Preparation, Characterization, and Activity of Sulfided Catalysts Promoted by Co(CO)₃NO Thermodecomposition

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Various Co–Mo/Al₂O₃ catalysts were prepared by deposition of Co(CO)₃NO either on oxidic or sulfided Mo/Al₂O₃. The thermodecomposition step was followed by IR spectroscopy, which showed that cobalt was preferentially deposited on the molybdenum phase. Thiophene hydrodesulfurization (HDS) activity was found to be higher when the precursor was deposited on sulfided Mo/Al₂O₃, while this catalyst was much more active than that prepared by the classical impregnation method. The nature and the amount of the surface sites of sulfided Co–Mo catalysts were assessed by Fourier transform infrared spectroscopy of adsorbed CO. Unpromoted and promoted coordinatively unsaturated Mo sites were identified on both ex-carbonyl nitrosyl and impregnated catalysts, but the ratio of the two types of sites was found to be strongly dependent on the preparation method. A good correlation was obtained between HDS activity and the integrated area of the IR band characteristic of CO adsorbed on the promoted sites. The high concentration of Co–Mo–S sites on ex-carbonyl nitrosyl catalysts may be related to the low amount of cobalt species on alumina, due to the mode of promoter introduction and to treatments subsequent to cobalt deposition which are milder on ex-carbonyl nitrosyl catalysts than on impregnated ones.   © 1996 Academic Press, Inc.

INTRODUCTION

Cobalt or nickel promoted molybdenum sulfide catalysts supported on alumina are widely used in hydrotreatment processes. The refining of heavier feedstock needs new catalysts with improved performances. Modifications of the sulfidation procedure (1–3) and the use of other carriers than alumina (4–6) or various precursors (7–13) have led to highly active catalysts. Among these different approaches, the preparation of the active phase using organometallic precursors has been developed (8–13). Maezawa *et al.* (8), starting from Mo(CO)₆, prepared sulfided catalysts supported on alumina which showed a higher catalytic activity for hydrodesulfurization of thiophene than that of corresponding conventional catalysts. Yermakov (9) found that the catalytic activity of monometallic or bimetallic NiW sulfides supported on SiO₂ prepared from organometallic precursors was much higher than that of conventional ones.

He explained their substantial activity increase by the formation of sulfide particles in the form of small filaments which induced an improved dispersion of the active phase. Bernadyuk *et al.* (11) showed that it was possible to promote supported or unsupported MoS₂ using Co₂(CO)₈ decomposition, the catalytic activity of the samples thus prepared being slightly higher than that of the corresponding classical ones. It was deduced that use of organometallic precursors yields a highly dispersed active phase using the minimum amount of metal.

In this work, our aim was to specify whether it is possible to increase the number of promoted sites on MoS₂ slabs of constant size. We therefore deposited the promoter cobalt as an organometallic complex on a conventional impregnated Mo/Al₂O₃ in the oxidized or sulfided state. Previously, we reported that deposition of nickel on sulfided Mo/Al₂O₃ using Ni(CO)₄ was successful since the number of Ni–Mo–S sites determined by CO chemisorption was much higher than on the conventional catalyst (12). In the present work, we have used Co(CO)₃NO, a convenient precursor due to its high vapor pressure (14, 15). In a first step, we followed the anchorage of carbonyl nitrosyl complex on oxidized or sulfided Mo/Al₂O₃ by IR spectroscopy. We further compared the activity of these catalysts for hydrodesulfurization of thiophene with that of a conventional CoMo/Al₂O₃ catalyst prepared by successive impregnations. We then characterized the nature and the amount of the different adsorption sites present on the catalysts so prepared by IR spectroscopy of CO adsorption. Indeed, CO allowed us to differentiate (Mo, W) sites, (Co, Ni) sites, and promoted sites (16–20). Good correlation between the intensity of the ν(CO) band characteristic of promoted sites and HDS activity was previously found (19, 20).

EXPERIMENTAL

The oxidic Mo/Al₂O₃ (8 wt% Mo sample) was prepared by pore filling impregnation of a γ-Al₂O₃ carrier (230 m² g⁻¹) with ammonium heptamolybdate, drying at 383 K and calcining at 773 K for 2 h.

The promotion of Mo/Al₂O₃ was directly realized either in an infrared cell using a catalyst in the form of a disc

$(5 \times 10^{-3}\,\mathrm{g\,cm^{-2}})$ or in a quartz microreactor using a catalyst in the form of powder with a grain size comprised between 0.2 and 0.5 mm. In order to achieve *in situ* $Co(CO)_3NO$ deposition, the IR cell or the reactor was connected to a vacuum device. A quantity of 6×10^{-4} mol of $Co(CO)_3NO$ per gram of catalyst was contacted either with oxidic Mo/Al_2O_3, calcined at 673 K under O_2 and then evacuated at 673 K (sample O_1) or with its sulfided form (sample S_1). Sulfidation was carried out by three successive treatments with 80 Torr H_2–H_2S (10% vol) at 673 K for 1 h, 1 h, and 15 h, respectively. Each sulfidation was followed by an evacuation for 20 min at 673 K. A third sample (sample S_2) was prepared by deposition of $Co(CO)_3NO$ on sulfided Mo/Al_2O_3 as on sample S_1, but the sample was contacted with air before $Co(CO)_3NO$ decomposition.

