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Deactivation of MoS_2/Al_2O_3 in Thiophene Hydrodesulfurization: An Infrared Spectroscopic Analysis by Adsorbed CO

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Fourier transform infrared spectroscopy on adsorbed carbon monoxide was used to study the deactivation and rejuvenation of a MoS_2/γ-Al_2O_3 catalyst during hydrodesulfurization (HDS) of thiophene. The study covered several sample pretreatment steps, each resembling a stage in the catalyst life. The number of active sites on the sulfided sample was correlated to the intensity of CO-stretch absorption bands in the infrared spectrum. It was concluded that with increasing HDS time on stream the intensity of bands correlated to CO adsorbed on edge and corner sites decreases, while simultaneously those in the carbon–carbon stretch region (1800–1200 cm^{-1}) increase in intensity. Rejuvenation of a spent catalyst under H_2S/H_2 at 673 K revealed an increase in the number of gas-phase exposed edge and corner sites of the MoS_2 slabs, while concurrently the intensities of bands correlated to carbon–carbon stretch vibrations decreased. Thus, it was concluded that catalyst deactivation was caused by preferential coke deposition on the active sites, which can be removed under H_2S/H_2. No differences were found in the coking behavior of edge and corner sites.

INTRODUCTION

An important process in oil refineries is hydrotreating, i.e., the removal of heteroatoms such as nitrogen, sulfur, and oxygen by using sulfided molybdenum- or tungsten-based catalysts. The main objective of sulfur and nitrogen removal is the protection of down-stream catalysts, e.g., catalysts applied for catalytic reforming or isomerization, which are sensitive for sulfur poisoning of the active sites. Another incentive for hydrotreating is the reduction of environmental pollution, improvement of color and odor, and the stability of the oil products produced.

It is known from refinery practice that the activity of hydrotreating catalysts decreases with time on-stream. This is mainly due to deposition of coke and metal sulfide particles on the catalyst surface and sintering of the active phase. Coke deposition on the catalyst surface can be roughly divided into two time regions. In the first period coke buildup is very rapid, causing a fast deactivation of the catalyst. The second region exhibits a rather stable catalyst activity, combined with a slow coke deposition (1, 2). Several authors (3–5) proposed a model for deactivation, based on research on commercial hydrotreating catalysts, i.e., alumina-supported NiMo or CoMo catalysts. This model describes coke deposition on the catalyst support, while a coke-free zone surrounding the metal sulfide ensures catalytic activity. Richardson *et al.* (3) proposed that, eventually, hydrogen deficiency on the catalyst surface will cause coke deposition even in the coke-free zone, leading to the deactivation of the catalytic site. In contrast, Marafi and Stanislaus (6) reported immediate blocking of active sites by coke deposits already after a short time on-stream. Obviously, it is important to know where the coke deposits are formed on the catalyst surface: on the carrier material, thus blocking the pore structure of the support but not the active sites, or preferentially on the active sites. This knowledge can then be used to facilitate the development of catalysts that withstand deactivation due to coke deposition and to design advanced catalyst rejuvenation methods. Burning the coke with oxygen is usually applied to regenerate deactivated catalysts. A more subtle approach could be followed in order to restore at least part of the activity by treating the catalyst in a mixture of H_2S/H_2. This more gentle procedure might be referred to as rejuvenation.

The current study has been carried out to provide insight on where the coke is deposited on the catalyst surface during the initial stage of the catalyst life in gas-phase thiophene hydrodesulfurization (HDS). As this research is a first step to a better understanding of the deactivation and rejuvenation of an HDS catalyst, a relatively simple catalyst system was chosen: MoS_2/γ-Al_2O_3, in the absence of such a promoter as Co. Fourier transform infrared analysis of low-temperature adsorbed carbon monoxide, FTIR(CO), has been chosen to acquire information on the surface of the MoS_2/Al_2O_3 catalyst, since the technique gives information on both the available active sites and the nature of the coke present. For this research, a setup has been used in which both chemical reactions and IR analyses can be carried out *in situ*.

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Over the years, Fourier transform infrared analysis of chemisorbed probe molecules has been extensively used in research on solid catalysts. Examples of these probe molecules are NO and CO. On the one hand, probing with NO has an advantage over CO in the fact that a high NO coverage can be established already at room temperature, whereas in the case of CO as probe molecule the sample temperature has to be lowered to 100–150 K to ascertain a sufficiently high surface coverage. On the other hand, the typical advantage of CO probing over that by NO is, as was shown by Delgado *et al.* (7), that it is more selective and less reactive than NO. As this research involves sulfided as well as deactivated (coked) catalysts, CO adsorption was considered the most appropriate.

