fact, the strong absorption around 675 and 400 nm for the sample CoAl (Fig. 2c) is quite similar to that in Co_3O_4 (Fig. 2b). For a sample of Co_3O_4, Ashley and Mitchell (*12*) had also observed absorption maxima around 370 and 660 nm, respectively. It might be recalled here that both the CoAl and the CoMoAl samples were prepared from a single batch of alumina support, contain the same amount of cobalt, and

have been calcined at the same temperature of 823 K for 24 hr. The observed differences in the electronic spectra imply that molybdenum has an influence on the coordinative environment of cobalt; in its absence, even though a part of Co^{2+} enters into a tetrahedral coordination in the alumina lattice, a significant portion occurs as small patches of an oxide of cobalt. In the presence of Mo^{6+}, the oxide phase is suppressed and a predominant portion of the Co^{2+} is surrounded tetrahedrally by oxygen. On calcination at 823 K for 24 hr no bulk $CoAl_2O_4$ phase could be detected by X-ray diffraction in either CoAl or CoMoAl. This phase is obtained only when calcination temperatures exceed 973 K.

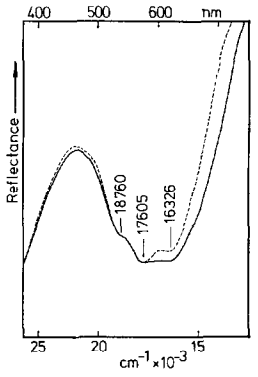


FIG. 4. The influence of water vapor on the visible spectrum of Co^{2+} in the Harshaw sample. (——) Sample evacuated at 823 K for 2 hr; (– – – –) H_2O adsorbed on the above at 298 K during 10 min under a pressure of 1300 Pa.

(*b*) *Trigonal* Co^{2+}. Figure 4 shows the influence of H_2O on the visible spectrum of Co^{2+} in the Harshaw catalyst. The changes observed on hydration were completely reversible. That is, on evacuation at elevated temperatures, the original spectrum (solid line) was obtained again. Identical results were obtained in the case of CoMoAl also. Even though there were spectral changes in the region 1000–2000 nm on adsorption of water, their interpretation is complicated by the absorption due to the alumina support in the same region. The latter absorption is especially sensitive to the degree of hydration of the sample. Similar changes, namely, a reduction in the intensity of absorption in the region 575 to 800 nm, together with a better resolution of the triplet bands due to tetrahedral cobalt were also observed on adsorption of pyridine, thiophene, and 1-butene. Such changes were, however, not observed in the case of CoAl. In the latter case, the absorption spectrum was not modified at all on adsorption of the above probe molecules. The spectral changes brought about by pyridine, thiophene, and 1-butene in the case of CoMoAl and Harshaw samples were not reversible. On evacuation at higher temperatures, strongly absorbing carbonaceous species were formed on the surface completely masking the spectra due to cobalt.

Since Co^{2+} ions are the only species responsible for the spectrum in Fig. 4, the observed changes imply that at least some of them occur on the surface layer and, in addition, chemisorb molecules like thiophene, 1-butene, pyridine, and water. Moreover, since CoAl does not exhibit such changes, it is the presence of molybdenum which has led to the exposure of such surface Co^{2+} ions. The observed diminution in intensity is evidently due to changes in the coordination number of Co^{2+} and not in its oxidation state. Co^{3+} in corundum (α-Al_2O_3) has an absorption maximum around 430 nm (*15*). The absence of such a maximum and, in fact, any changes in this spectral region in Fig. 4 rule out the involvement of Co^{3+} in this process. Moreover, the similar spectral changes brought about by such diverse molecules like water and 1-butene suggest that Co^{2+} ions undergo a change in their coordination number on adsorption of these molecules. It is suggested that trigonally coordinated Co^{2+} ions (of C_{3v} or D_{3h} symmetry; it is difficult to distinguish between the two due to the absorption band of molybdenum below 450 nm) adsorb the probe molecules and attain a tetrahedral coordination. The