The decomposition of the carbonyl nitrosyl complex in vacuum ($P = 2 \times 10^{-5}$ Torr) was followed by IR spectroscopy, at increasing temperature. CO adsorption was performed on the samples promoted by $Co(CO)_3NO$ and further sulfided under H_2–H_2S at 673 K. IR spectra were recorded with a Fourier Transform Nicolet 60SX spectrometer.

For reactivity measurements, after $Co(CO)_3NO$ decomposition, the microreactor was connected to a reactivity device without any contact with air. Before tests, catalysts were sulfided for 4 h at 673 K under a flow of H_2–H_2S (15% vol). The hydrodesulfurization of thiophene was performed at 673 K under atmosphere pressure with a mixture of H_2–H_2S–thiophene (90:2:8). The conversion to butene was measured under steady state conditions after 3 h on stream. Activity measurements, expressed as the pseudo first-order rate constant, were compared to that of a conventional $CoMo/Al_2O_3$ catalyst prepared by successive impregnation and sulfided under the same conditions. Chemical analysis of cobalt and molybdenum was performed by CNRS (Vernaison).

RESULTS

The cobalt contents are reported in Table 1 for the various preparations. $Co(CO)_3NO$ decomposition gives rise to

TABLE 1

Composition and Activity for Thiophene Hydrodesulfurization of Catalysts after Sulfidation

Catalyst	Type of preparation	Co (%)	Mo (%)	Rate constant k_{HDS} ($l \cdot h^{-1} \cdot g^{-1}$)
O_1	$Co(CO)_3NO$ on oxidic Mo/Al_2O_3	1.3	8.0	20.8
S_1	$Co(CO)_3NO$ on sulfided Mo/Al_2O_3	3.6	8.0	74.4
S_2	$Co(CO)_3NO$ on sulfided Mo/Al_2O_3, exposed to air	2.8	8.0	53.3
REF	Impregnated catalyst	2.6	9.3	27.5

a lower amount of cobalt on sample O_1 than on sulfided samples, particularly on the sample S_1. Sample S_2, which was exposed to air after metal carbonyl nitrosyl adsorption, fixes an intermediate cobalt concentration. Therefore, although the metal carbonyl nitrosyl was introduced in the same way (contact with 6×10^{-4} mol g^{-1}), the amount of cobalt deposited is quite different according to the state of the molybdenum phase. The composition of S_2 catalysts is close to that of the reference catalyst prepared by impregnation.

1. Adsorption and Decomposition of Co(CO)₃NO

The IR spectrum of gaseous $Co(CO)_3NO$ mainly shows two $\nu(CO)$ bands at 2107 and 2046 cm^{-1} and a $\nu(NO)$ band at 1823 cm^{-1} (14).

Adsorption and decomposition of $Co(CO)_3NO$ on γ-alumina has already been reported by Roustan *et al*. (14). On the spectra, two regions can be distinguished corresponding to $\nu(CO)$ (2150–1950 cm^{-1}) or $\nu(NO)$ (1900–1600 cm^{-1}) vibrations. In agreement with Roustan *et al*. (14), when $Co(CO)_3NO$ is introduced on Al_2O_3 (Fig. 1), three $\nu(CO)$ bands are observed at 2130, 2078, and 2045 cm^{-1}. Their intensity decreases with contact time and the bands disappear upon evacuation. They were assigned to $\nu(CO)$ vibrations of the $Co(CO)_3NO$ complex adsorbed via the oxygen atom of the nitrosyl group (14). In the $\nu(NO)$ range, two bands are present at 1790 and 1695 cm^{-1} and were previously assigned to mononitrosyl species (14). They also disappear upon evacuation. After a contact for 30 min, new bands at 1870 and 1795 cm^{-1} appear; they were assigned to dinitrosyl species (14). In addition, as soon as $Co(CO)_3NO$ is introduced, isocyanate species (bands around 2230 cm^{-1}) are observed. Their number increases with contact time and is maximum at 373 K.