To the best of our knowledge, up to now, investigations of hydrotreating catalysts by FTIR(CO) have been confined to either "sulfided catalysts," i.e., a molybdenum catalyst prior to actually performing an HDS reaction, or its oxidic precursor. As the present study focuses on the deactivation of the catalyst due to coking, FTIR(CO) was applied on sulfided and "spent" samples. Rejuvenated samples were included in the study also.

Two simultaneously occurring processes usually describe the chemisorption of CO on surfaces: σ-donation (8) and π-back donation (8, 9), and they affect the bond strength between carbon and oxygen. σ-Donation takes place between the 5σ molecular orbital, "MO," of the CO and an electron-deficient site on the catalyst surface. An electron from the lone pair in the 5σ-MO of CO is shared with the surface atom, resulting in a stronger CO bond, thus causing a shift of the absorption band to higher wave numbers compared to gaseous CO. An example of this σ-donation is the adsorption of CO on alumina –OH groups, which results in an absorption band at 2154–2166 cm^{-1} (8–10).

In the case of CO adsorption on Mo^{2+} sites in MoS_2 π-back donation also occurs. Then, d-electrons are back-donated from the Mo^{2+} ions into the anti-bonding $2\pi^*$-MO of the CO molecule. This results in a weakening of the CO bond and, hence, a shift of the absorption band to a lower wave number. Various authors (8–11) reported the appearance of an IR absorption band in the region of 2100–2110 cm^{-1} for CO adsorbed on a sulfided molybdenum/alumina catalyst. This band was ascribed to CO adsorbed on the catalytically active sites for HDS, located at the edges of MoS_2 slabs. The activity of these sites is thought to originate from sulfur ion vacancies, commonly referred to as coordinatively unsaturated sites (cus sites) (12–20).

EXPERIMENTAL

Catalyst Preparation

The catalyst investigated consisted of 10 wt% MoO_3 on γ-Al_2O_3. The specific surface area of the alumina was 281 m^2/g, as determined from N_2 adsorption at 77 K in a Quantachrome Autosorb-6B. The alumina contains mesopores with a diameter of 4 to 10 nm, the total pore volume being $0.66 \cdot 10^{-6}$ m^3/g. The alumina support was pore volume impregnated with an aqueous solution of ammonium heptamolybdate, dried for 2 h at 393 K, and subsequently calcined for 1 h at 773 K.

Experimental Setup

A schematic representation of the infrared *in situ* setup (IRIS) is shown in Fig. 1. The IRIS can be divided into two main sections: the high temperature reactor (HTR) and the infrared transmission cell (IRTC), which are separated by a pneumatic gate valve. The spectrometer used was a Magna-IR spectrometer 550 (Nicolet). In the HTR the sample can be subjected to various reactions of interest, e.g., calcination, sulfidation, and thiophene HDS. The heating is temperature controlled, thus enabling a linear temperature increase to a maximum of 1273 K. During the reactions gases are led over the sample in the HTR using mass flow controllers, while the pneumatic gate valve is closed

