FT–IR Study of CO Adsorption on Sulfided Mo/Al$_2$O$_3$ Unpromoted or Promoted by Metal Carbonyls: Titration of Sites

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The IR study of CO adsorption at low temperature has been used to follow the transformation of unpromoted Mo sites into promoted ones on sulfided Mo/Al$_2$O$_3$ catalysts. The promotion is realized by thermal decomposition of different amounts of Co(CO)$_3$NO on sulfided Mo/Al$_2$O$_3$. The determination of integrated molar extinction coefficients of the ν(CO) bands corresponding to the different sites has been performed. For the unpromoted catalyst, the titration technique used leads to a number of Mo sites, which is in good agreement with that provided from the geometrical model. Evidence that the formation of one promoted site occurs at the expense of one unpromoted site is provided. However, the number of detected promoted sites is lower than that expected from the amount of cobalt introduced: introduction of six cobalt atoms leads to the creation of only one promoted site. The migration of cobalt atoms into intercalated positions or into alumina is consid-considered. © 1992 Academic Press, Inc.

INTRODUCTION

Probe molecules have been extensively used to characterize hydrotreating catalysts [Co(Ni)–Mo(W)/Al$_2$O$_3$] in the sulfided state (1–8). For unpromoted catalysts, O$_2$ and CO chemisorption correlate well with the HDS activity (1, 2). Their adsorption is more complex on promoted catalysts. Consequently, the determination of the nature and the amount of the different adsorption sites is required. IR spectroscopy can provide such information. Particularly, the study of NO adsorption has provided evidence for different IR bands corresponding to the adsorption on (Mo,W) or (Co,Ni) sites (3, 4). However, a direct correlation with the catalyst activity is not straightforward. More specifically, CO has allowed us to differentiate between three types of sites: (Mo,W) sites, (Co,Ni) sites, and promoted sites (5–7). For example, CO adsorption on Mo sites on a Mo/Al$_2$O$_3$ sulfided catalyst gives rise to a band at 2115 cm^{-1}, which is completely re-

moved by evacuation at room temperature (RT). On sulfided Co/Al$_2$O$_3$ catalysts, a band is observed at 2055 cm^{-1}, corresponding also to a reversible CO adsorption at RT. On sulfided Co–Mo/Al$_2$O$_3$ catalysts, a new band appears at 2065 cm^{-1}; it partially remains after evacuation at RT. This band characterizes the interaction between Co and Mo in the sulfided state. A good correlation between the intensity of the irreversible part of the band at 2065 cm^{-1} and the HDS activity has been found. Recently, the correlation with activity has been extended to sulfided supported Ru–Ni catalysts (8).

According to the "decoration" model proposed by Topsøe et al. (9), it seems possible to introduce the promoter directly from a metal carbonyl decomposition on the sulfided form of a Mo/Al$_2$O$_3$ catalyst. A first approach has been performed using Ni(CO)$_4$ (10). Although the final catalyst presented a Ni content as low as 0.1%, the IR spectrum of adsorbed CO indicated a very high degree of promotion compared to the catalysts prepared by the classical impregnation method. Another series of catalysts has been pre-

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pared by thermal decomposition of Co (CO)₃NO (*11*). For compositions similar to that of the conventional Co–Mo/Al₂O₃ catalysts, the ratio between promoted and unpromoted Mo sites was greatly enhanced. This was confirmed by a twofold increase in thiophene HDS activity. As a matter of fact, promotion by metal carbonyls appears to ensure the maximum amount of the "Co–Mo–S type" structure.

In this study, we have followed the transformation of unpromoted Mo sites into promoted ones by thermal decomposition of different amounts of Co(CO)₃NO on a sulfided Mo/Al₂O₃ catalyst. To achieve this, we used CO as a probe molecule, since it differentiates promoted and unpromoted sites well. At room temperature, CO adsorbs only on Mo, Co, or CoMo sites of sulfided alumina-supported catalysts, which allows the determination of the integrated molar extinction coefficients $\bar{\varepsilon}$ of CO adsorbed on these sites. However, under such conditions, the sites are not completely saturated, even in the presence of a CO pressure. Therefore to titrate all these sites, it is necessary to adsorb CO at 100 K even though, at this temperature, CO adsorption also occurs on Al₂O₃, which makes spectra decomposition necessary. This titration method has been applied to the determination of the number of promoted sites in the case of a catalyst prepared by the classical impregnation.