Figure 2 presents the spectra (2400–1500 cm^{-1} range) of species formed when $Co(CO)_3NO$ is adsorbed on the oxidic Mo/Al_2O_3 (sample O_1). After introduction of $Co(CO)_3NO$ (Fig. 2a), we note the presence of bands at 2130 (shoulder); 2106, 2047, 2010 (sh); 1887, 1806 (broad); and 1687 cm^{-1}. Those at 2106 and 2047 cm^{-1} are close to those present in the spectrum of $Co(CO)_3NO$ gas. After 30 min (Fig. 2b) the intensity of the 1887 cm^{-1} band increases, whereas that of the 1687 cm^{-1} band decreases. A shoulder also appears at 1792 cm^{-1}. Upon evacuation at 373 K, the $\nu(CO)$ bands disappear while those at 1887 and 1792 cm^{-1} persist. No band resists an evacuation up to 473 K (Fig. 2d).

The assignment of the different bands can be proposed according to literature results obtained from CO and NO adsorption on alumina-supported Co, Mo, and Co–Mo oxidic catalysts (Table 2). These results show that on the Co–Mo catalyst, NO adsorption occurs simultaneously on cobalt atoms in interaction with molybdenum atoms (bands at 1880 and 1796 cm^{-1}) and on unpromoted molybde-
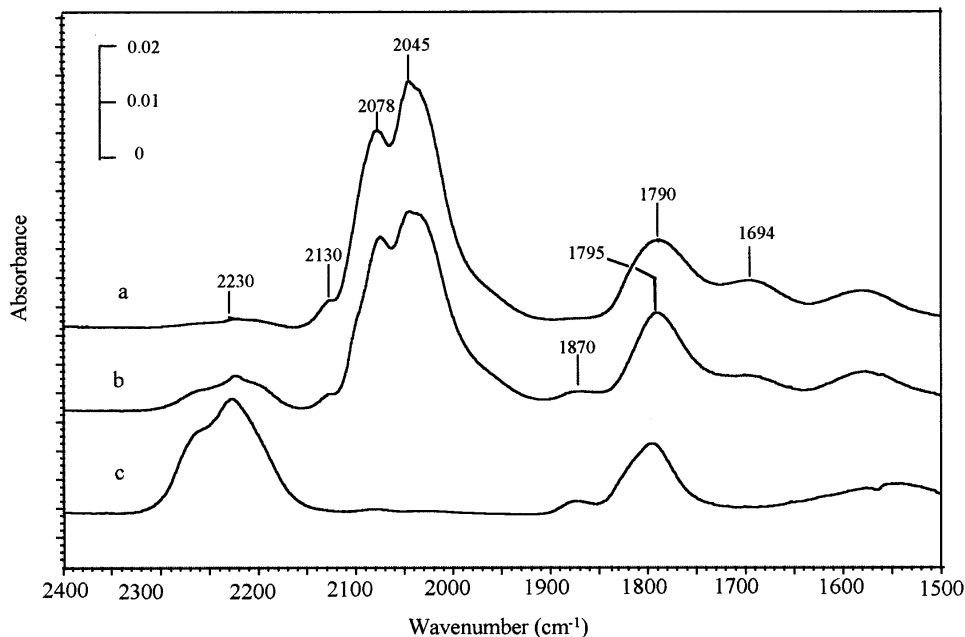
FIG. 1. Co(CO)$_3$NO adsorption on alumina activated at 673 K: (a) after carbonyl nitrosyl introduction; (b) after 30 min of contact; (c) after evacuation at 373 K.

num atoms (bands at 1796 and 1696 cm^{-1}). On sample O$_1$, the 1887 and 1792 cm^{-1} bands which persist after evacuation (Fig. 2c) are clearly attributed to ν_a and ν_s vibrations of dinitrosyl species adsorbed on cobalt sites of oxidic Co–Mo/Al$_2$O$_3$. Before evacuation, the 1687 cm^{-1} band and the shift of that at 1806 cm^{-1} to 1792 cm^{-1} reveals the presence of other species. They can be related either to mononitrosyl species in accordance with results reported on alumina (14) or dinitrosyl species formed on Mo sites.