TABLE 2

Electronic Transitions of Co^{2+}

Matrix	Symmetry	Electronic transition (cm^{-1})	Reference
$MgAl_2O_4$	T_d	16,130; 16,780; 17,240;	(*27*)
$Co(Me_6tren)Cl^+$	D_{3h}	12,500; 15,600; 16,100; 20,000;	(*28*)
Sapphire	C_{3v}	15,875; 22,730;	(*29*)
Zeolite *y*	C_{3v}	13,890; 15,400; 16,800;	(*30*)
Zeolite A	D_{3h}	13,700; 15,750; 16,772; 18,425; 24,000;	(*17*)
SiO_2	D_{3h}	14,000; 16,000; 20,000;	(*16*)
Co-Mo-Al_2O_3		15,500; 16,700; 18,000;	(*12*)
Co-Mo-Al_2O_3		16,000; 17,000; 18,500;	(*6*)
Harshaw		16,326; 17,605; 18,760;	Present study
CoMoAl		16,000; 17,391; 18,691;	Present study

diminution in intensity seen in the spectra of Fig. 4 follows from the increase in local symmetry at Co^{2+} from C_{3v} or D_{3h} to T_d. Table 2 compares the electronic transitions of Co^{2+} in various trigonal and tetrahedral symmetries. Of special relevance, in the present context, are the studies of Kazansky *et al.* (*16*) and Klier (*17*). The former, investigating the optical spectrum of Co^{2+} in Aerosil, attributed the absorption maxima at 714 nm to Co^{2+} ions in D_{3h} symmetry. On adsorption of olefins or saturated hydrocarbon molecules, these formed tetrahedral complexes. Trigonal Co^{2+} ions in D_{3h} symmetry were also observed by Klier (*17*) in Co(II)-exchanged, dehydrated type A zeolite. The decrease in reflectance along with a better resolution of the triplet bands of tetrahedral Co^{2+} on adsorption of H_2O observed by Klier [see Fig. 2 of Ref. (*17*)] is quite similar to our results in Fig. 4. This lends additional support to our conclusion that, on the surface of both the Harshaw and CoMoAl samples, trigonally coordinated Co^{2+} ions are present which can form surface complexes with adsorbed molecules.

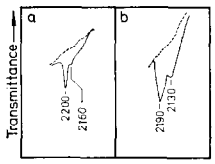


FIG. 5. Infrared spectra of carbon monoxide adsorbed on Harshaw (a) and CoMoAl (b) samples. (– – – –) Samples evacuated at 823 K for 2 hr before adsorption of Co; (——) adsorption of CO at 353 K and a pressure of about 1.3×10^4 Pa.

(*c*) *Adsorption of carbon monoxide on trigonal* Co^{2+}. If trigonal Co^{2+} ions are exposed on the surface, then selective chemisorption measurements with CO may be used to confirm their existence. No ir bands due to chemisorbed CO could be discerned on Al and MoAl samples. On CoAl only a very weak band around 2185 cm^{-1} could be seen (see Fig. 7). On CoMoAl and Harshaw samples, however, a sharp intense band at 2200 and a weak shoulder at around 2160 cm^{-1} (in the case of the Harshaw sample) could clearly be distinguished (Fig. 5). As the frequencies correspond very well with those of Angell and Schaffer (*18*) for the adsorption of CO on Co^{2+} ions in zeolite X, these bands are clearly assigned as stretching vibrations of CO molecules coordinated to exposed Co^{2+} ions, most probably in the tricoordinated state. The coordinative bond is, however, weak as it disappears on pumping at 353 K.

Yao and Shelef (*19*) had earlier found that, while Co_3O_4 adsorbs CO molecules, the Co^{2+} ions in $CoAl_2O_4$ do not do so and hence are well shielded. The observation of a CO stretching band in our CoAl sample

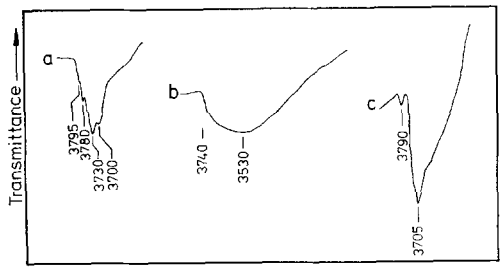


FIG. 6. Infrared spectra of hydroxyl groups on CoAl, MoAl, and Harshaw samples (a, b, and c, respectively). The samples were evacuated at 823 K for 2 hr. The numbers refer to the positions of the ir bands (per centimeter).