EXPERIMENTAL

Mo/Al₂O₃ (12% MoO₃) was prepared by pore filling impregnation of a γ-Al₂O₃ from Rhône-Poulenc (230 m² g⁻¹) with ammonium heptamolybdate, drying at 383 K, and calcination at 773 K for 2 h. The catalyst, pressed into a self-supporting disc (10 mg, ϕ = 16 mm), was activated *in situ* in the IR cell. After calcination at 673 K under O₂, followed by evacuation at the same temperature, the sample was sulfided by three successive treatments with 80 Torr of H₂S (10%) + H₂ at T = 673 K, respectively, for 1 h, 1 h, and 15 h. Each sulfidation was

followed by an evacuation for 20 min at 673 K. The promotion of the catalyst was realized *in situ* in the IR cell. Doses of Co(CO)₃NO (from Ventron) were calibrated by introducing a given pressure of this compound, measured by a gauge (Datametrics, accuracy 10⁻³ Torr), in a well-known volume (v = 1.57 cm³). They were contacted at RT with the sulfided Mo/Al₃O₃ disc (*11*). The carbonyl was further decomposed under evacuation at 673 K.

The integrated molar extinction coefficients $\bar{\varepsilon}$ of CO adsorbed on sulfided catalysts were determined in the IR cell at RT by introduction of very small doses of CO (0.05 μmol) measured by the same volumetric method as for Co(CO)₃NO admission. Introduction of the first doses led to a complete CO adsorption as shown by the absence of a gas phase ($P < 10^{-3}$ Torr) as indicated by a second gauge directly connected to the cell. Before admission, CO was purified by passing through a trap cooled by liquid nitrogen. Spectra were recorded on a Fourier Transform Nicolet 60SX spectrometer.

For quantitative site titration, IR spectra were recorded at low temperature, in a cell equipped with double walls with a space for cooling agent between them. To achieve a better thermal contact of the sample with the cooled walls, about 0.5 Torr of helium was admitted to the cell. Using liquid nitrogen as coolant, a sample temperature of about 100 K was obtained.

RESULTS

(1) CO Adsorption on Mo/Al₂O₃

CO adsorption at 295 K on the sulfided Mo/Al₂O₃ catalyst gives rise to a band at 2110 cm⁻¹. It corresponds to CO adsorption on Mo sites with a low oxidation state (*12, 13*). The band completely disappears upon degassing at RT. Introduction of very small amounts of CO allows us to determine the integrated molar extinction coefficient $\bar{\varepsilon}$2110 cm⁻¹ (Fig. 1A). The value obtained is $\bar{\varepsilon}$2110 cm⁻¹ = 16 ± 4 μmol⁻¹ cm.