Figure 3 shows the spectrum of oxidic Mo/Al$_2$O$_3$; it provides evidence for a band at 1007 cm^{-1} characterizing Mo=O bonds of molybdena species, as reported previously (26, 27). After Co(CO)$_3$NO introduction, the difference spectrum (Fig. 3.b1) shows that this band vanishes,
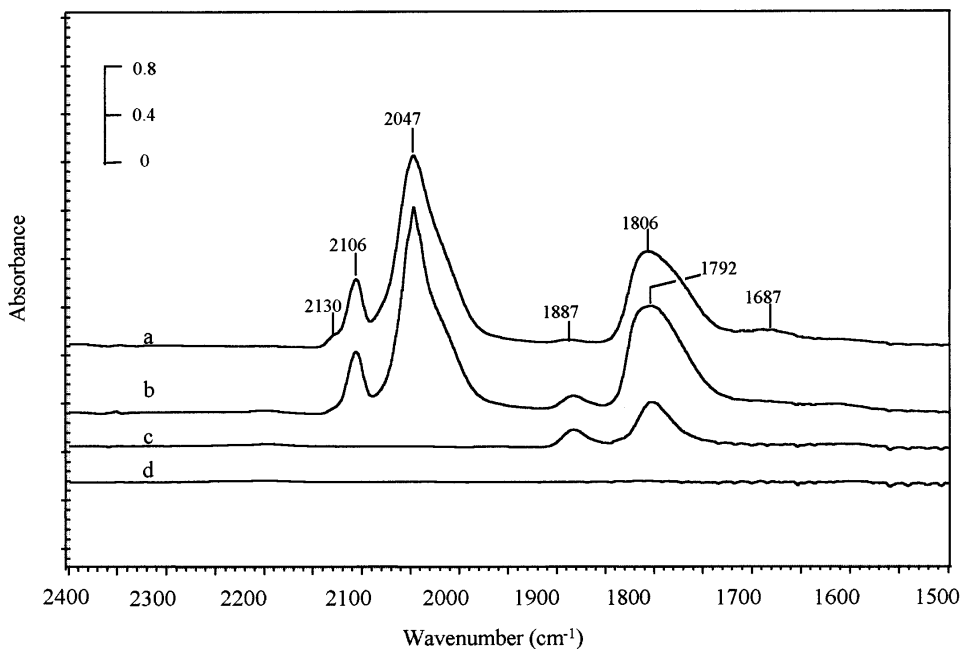

FIG. 2. Co(CO)$_3$NO adsorption on oxidic Mo/Al$_2$O$_3$ after various contact times at room temperature: (a) after carbonyl nitrosyl introduction; (b) after 30 min of contact and after evacuation at different temperatures; (c) 373 K; (d) 473 K.

TABLE 2

Wavenumbers (in cm^{-1}) of IR Bands for CO or NO Adsorbed on Oxidic or Sulfided Mo, Co, and Co–Mo Supported on Alumina

	$v(CO)$	$v(NO)_2$
Mo/Al$_2$O$_3$		
Oxidic	—	1804, 1693w^b
Sulfided	2110^a	1780, 1685^b
Co/Al$_2$O$_3$		
Oxidic	2165^a	1860, 1780^b
Sulfided	2055^a	1842, 1778^b
Co–Mo/Al$_2$O$_3$		
Oxidic	2165^a	1880, 1796, 1696w^b
Sulfided	2112 + 2065^a	1850, 1785, 1690^b

Note. w = weak.

^{a} Refs. (13, 16, 18, 21, 22).

^{b} Refs. (23–25).

indicating an interaction between the molybdenum phase and the cobalt complex. After evacuation at 373 K (Fig. 3.b2) and 473 K, this interaction is still observed.

Figure 4 shows results obtained when Co(CO)₃NO is introduced to sulfided Mo/Al₂O₃ (sample S₁); it clearly appears that the band intensities are more intense than those observed for sample O₁. The wavenumbers are also slightly different: in the 1900–1700 cm^{-1} range, the spectrum (Fig. 4a) presents v(NO) bands at 1810 and 1680 cm^{-1} (weak); in the 2300–1900 cm^{-1} range v(CO) bands are observed at 2124, 2102, 2070, and 2046 cm^{-1}. After contacting for 30 min (Fig. 4b), a band at 1855 cm^{-1} clearly appears

and the wavenumber of the most intense v(NO) band is shifted from 1810 to 1790 cm^{-1}. In the v(CO) range, the shoulder at 2070 cm^{-1} becomes marked. We also note the formation of isocyanate species characterized by a band at 2195 cm^{-1}, with a shoulder at 2232 cm^{-1}, whereas such species were not observed on sample O₁. After evacuation at 373 K (Fig. 4c), isocyanate species persist and nitrosyl species (band at 1824 cm^{-1}) are noted. They are both eliminated upon evacuation at above 573 K (Fig. 4e). The same features are observed on sample S₂.

The assignment of the v(NO) bands at 1810 and 1680 cm^{-1} observed as soon as Co(CO)₃NO is introduced is rather difficult. As on sample O₁, they can be related to mononitrosyl species but their wavenumber is also close to that of dinitrosyl species observed on unpromoted molybdenum atoms in the sulfided state (Table 2). On the other hand, the bands which appear at 1855 and 1790 cm^{-1} after 30 min well characterize dinitrosyl species formed on cobalt sites of sulfided Co–Mo/Al₂O₃. After evacuation at 373 K, the only v(NO) band detected at 1824 cm^{-1}, at a wavenumber value halfway between the v_a and v_s vibrations of dinitrosyl species, may be due to mononitrosyl species adsorbed on the same site.