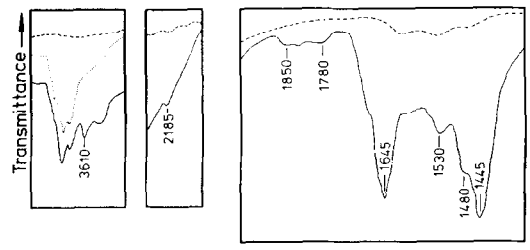
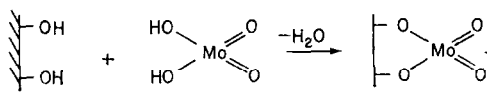


FIG. 7. Infrared spectral changes on adsorption of CO (1.3×10^4 Pa) on CoAl and MoAl samples. (·····) Background for CoAl; (——) and (– – – –) adsorption of CO on CoAl and MoAl, respectively. The numbers refer to the positions of ir bands (per centimeter).

is therefore due to adsorption on the Co_3O_4 patches present on the surface of CoAl and supports our assignment of the bands in the optical spectrum (curve b, Fig. 2) to Co_3O_4. Since only the Co^{2+} ions in octahedral sites adsorbed CO (*19*), the absence of changes in the optical spectrum of CoAl on adsorption of H_2O is quite understandable since the extinction coefficient for such bands is very small. Changes in the intensity of the spectrum of octahedral Co^{2+} on adsorption of water or pyridine are expected to be negligible.

2. Surface Hydroxyl Groups

Figure 6 shows the ir spectra in the OH stretching region for CoAl, MoAl, and Harshaw samples. The spectrum of CoAl is typical of that of pure alumina (*2*). Cobalt ions apparently do not disturb the nature of surface hydroxyls on alumina. In the case of MoAl, a broad band centered around 3550 cm^{-1} and extending down to 3000 cm^{-1} is observed. The hydroxyl groups of alumina absorbing in the region 3700 to 3800 cm^{-1} have been either eliminated or shifted to lower wavenumbers on deposition of molybdenum oxide. They may be eliminated by reaction with the molybdenum species as shown below.



Defaux *et al.* (*20*) had also arrived at a similar conclusion from thermogravimetric measurements. The extension down to 3000 cm^{-1} of the OH band in MoAl implies the presence of acidic hydroxyl groups (probably hydrogen bonded) on it. These hydroxyl groups are the probable source of protons in the formation of pyridinium ions on adsorption of pyridine (*3*).

The differences in the nature of the interaction of cobalt and molybdenum species with the OH groups of alumina are illustrated further in Fig. 7 which shows the spectral changes on adsorption of CO on CoAl and MoAl. On CoAl, in addition to the C≡O stretching band at 2185 cm^{-1}, a new OH stretching band is observed at 3610 cm^{-1} and a whole series of absorptions are seen in the region 1400 to 1900 cm^{-1}. This behavior is very similar to that observed on adsorption of CO on alumina and is characteristic of the formation of carbonate and bicarbonate species due to the interaction between adsorbed CO and the alumina hydroxyl groups (*21*, *22*). The absence of similar hydroxyl groups on MoAl is the reason for the presence of only weak bands in its spectrum.

When both cobalt and molybdenum are present together (Fig. 6, curve c), only two OH bands at 3790 and 3705 cm^{-1} are observed. The original central bands of alumina in the region 3730 to 3740 cm^{-1} have disappeared, presumably due to reac-

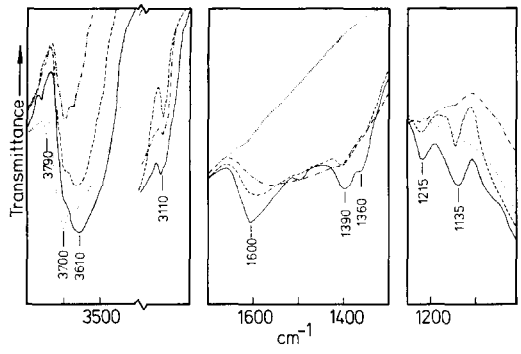


FIG. 8. Infrared spectra of thiophene adsorbed on the Harshaw sample; the adsorption was carried out at 353 K and 1300 Pa for 10 min. (·····) Background; thiophene desorbed at (——) 353 K, (– – – –) 423 K, and (–·–·–) 563 K.