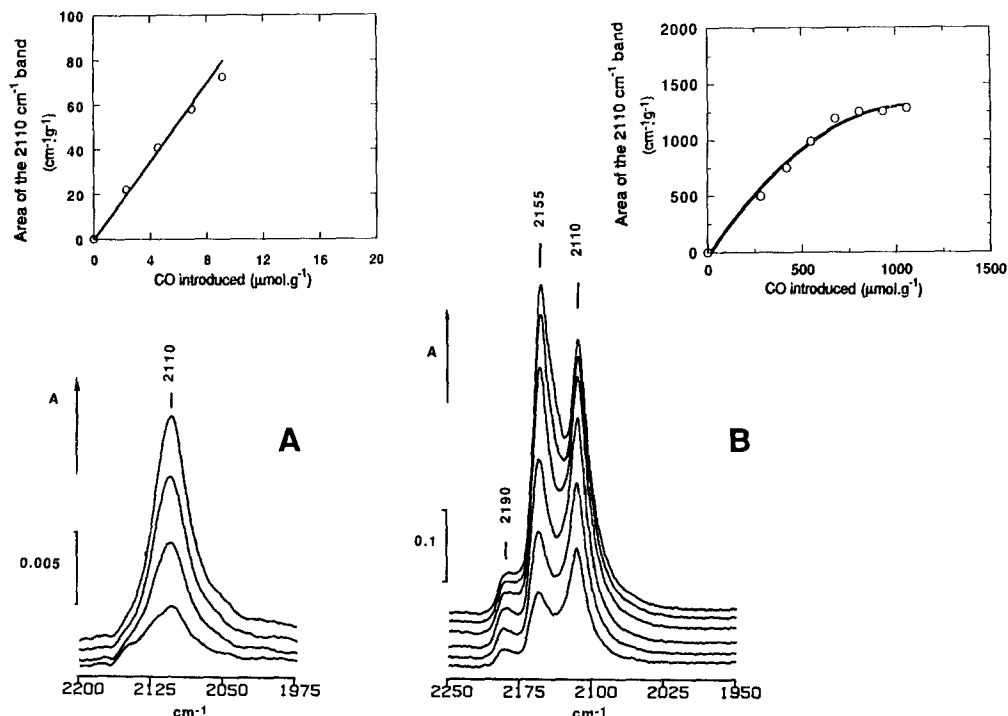CO adsorption at 100 K leads to the appearance of three bands at 2190, 2155, and

FIG. 1. IR spectra of CO species resulting from introduction of small doses of CO on the sulfided Mo/Al₂O₃ at 295 K (A) or 100 K (B). Inserted: Area of the 2110 cm^{-1} band versus the amount of CO introduced.

2110 cm^{-1} (Fig. 1B). Upon degassing at 100 K the band at 2110 cm^{-1} partially remains whereas that at 2155 cm^{-1} only persists as a shoulder. The band at 2190 cm^{-1} disappears making apparent a weaker one at 2208 cm^{-1}. The 2208 cm^{-1} and 2190 cm^{-1} wavenumber values characterize CO adsorption on coordinative unsaturated (cus) Al^{3+} sites (14). Study of the ν(OH) range shows a concomitant perturbation of the alumina ν(OH) bands, suggesting the formation of H-bonded species, characterized by the ν(CO) band at 2155 cm^{-1} (14). The persistence of the 2110 cm^{-1} band upon evacuation at low temperature allowed us to model its shape and therefore to determine its extent on the spectra of CO adsorbed at 100 K. The variation of this band area versus the total number of CO micromoles added is reported in Fig. 1B. The curve clearly indicates a saturation of Mo sites. From the corresponding band

area and from the value of $\bar{\varepsilon}$2110 cm^{-1}, the number of CO species adsorbed on Mo sites can be estimated to be 150 micromol g^{-1} of catalyst.