2. Hydrodesulfurization of Thiophene

Reactivity data reported in Table 1 provide evidence for the high activity, by a factor of 2 to 3, of samples S₁ and S₂ compared to the reference catalyst; it is worthwhile noticing that the O₁ catalyst is less active. The variation of HDS activity versus cobalt content is reported in Fig. 5, which
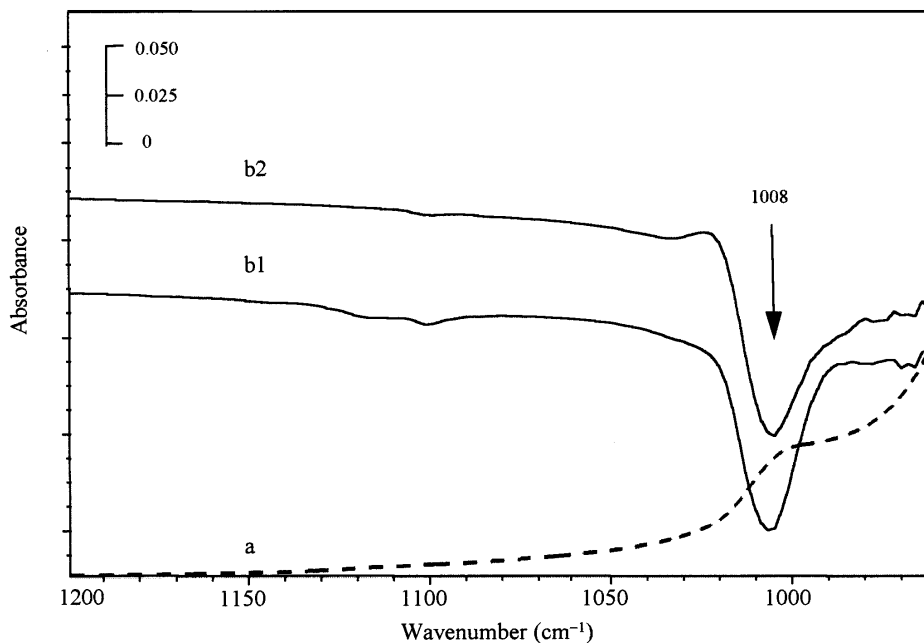

FIG. 3. IR spectra in the zone of the Mo–O vibrations: (a) oxidic Mo/Al₂O₃; (b) Difference spectra corresponding to (b1) Co(CO)₃NO adsorption on oxidic Mo/Al₂O₃-a; (b2) evacuation at 373 K-a.
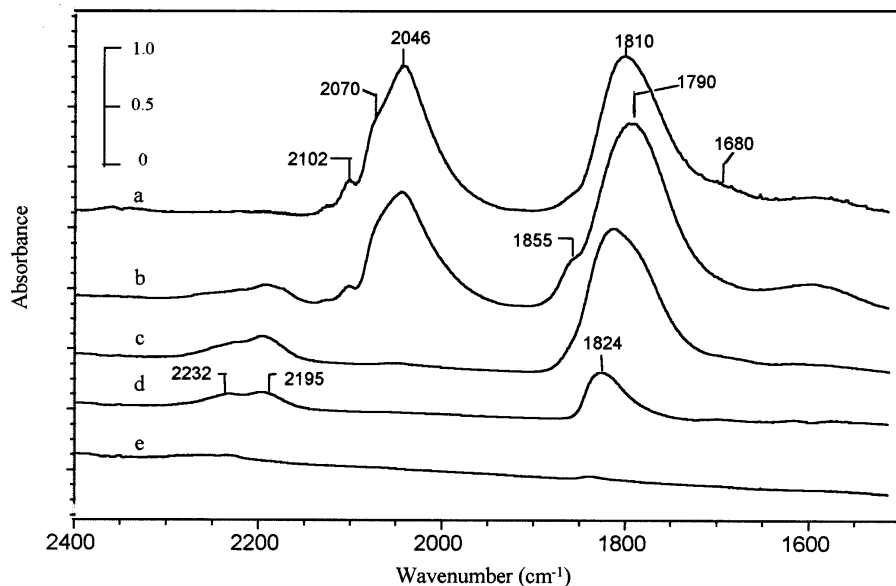
FIG. 4. Co(CO)$_3$NO adsorption on sulfided Mo/Al$_2$O$_3$ after various contact times at room temperature: (a) after carbonyl nitrosyl introduction; (b) after 30 min of contact, and after evacuation at different temperatures: (c) 373 K; (d) 473 K; (e) 573 K.

shows that the ex-carbonyl nitrosyl catalyst activity is proportional to the amount of cobalt deposited. Conversely, the conventional catalyst is less active than expected from its cobalt content.