tion with the molybdenum species. An important influence of cobalt in controlling the interaction of molybdenum with the alumina support is apparent here. In the absence of cobalt, the molybdenum species interacts indiscriminately with all hydroxyl groups of alumina. In its presence, however, only those OH groups responsible for the bands at 3730 to 3740 cm^{-1} react selectively with molybdenum. What is the structural nature of these hydroxyl groups? A new model for the surface OH groups on alumina has recently been presented (*2*). According to this model, those OH groups which absorb in the range 3730 to 3740 cm^{-1} [configurations IIa and IIb of Ref. (*2*)] correspond to bridging hydroxyls in either the A and B layers of the (111) face or in the C layer of the (110) face. These are aligned in parallel rows on the alumina surface (*2*). If the positions previously occupied by these rows of OH groups are now occupied by molybdenum moieties (see diagram above) we are then led to a surface model wherein a significant portion of the Mo occurs in one-dimensional chains. The mechanism through which cobalt exerts this influence is not clear. From gravimetric measurements of the rates and stoichiometry of sulfidation of a 8% Mo/γ-alumina catalyst, Massoth had earlier postulated (*23*) a surface model for Mo/alumina samples consisting of one-dimensional chains of MoO_2 over the alumina substrate. The third O associated with Mo was placed in vacancies in the alumina lattice. In agreement with our results, he had also found a lower OH concentration on the Mo/alumina sample compared to alumina. In addition, the infrared spectrum of a sample of 3% Mo/γ-alumina showed that two of the OH bands of the γ-alumina had disappeared and one new absorption band had appeared (*23*). The disappearance of *all* the OH bands in our sample, MoAl, is perhaps due to the larger Mo concentration in it. However, it should be noted that all the above observations of Massoth were made on a Mo/alumina sample, whereas the similar results observed by us were obtained on the Co–Mo–alumina catalyst. It is probable that cobalt enables the selective interaction between molybdenum moieties and alumina hydroxyl groups to occur even at higher concentrations of molybdenum.

3. *Adsorption of Thiophene and Pyridine*

Cobalt–molybdenum catalysts are used mainly in desulfurization reactions where thiophene or its derivatives like benzo- and dibenzothiophenes form a significant fraction of the molecules containing sulfur in the feedstock. Before use, the oxide catalysts are presulfided in an atmosphere of H_2 and any one of a variety of sulfur-containing species like H_2S, CS_2, $(CH_3)_2S$, or even the feedstock itself. An infrared spectroscopic study of the interaction of thiophene with the oxide form of the catalyst is, therefore of intrinsic interest. Figure 8 shows the ir spectra of thiophene adsorbed on the Harshaw catalyst which was previously evacuated at 873 K for 4 hr. After adsorption at 353 K, the sample was evacuated progressively at 353, 503, and 563 K. The ir frequencies of the species remaining after desorption along with their probable assignments are collected together in Table 3.

TABLE 3

Thiophene ir Bands

Vapor	Chemisorbed after desorption at			Assignment
	AT[a]	423 K	563 K	
3126 (m)	3120	3110	3100	 C–H stretching
3098 (s)				
3086 (s)				
1583 (s)	1600	1595	1580	Conjugated
1575 (s)				
1409 (s)	1395	1400	1400	 Rocking
1393 (s)	1360	1360	—	
1256 (s)	1215	1220	—	
1083 (s)	1135	1140	1140	

[a] Ambient temperature.

No ir bands characteristic of molecular thiophene (the strong bands at 3086 and 3098 cm^{-1}, for example) are observed in Fig. 8, even at 353 K. The oxide surface is, hence, a highly reactive one and decomposes the adsorbed thiophene molecules even at relatively low temperatures. This conclusion is further supported by the fact that ir bands of decomposed products (like that at 1135 cm^{-1}, representing the C=S group) are present even at 353 K. The various groups responsible for the ir bands in Table 3 may constitute a single or several surface species, probably the latter. The intensities of the different bands, for example, do not vary in the same direction on evacuation at higher temperatures. In addition to the observation of such hydrocarbon moieties, major irreversible changes are also seen in the OH stretching region. Even though there is a fractional elimination of all the hydroxyl groups, the OH groups absorbing at 3790 cm^{-1} have undergone complete selective elimination. It may be noted here that it is precisely this type of OH group [called type Ia in Ref. (*2*)] which has been postulated to constitute part of the active center for adsorption and catalytic reactions on the alumina surface. Their perturbation and disappearance is caused presumably by their reaction or sulfidation on adsorption of thiophene. This phenomenon further reveals that, even though the molybdenum and cobalt species may constitute the principal reaction centers for the desulfurization reaction, the alumina surface also takes part in the adsorption and reaction of thiophene molecules at least during the initial presulfidation.