The 2110 cm^{-1} band is due to CO adsorption on Mo cus sites. Therefore, the number of CO adsorbed molecules may depend on the extent of reduction of the catalyst. To study this point, we have compared the CO adsorption at 100 K after H₂S + H₂ sulfidation to that obtained on the same sulfided catalyst further reduced by pure H₂ at 773 K or treated by pure H₂S at 623 K, followed by an evacuation at the treatment temperature (Fig. 2). On the H₂S post-treated catalyst, almost no CO adsorption occurs on the Mo sites showing that they are saturated by H₂S adsorption. On the other hand, the area of the 2110 cm^{-1} band is nearly the same after H₂S + H₂ sulfidation as after the subsequent treatment of the catalyst by pure H₂. This shows that the H₂S + H₂ treatment used is
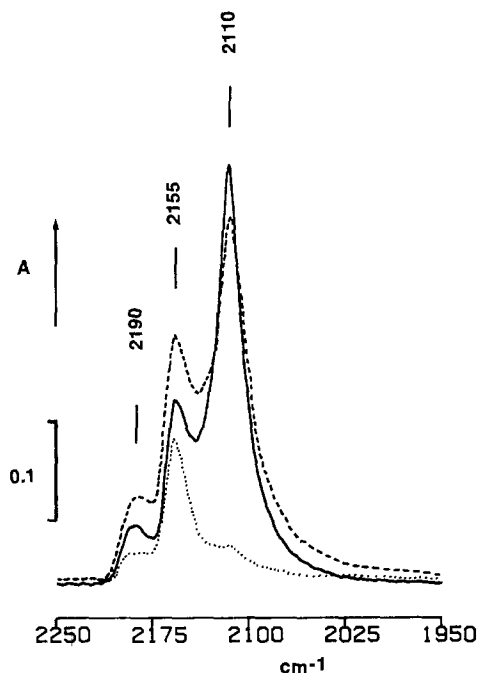
FIG. 2. IR spectra of CO species for Mo sites saturation at 100 K on (—) Mo/Al$_2$O$_3$ sulfided by H$_2$S + H$_2$ at 673 K and evacuated at 673 K (A catalyst). (---) A catalyst further reduced by H$_2$ at 773 K and evacuated at 773 K. (···) A catalyst further treated by H$_2$S at 673 K and evacuated at 673 K.

sufficient to reveal all the CO adsorption sites of the MoS$_2$ sheets.

(2) CO Adsorption on Co/Al$_2$O$_3$

On the sulfided alumina support, 225 μmol g^{-1} of Co(CO)$_3$NO were introduced and then decomposed by heating under vacuum up to 673 K. CO adsorption at room temperature on such a catalyst gives rise to a broadband at 2160 cm^{-1} (Fig. 3). No species remain after evacuation. According to the literature (15), this may be accounted for by CO adsorption on Co^{2+} sites. After further sulfidation at 673 K by H$_2$S + H$_2$ of the Co/Al$_2$O$_3$ catalyst so obtained, CO adsorption at RT gives rise to a band at 2051 cm^{-1} with two weak ones at 2152 and 2127 cm^{-1}. These bands completely disappear by evacuation at RT. The main band shows the presence of cobalt in an oxidation state close to

zero (15) as already observed on sulfided Co/Al$_2$O$_3$ catalysts prepared by the conventional impregnation method (5). Even after introduction of very small amounts of CO, the presence of CO gas is detected, preventing the determination of the integrated molar extinction coefficient $\bar{\varepsilon}$ of the 2051 cm^{-1} band.

(3) CO Adsorption on Sulfided Mo/Al$_2$O$_3$ Promoted by Thermal Decomposition of Co(CO)$_3$NO