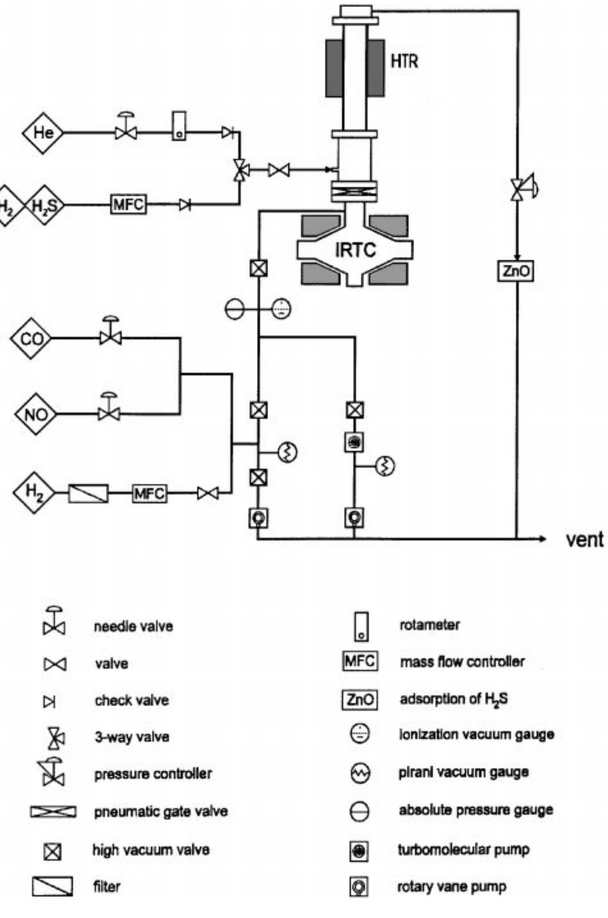

FIG. 1. A schematic representation of the infrared *in situ* setup (IRIS).

to prevent contamination of the IRTC. The pressure in the HTR is controlled by a Brooks Series 5866 backpressure regulator. The maximum pressure in the complete setup is approximately 3 bar and it was operated routinely at 1.7 bar to ensure a steady flow of the gases.

After the reaction in the HTR, the reactive gases are purged with helium or argon to avoid contamination of the IRTC and next the IRIS is evacuated with a turbomolecular pump. The base pressure, which is monitored by an ionization manometer, is about 10^{-5} Pa. Prior to FTIR(CO) analysis, the temperature in the IRTC is decreased to 133 K using liquid N_2 and the sample is lowered into the IRTC. Using an absolute pressure gauge (Granville-Phillips Cat. No. 275), the catalyst sample is exposed to defined pressures of CO. The CaF_2 windows of the IRTC are heated with a stream of hot air to prevent condensation of water from the air on the outside of the windows.

Sample Preparation

The molybdenum catalyst was powdered and about 10–15 mg of the powder was pressed into a self-supporting rectangular wafer with a surface of approximately 1.5 cm^2, using a pressure of 3 tons during 60 s. The wafer is then placed in the sample holder, which is inserted into the HTR.

Calcination of the Oxidic Precursor

The temperature in the high-temperature reactor was linearly increased at a rate of 0.17 K/s from ambient temperature to 673 K in a flow of air to remove impurities from the catalyst sample, introduced by handling it. After calcination, the HTR was flushed with helium for 0.5 h at 673 K and cooled to ambient temperature under a helium flow. The pneumatic gate valve was opened and the complete setup was evacuated overnight.

Sulfidation of the Oxidic Precursor

The sample was sulfided in a mixture of $4.5 \cdot 10^{-7}$ m^3/s H_2, $4.5 \cdot 10^{-7}$ m^3/s Ar, and $0.5 \cdot 10^{-7}$ m^3/s H_2S. The sample was sequentially subjected to 0.5-h sulfidation at ambient temperature and heated to 673 K at a rate of 0.17 K/s, followed by an isothermal sulfidation at 673 K for 2 h. Afterward, the HTR was flushed with helium at 673 K for 1 h and cooled to 473 K in the absence of a gas flow. To remove excess sulfur (9), the sample was treated for 0.5 h at 473 K in a flow of H_2 ($1.7 \cdot 10^{-7}$ m^3/s). Finally, the HTR is flushed with helium for 0.5 h, cooled to ambient temperature in a flow of He, and evacuated overnight.

Thiophene HDS

Thiophene HDS consisted of the following steps. Under a flow of thiophene, Ar, and H_2, the temperature in the HTR was increased to 673 K at a rate of 0.17 K/s, followed by thiophene HDS. The reaction mixture consisted of 66.7 vol% H_2 and 33.3 vol% thiophene/Ar at a total flow of $5.0 \cdot 10^{-7}$ m^3/s. The partial pressure of thiophene was 5 kPa. The duration of the HDS reaction was varied from 1 to 12 h. Since the setup was not designed for kinetic studies, conversion levels of the thiophene were not determined.

After the reaction, the temperature in the HTR was decreased to 473 K under a flow of the reaction gas mixture. Subsequently, a flow of $5.0 \cdot 10^{-7}$ m^3/s Ar was used to cool the HTR to ambient temperature in Ar, followed by evacuation of the complete setup. For comparison, a sulfided alumina sample was exposed to 8-h thiophene at 673 K.