What is the structural nature of the sites which adsorb thiophene? It was earlier shown (section 1b) that at least part of the thiophene is adsorbed on trigonal Co^{2+} ions, converting them to the tetrahedral coordination state in the process. To investigate the nature of the other sites which also adsorb thiophene, selective poisoning was done with pyridine, a Lewis base. After adsorption of pyridine on the Harshaw sample at 473 K, the material was evacuated for 30 min at 473 K. On such a pyridine-covered surface, when thiophene was contacted at 353 K, only physical adsorption occurred. Only weak bands due to molecular thiophene were observed

which were easily removed on pumping at 353 K leaving the original spectrum of adsorbed pyridine undisturbed. Thus, both pyridine and thiophene are chemisorbed on the same Lewis acid sites, and pyridine being a stronger Lewis base successfully competes for it.

The spectrum of adsorbed pyridine revealed the presence of both Lewis and Brønsted acid sites on the surface of MoAl and Co–Mo–alumina catalysts, confirming the similar observations of Kiviat and Petrakis (*3*). These authors, had, however, not reported the influence of adsorbed pyridine on the surface hydroxyl groups. In our study on adsorption of pyridine at 353 K, the band at 3700 cm^{-1} (type III) is reduced in intensity, the band at 3790 cm^{-1} (type Ia OH groups) disappears, and there is a new broad OH band at 3600 cm^{-1}. These changes are irreversible in that desorption up to 573 K does not significantly affect the spectrum. On the MoAl sample, on adsorption of pyridine under the same conditions, there is a reduction in the intensity of the broad OH band in the region 3340 to 3740 cm^{-1}. Since the presence of pyridinium ions is simultaneously detected on both these samples, it is likely that the reduction in the OH band intensity is due to the transfer of some protons of these hydroxyls group to adsorbed pyridine molecules. The ir spectrum of pyridine adsorbed on the Harshaw sample, which had been sulfided with a mixture of H_2 and CS_2 (10:1) at 523 K for 4 hr in a flow system, revealed the presence of only Lewis acid sites. The ir band at 1545 cm^{-1} characteristic of the pyridinium ion was absent. The concentration of the Lewis acid sites was also lower compared to the same catalyst in the oxide state. Hence, it is doubtful whether Brønsted acid sites play a role in the desulfurization reactions over the sulfided catalyst. It was earlier stated (section 1c) that adsorption of pyridine induced changes in the electronic spectrum of trigonal Co^{2+}. It was also shown there that CO adsorbs selectively on trigonal Co^{2+}. Competitive adsorption experiments involving pyridine and CO revealed that preadsorption of pyridine blocks completely the sites for CO adsorption. Trigonal Co^{2+} ions on the surface should, hence, also be included among the Lewis acid sites.

The phenomenon of selective elimination of the 3790 cm^{-1} band on adsorption of pyridine or thiophene is also similar to that observed on pure alumina (*24*). Lewis acid sites, probably the same as the "X sites" of pure alumina (*2*), are present also on the surface of Co–Mo–alumina and adsorb molecules like thiophene and pyridine. Their possible role during the presulfidation and desulfurization reaction processes should be understood before any meaningful picture of the "active center" can be formulated.

IV. CONCLUSIONS

Three important conclusions regarding the surface structure of Co–Mo–alumina catalysts in the oxide state may be drawn from our results.

(i) Even though a major portion of cobalt occurs in a tetrahedral environment of oxygen ions, a significant fraction of them occurs on the surface with a trigonal (C_{3v}) symmetry coordination of oxygen ions. Being coordinatively unsaturated and well exposed they adsorb molecules like thiophene, pyridine, water, and CO. Their formation is enhanced by molybdenum since in its absence the optical spectrum does not reveal the presence of trigonal Co^{2+}.

(ii) Cobalt ions exert a major control in the mode of interaction of molybdenum species with the surface hydroxyl groups of alumina. In the presence of cobalt, reaction of selective hydroxyl groups with molybdenum-containing species occurs, leading to the presence of molybdenum in specific sites (probably in parallel rows) on the alumina surface.

(iii) Both Lewis and Brønsted acid sites occur on the oxide surface. At least some of the Lewis acid sites are composed of trigonal Co^{2+} ions and the "X sites" of the pure alumina portion of the surface (*2*). Cobalt ions should, hence, be considered not only as structural promoters but also as adsorption and reaction centers for sulfur-bearing molecules at least during the presulfidation of the catalyst. Even though Lewis acid sites are still present on the sulfided surface, Brønsted sites are absent.

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