On the sulfided Mo/Al$_2$O$_3$ catalyst, successive doses of Co(CO)$_3$NO have been introduced and decomposed by evacuation at 673 K. After thermal decomposition of each dose, CO adsorption at RT has been used to follow the degree of the promotion (Fig. 4A). Spectra show the presence of two bands at 2110 and 2065 cm^{-1}. Upon evacuation at RT, the former completely disappears, whereas the latter partially persists. As already reported on catalysts prepared by the classical impregnation (5), these
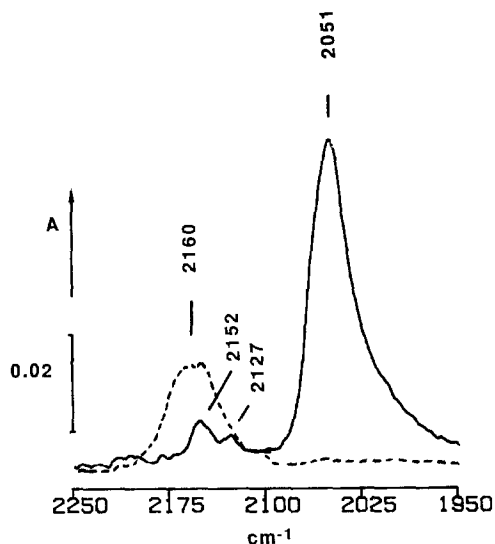
FIG. 3. IR spectra of CO species formed by introduction of CO (P_e = 10 Torr, RT) on Co/Al$_2$O$_3$ prepared by thermal decomposition of Co(CO)$_3$NO on sulfided alumina. The Co/Al$_2$O$_3$ catalyst was not (---) or was (—)resulfided by H$_2$S–H$_2$ at 673 K and then evacuated at the same temperature before CO introduction.
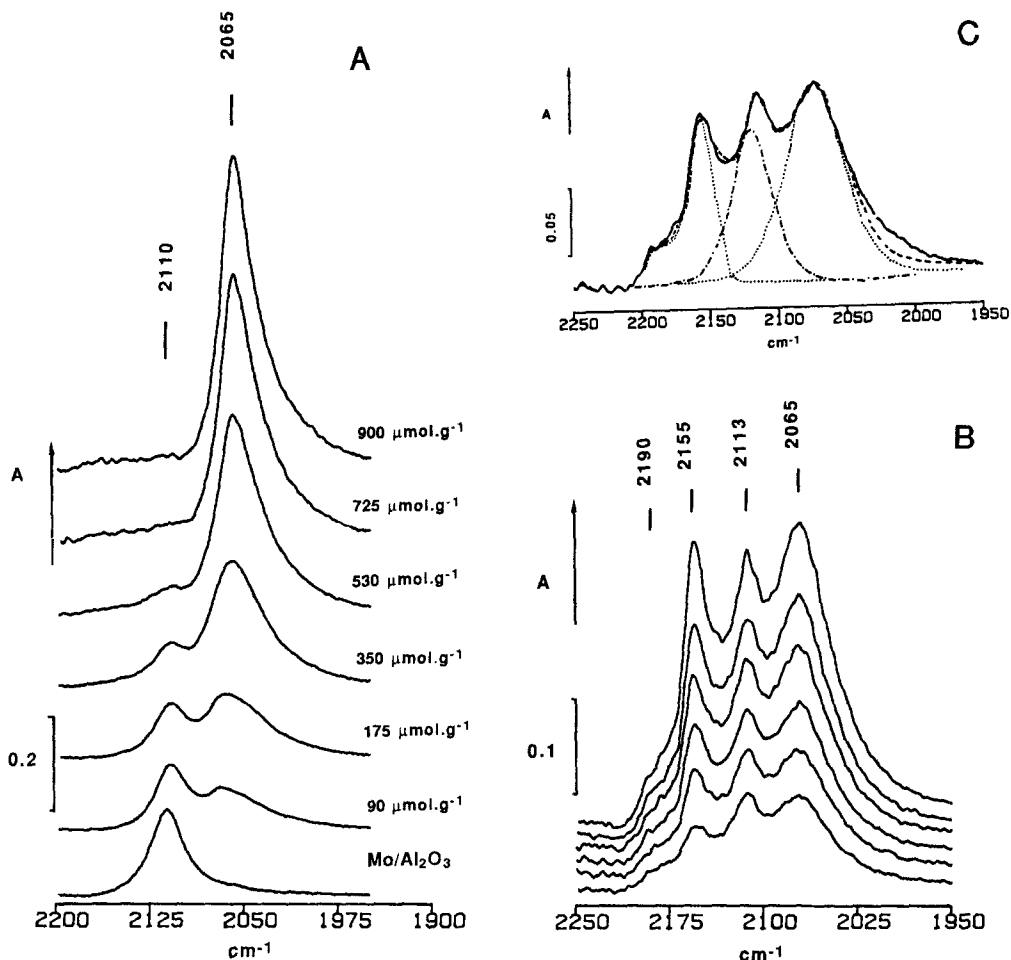
FIG. 4. CO adsorption on sulfided Mo/Al₂O₃ promoted by thermal decomposition of Co(CO)₃NO. (A) Variation of the IR spectra with the amount of cobalt introduced (P_e(CO) = 10 Torr, RT). (B) Variation of the IR spectra with the amount of CO introduced at 100 K (CoMo/Al₂O₃ catalyst prepared by thermodecomposition of 400 μmol g⁻¹ of Co(CO)₃NO). (C) An example of IR band decomposition.