3. CO Adsorption on Sulfided Catalysts

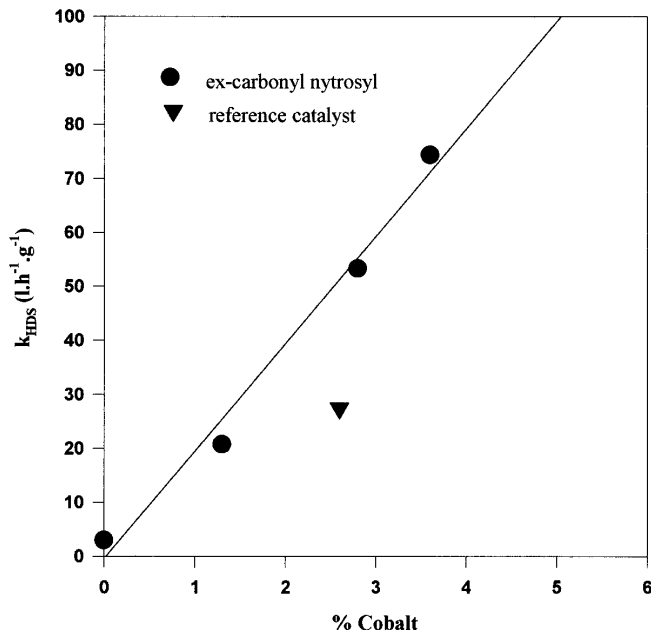In order to assess the nature and the amount of surface sites after sulfidation, CO adsorption has been stud-

FIG. 5. Rate constant for hydrodesulfurization of thiophene versus cobalt content.

ied by infrared spectroscopy. Spectra are reported in Fig. 6. All the catalysts present two bands at 2110 and 2065 cm^{-1} indicating the presence of unpromoted and promoted sites, respectively (13, 16, 18). No shoulder clearly appears near 2055 cm^{-1}, indicating that CO does not adsorb on cobalt sites; we conclude that cobalt atoms are mainly in interaction with the molybdenum phase. We note that on samples S$_1$ and S$_2$ the number of unpromoted sites (band at 2110 cm^{-1}) is lower than on the reference catalyst, whereas the number of promoted sites (band at 2065 cm^{-1}) is clearly higher, particularly on sample S$_1$. These results are in agreement with the higher activity of the latter. On sample O$_1$, the intensity of the band characteristic of unpromoted sites is close to that observed on the reference catalyst, whereas that corresponding to promoted sites is slightly lower. This can be related to the lower cobalt content of the O$_1$ catalyst and explains its lower activity.

DISCUSSION

Anchorage of Cobalt

Taking into account the previous work of Roustan *et al.* (14) on the adsorption of Co(CO)$_3$NO on Al$_2$O$_3$ and the present results, the anchorage of Co(CO)$_3$NO on the oxidic Mo/Al$_2$O$_3$ can be interpreted as the mechanism of carbonyl nitrosyl adsorption, illustrated in Scheme 1.

The first step would be an interaction of Co(CO)$_3$NO with the surface by the oxygen atom of the NO group (species I:ν(NO) = 1806 cm^{-1}), the second step an interaction of the cobalt atom of species I with the surface (species II:ν(NO) = 1687 cm^{-1}), leading to the appearance of CO in the gas phase. This is supported by the ν(NO)
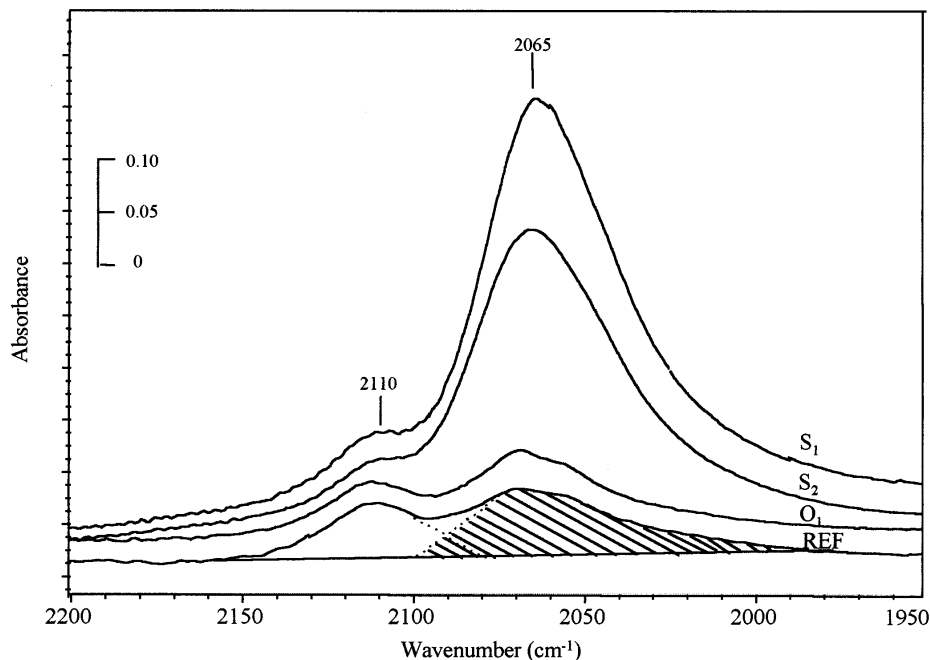
FIG. 6. IR spectra of CO adsorbed ($P_{eq} = 10$ Torr) after sulfidation of the different catalysts.