bands respectively characterized unpromoted and promoted sites. Introduction of increasing amounts of cobalt decreases the intensity of the band characteristic of unpromoted sites whereas that corresponding to promoted ones increases. From the profile of the ν(CO) band observed on the unpromoted catalyst and from that of the band remaining after evacuation, it is possible to decompose the ν(CO) absorption into two components. However, to access the number of sites, it was necessary to determine the integrated molar extinction coefficient

of the band at 2065 cm⁻¹. The strong IR absorption of the sulfided promoted catalysts and the rapid surface saturation of these catalysts even after the introduction of small doses of CO made it difficult. However, we succeeded with a sulfided Mo/Al₂O₃ promoted by thermal decomposition of Co(CO)₃NO (12% MoO₃–1.7% CoO) since, for the first doses of CO introduced, only the band characteristic of promoted sites was formed. From several experiments, we determined $\bar{\varepsilon}$2060 cm⁻¹ = 43 ± 12 μmol⁻¹ cm.
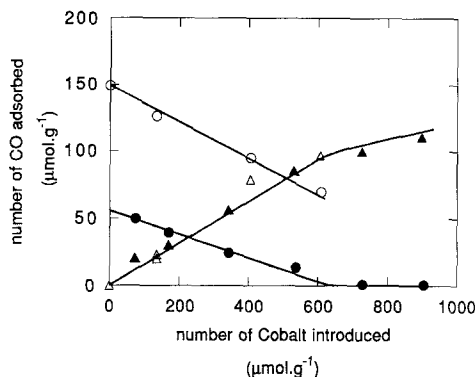
FIG. 5. Variation of the amount of CO adsorbed on unpromoted Mo (2110 cm^{-1}, circles) or promoted Mo (2065 cm^{-1}, triangles) at RT (solid symbols) and at 100 K (open symbols) versus the amount of Co added.

Figure 5 shows the variation of the number of unpromoted and promoted sites obtained from CO adsorption at RT with the cobalt content (solid symbols). We observe that complete promotion occurs for 600 μmol g^{-1} (4.5% CoO): when the amount of cobalt increases from 4.5 to 6.8% CoO, evidence for the completion of the promotion is given by the absence of variation of the band intensity remaining after evacuation. The increase of the area of the 2065 cm^{-1} band observed in the presence of a CO gas phase (P_e = 10 Torr), for high cobalt loading, therefore can be related to an adsorption of CO on cobalt sites noninteracting with molybdenum sites. The cobalt content necessary for a complete promotion is not very different from that present in the optimized Co–Mo catalysts prepared by the classical impregnation method (HR306 : 3% CoO–12% MoO$_3$).

At 100 K, CO adsorption gives rise to the same bands as on the unpromoted catalyst with an additional band at ~2065 cm^{-1}, characterizing the presence of promoted sites (Fig. 4B). Only CO adsorbed on unpromoted and promoted sites partially remains after evacuation at 100 K. From the spectra obtained on the unpromoted catalyst (Fig. 1B), and after spectra decomposition, it is possible to access the area of the bands due

to promoted and unpromoted sites. Figure 5 reports the number of CO adsorbed on each type of site at 100 K (open symbols) for a coverage corresponding to saturation and for the different amounts of Co(CO)$_3$NO introduced. A similar trend to that observed at RT is obtained. This figure shows that the number of unpromoted sites detected at 100 K is considerably higher than that measured at RT, whereas for the promoted sites, all the sites are detected at RT. It clearly appears that the total number of promoted and unpromoted sites is constant whatever the cobalt loading.

DISCUSSION

The appearance of only one symmetrical ν(CO) band on molybdenum catalysts allows us to deduce that, under the conditions used, only one CO molecule is adsorbed per Mo site. The ratio of the number of Mo sites detected by CO adsorption at 100 K compared to the total number of Mo present in the sample is close to 0.2. For catalysts presenting the same coverage ratio, Pratt et al. (16) have measured, by electron microscopy, the mean size of the MoS$_2$ sheets, which is close to 45 Å. Supposing hexagonal slabs, following the model of Kastzelan et al. (17), sitting vertically to the support according to Pratt et al. (16), and taking into account the MoS$_2$ structure that implies a Mo–Mo distance of 3.16 Å (18), it is possible to calculate the number of accessible Mo sites and to compare it with the number of Mo atoms present in the slabs. The ratio obtained is 0.21; it is in good agreement with the experimental ratio, which provides a validation of the titration technique used.

Thermal decomposition of increasing doses of Co(CO)$_3$NO on sulfided Mo/Al$_2$O$_3$ leads to the creation of promoted sites while unpromoted ones disappear. From CO site titration at 100 K, it is shown that the appearance of one promoted site corresponds to the disappearance of one unpromoted site (Fig. 5). This quantitative study proves that promoter atoms are located on the MoS$_2$

edges, blocking Mo sites as described in the decoration model. However, Fig. 5 indicates that the number of promoted sites detected by CO compared with the amount of cobalt atoms introduced is surprisingly low, since the introduction of six cobalt atoms leads to the creation of only one promoted site. Several hypotheses can be put forward for locating the extra Co atoms:

(i) The presence of other surface cobalt species. However, no bands are detected at 2160 cm^{-1} (oxidic cobalt) or 2051 cm^{-1} (metallic cobalt), at least for low Co content catalysts (CoO < 4%).

(ii) Incorporation of cobalt into alumina. A migration of cobalt atoms into the alumina lattice may occur during the carbonyl decomposition at 673 K. Although Fig. 3 suggests that an important part of the cobalt stays on the surface of the support after such a decomposition, we cannot rule out some migration into the alumina.

(iii) The presence of cobalt in intercalated positions. Pratt et al. (16) observed that MoS₂ slabs on alumina formed stackings of up to five layers. Therefore, the presence of cobalt atoms in intercalated positions between two MoS₂ slabs can be envisaged (19). This cobalt would be detectable by CO and would not participate in the Co–Mo–S phase. It could arise from a cobalt migration due to the thermal treatment necessary to decompose Co(CO)₃NO.

The nature of the promoted sites that give rise to a band at 2065 cm^{-1} is difficult to specify. Such a wavenumber value is lower than that observed on Mo sites (2110 cm^{-1}) but higher than that observed for Co ones (2051 cm^{-1}). It proves, in agreement with Harris and Chianelli (20), that an interaction occurs between Co and Mo by an electronic transfer from cobalt to molybdenum. Even so, it does not allow us to specify more precisely the nature of the site. However, the blocking of Mo sites by cobalt atoms would suggest that CO adsorption occurs on Co sites in interaction with molybdenum.

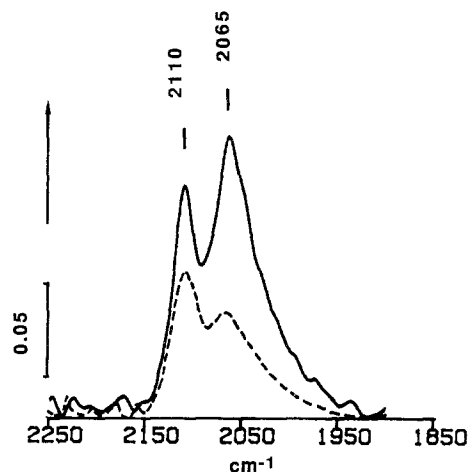It was interesting to apply the results rela-

FIG. 6. IR spectra of CO adsorbed (P_e = 10 Torr, RT) on CoMo/Al₂O₃ catalysts prepared by impregnation: 3% CoO–12% MoO₃ (—), 1.5% CoO–6.1% MoO₃ (---).