wavenumber of species I, lower than that of the parent compound (1823 cm^{-1}) and higher than that of species II. Moreover, it explains the presence of a ν(CO) band (shoulder at 2130 cm^{-1}) at a higher frequency than those observed in the spectrum of Co(CO)₃NO gas. Further interaction of cobalt with the surface (third step) releases CO and NO to the gas phase. They can be subsequently readsorbed in the form of carbonyl or nitrosyl species (species III). Previous results on sulfided NiW/Al₂O₃ catalysts showed that NO is preferentially adsorbed relative to CO (28). The wavenumbers of ν(NO) bands so formed are similar to those reported by Topsøe and Topsøe (23) when adsorbing NO on cobalt atoms of oxidic Co–Mo/Al₂O₃ (Table 2). Therefore, it indicates that cobalt is deposited on the molybdenum phase and not on alumina. In addition, the perturbation of the ν(Mo = O) band at 1008 cm^{-1}, even after carbonyl nitrosyl decomposition, confirms the interaction between molybdenum and cobalt.

Another possible assignment of the 1806 and 1687 cm^{-1} bands when Co(CO)₃NO is contacted with oxidic Mo/Al₂O₃ is the formation of dinitrosyl species on molybdenum sites. This would mean that part of the NO released into the gas phase may adsorb on molybdenum sites not involved in cobalt deposition. At longer contact times, these bands are no longer detected. This would indicate that when the amount of cobalt deposited increases, NO would be progressively displaced from molybdenum to cobalt sites in interaction with molybdenum. Whatever the assignment, the ν(NO) wavenumber of bands presented in Figs. 2b and 2c shows the formation of an oxidic Co–Mo/Al₂O₃ sample.

Adsorption of Co(CO)₃NO on sulfided Mo/Al₂O₃ follows the same three steps (Scheme 1): (i) the dinitrosyl species (bands at 1855 and 1790 cm^{-1}) which are characteristic of cobalt in interaction with sulfided molybdenum, reveal that the cobalt carbonyl nitrosyl decomposition occurs on the molybdenum phase, as in the case of the oxidic catalysts; (ii) the shoulder at 2070 cm^{-1} on sample S₁ (Figs. 4a–b) is characteristic of CO adsorption on promoted sites (13, 16, 18); and (iii) in all cases (oxidic and sulfided states) after evacuation at 373 K, no dinitrosyl species adsorbed on molybdenum sites are detected. This indicates that molybdenum sites are no longer accessible due to a complete coverage by cobalt species. Moreover, the higher

SCHEME 1
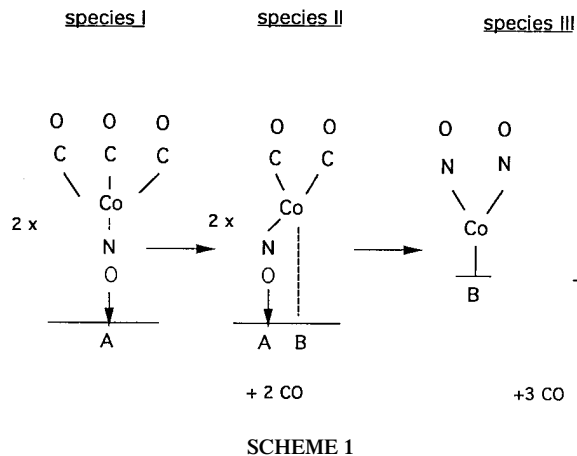
intensity of the band around 1790 cm^{-1} on S$_1$ (Fig. 4) than on the O$_1$ sample (Fig. 2) is explained by an increase of the number of anchorage sites after sulfidation. This is in agreement with the higher cobalt content measured by chemical analysis (Table 1). As for isocyanate species, Roustan *et al.* (14) proposed that their formation occurs through interaction between two Co(CO)$_3$NO adsorbed species. Since the concentration of these latter are higher on S$_1$ than on the O$_1$ sample, it could explain why NCO species are detected on the former but not on the latter.

On alumina (14), species I and II are expected to be formed on a pair of coordinatively unsaturated sites, namely, Al^{3+} (A site) and O^{2-} (B site). We propose that over an oxidic or sulfided Mo/Al$_2$O$_3$ sample, their formation involves a pair of surface sites: coordinatively unsaturated molybdenum (A site) and oxygen or sulfur sites (B site).