tive to the integrated molar extinction coefficients determined in the present study to catalysts prepared by the classical impregnation method. Since all the promoted sites are detected by CO adsorption at RT, the determination of their number is easy to obtain. Figure 6 shows the ν(CO) bands arising from CO adsorption at RT on the optimized catalyst HR 306 (3% CoO–12% MoO₃) and on a Co–Mo/Al₂O₃ (1.5% CoO–6.1% MoO₃) sulfided in situ. It appears that part of the Mo sites are not promoted, as shown by the ν(CO) band at 2110 cm^{-1}, even in the case of the optimized catalyst. Moreover, the number of CO molecules adsorbed on the promoted sites determined from the area of the 2065 cm^{-1} band is respectively of 42 and 17 μmol g^{-1}. Thus the ratio of the promoted sites compared to the amount of cobalt introduced is lower than in the case of the ex-carbonyl catalyst, since for both conventional catalysts only one promoted site is detected for 10 cobalt atoms introduced. This confirms the greater ability of cobalt carbonyl to form a Co–Mo–S phase. This result explains the higher HDS activity previously reported on ex-carbonyl catalysts for a given cobalt content (11).

REFERENCES

1. Tauster, S. J., Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **63,** 515 (1980).
2. Bachelier, J., Duchet, J. C., and Cornet, D., *Bull. Soc. Chim. Belg.* **90,** 1301 (1981).
3. Topsøe, N. Y., and Topsøe, H., *J. Catal.* **84,** 386 (1983).
4. Ouafi, D., Maugé, F., and Lavalley, J. C., *Bull. Soc. Chim. Fr.* **3,** 363 (1989).
5. Bachelier, J., Tilliette, M. J., Cornac, M., Duchet, J. C., Lavalley, J. C., and Cornet, D., *Bull. Soc. Chim. Belg.* **93,** 743 (1984).
6. Duchet, J. C., Lavalley, J. C., Housni, S., Ouafi, D., Bachelier, J., Lakhdar, M., Mennour, A., and Cornet, D., *Catal. Today* **4,** 71 (1988).
7. Maugé, F., Duchet, J. C., Lavalley, J. C., Houenssenbay, S., Payen, E., Grimblot, J., and Kasztelan, S., *Catal. Today* **10,** 561 (1991).
8. De Los Reyes, J. A., Vrinat, M., Beysse, M., Maugé, F., and Lavalley, J. C., *Catal. Lett.,* **13,** 213 (1992).
9. Topsøe, H., Clausen, B. S., Candia, R., Wivel, C., and Mørup, S., *J. Catal.,* **68,** 433 (1981).
10. Angelo, M., Maugé, F., Duchet, J. C., and Lavalley, J. C., *Bull. Soc. Chim. Belg.* **96,** 925 (1987).
11. Maugé, F., Vallet, A., Bachelier, J., Duchet, J. C., and Lavalley, J. C., *Catal. Lett.* **2,** 57 (1989).
12. Peri, J. B., *J. Phys. Chem.* **86,** 1615 (1982).
13. Delgado, E., Fuentes, G. A., Hermann, C., Kunzmann, G., and Knözinger, H., *Bull. Soc. Chim. Belg.* **93,** 735 (1984).
14. Zaki, M. I., and Knözinger, H., *Mater Chem. Phys.* **17,** 201 (1987).
15. Sheppard, N., and Nguyen, T. T., *Adv. Infrared Raman Spectrosc.* **5,** 67 (1978).
16. Pratt, K. C., Sanders, J. V., and Christov, V., *J. Catal.* **124,** 416 (1990).
17. Kasztelan, S., Toulhoat, H., Grimblot, J., and Bonnelle, J. P., *Appl. Catal.* **13,** 127 (1984).
18. Clausen, B. S., Topsøe, H., Candia, R., Villadsen, J., Lengeler, B., Als-Nielsen, J., and Christensen, F., *J. Phys. Chem.* **85,** 3869 (1981).
19. Farragher, A. L., and Cossee, P., *in* "Proceeding, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1301 North Holland, Amsterdam, 1973.
20. Harris, S., and Chianelli, R. R., *J. Catal.* **98,** 17 (1986).