Active Sites on Sulfided Catalysts

Figure 5 shows a good relation between the ex-carbonyl nitrosyl catalyst activity and the amount of cobalt deposited. Therefore, the introduction of cobalt before or after Mo sulfidation changes the amount of deposited cobalt but not the HDS activity per cobalt site. However, this result does not explain the two times lower activity, for the same cobalt content, of the impregnated catalyst relative to the ex-carbonyl nitrosyl one.

The IR study of adsorbed CO on sulfided Co–Mo (Fig. 6) provides evidence that the nature of the sites present on the ex-carbonyl nitrosyl and impregnated catalysts is similar, but that their distribution between promoted and unpromoted sites is different. Indeed, samples S$_1$ and S$_2$ present a much more intense IR signal characteristic of promoted sites (2065 cm^{-1} band) than the impregnated and sulfided O$_1$ catalysts. In particular, sample S$_2$ which presents an amount of total cobalt close to the reference catalyst exhibits a strongly higher number of cobalt atoms in interaction with molybdenum atoms. In order to obtain an accurate measurement of the absorbance of the band characteristic of promoted sites, we have decomposed the ν(CO) massif into two components as exemplified in Fig. 6. Figure 7 reports the HDS activity versus the integrated area of the component at 2065 cm^{-1} (promoted sites). The correlation, which includes the data relative to the impregnated catalyst, is fairly good. This confirms that, whatever the precursor, the nature of promoted sites and their intrinsic activity are similar. It also shows, conversely to conclusions of a recent paper (29), that infrared spectroscopy of adsorbed CO is a well-adapted tool to describe and to predict the relative activity of sulfide hydrotreating catalysts.

Our study clearly demonstrates that deposition of the promoter by a metal carbonyl on a previously sulfided Mo/Al$_2$O$_3$ sample is a very efficient way to promote molybdenum. Use of the carbonyl nitrosyl complex in the gas phase favors the anchorage of cobalt on molybdenum and
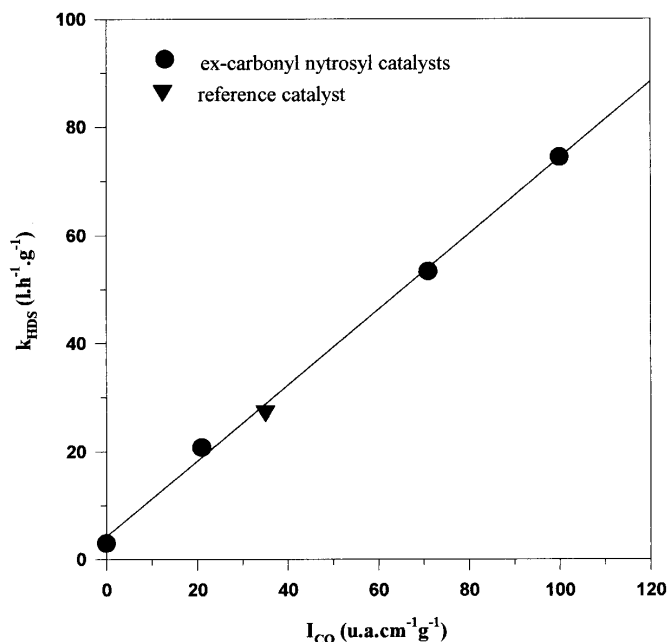

FIG. 7. HDS rate constant versus area of the ν(CO) band characteristic of the promoted sites (band at 2065 cm^{-1}).

avoids the formation of cobalt species on alumina, resulting in an increased amount of Co–Mo–S sites. Moreover, the excarbonyl nitrosyl preparation prevents extensive migration of cobalt in the alumina lattice due to the lower temperature of the post treatment; namely, sulfidation at 673 K, instead of calcination at 773 K for the impregnated catalyst.

CONCLUSION

IR characterizations allowed us to account for the anchorage of Co(CO)$_3$NO on oxidic and sulfided Mo/Al$_2$O$_3$ catalysts. The carbonyl nitrosyl complex was first bound to molybdenum sites and then to surface oxygen or sulfur ions, according to the state of the molybdenum phase. CO and NO released when adsorbing Co(CO)$_3$NO are used as intrinsic probe molecules and showed that cobalt was preferentially deposited on the molybdenum phase. This induced a higher amount of promoted sites than on the impregnated catalyst. This was confirmed by CO adsorption which detected a higher number of promoted sites on the ex-carbonyl nitrosyl catalysts than on the impregnated one for the same cobalt content and by the higher activity per total cobalt atom of the ex-carbonyl nitrosyl catalyst for thiophene hydrodesulfurization.

It was concluded that the higher activity of ex-carbonyl nitrosyl catalysts is not related to a modification of the nature of sites but to a greater ability of the carbonyl nitrosyl complex to form promoted sites and to provide for milder subsequent treatments.

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