Rejuvenation of the Spent Catalyst

Catalysts deactivated for 12 h were rejuvenated in a mixture of $4.5 \cdot 10^{-7}$ m^3/s H_2, $4.5 \cdot 10^{-7}$ m^3/s Ar, and $0.5 \cdot 10^{-7}$ m^3/s H_2S. The procedure consisted of an isothermal treatment at room temperature for 0.5 h, heating to 673 K at 0.17 K/s, and a 2-h isothermal stage at this temperature. Then, the HTR was flushed with He for 1 h at 673 K and cooled to ambient temperature under a helium flow, followed by evacuation overnight.

Infrared Analysis of Adsorbed CO

After cooling the IRTC to 133 K, the sample was lowered therein and a spectrum with a resolution of 4 cm^{-1} was obtained by accumulating 256 scans in the absence of CO, the “0-kPa” spectrum. This spectrum was used as a baseline correction (subtraction method) to allow a better comparison of the catalyst after various reactions. Then, the CO pressure in the IRTC was stepwise increased to 0.1, 1.0, 5.0, and 7.5 kPa and FTIR(CO) spectra were collected at each of these pressures. After each recorded spectrum, a new background spectrum was taken, i.e., about every 5 min. In the various figures, the spectra have been shifted vertically to ease the interpretation. Within each figure, the absorption units are the same.

RESULTS

Oxidic Catalyst Precursor

In Fig. 2 FTIR(CO) spectra on the freshly calcined, oxidic precursor are presented. The largest absorption band can be found at 2162 cm^{-1}, there is a weak band at ca. 2189 cm^{-1}, and a shoulder on the main band can be seen at 2140 cm^{-1} at higher CO pressures.

Sulfided Catalyst

Figure 3 shows the 7.5-kPa spectra of a freshly sulfided sample, “sulfided,” and the same sample after a mild reductive treatment at 473 K in a flow of hydrogen, “reduced-sulfided.” In the spectrum of the freshly sulfided sample a large absorption band can be observed at 2156 cm^{-1}, a

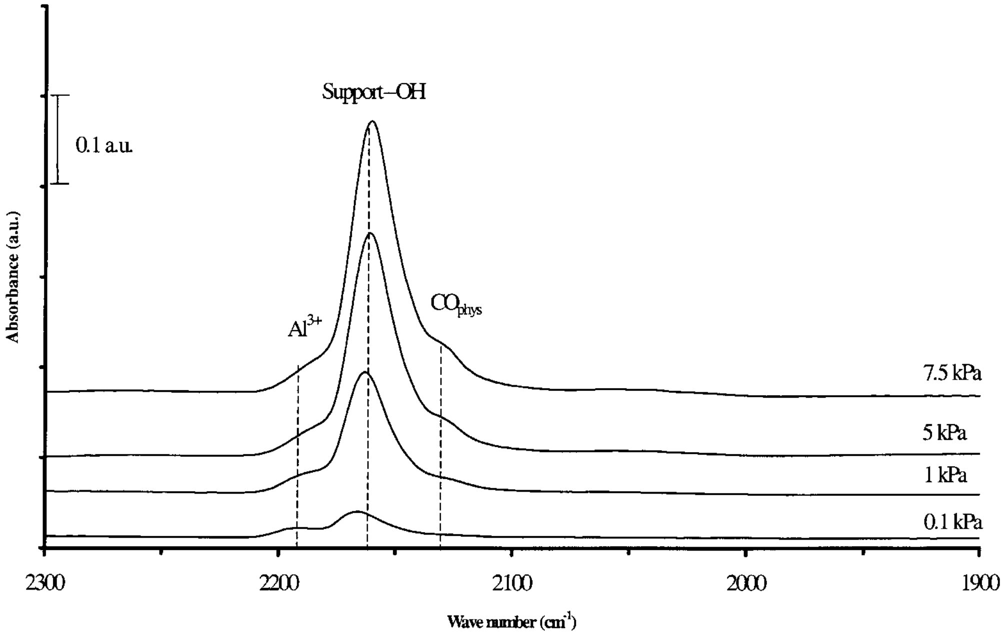

FIG. 2. Infrared spectra of CO adsorbed on the oxidic precursor. All spectra were recorded at a sample temperature of 133 K; the CO pressure is indicated at the various spectra.

small one at approximately 2140 cm^{-1}, and a broad band at approximately 2106 cm^{-1}. The intensity of the latter increases *after* treatment of the sample with hydrogen at 473 K, while that of the 2156-cm^{-1} band does not change. The main contribution in the 7.5-kPa CO spectrum of the reduced-sulfided sample is present at 2106 cm^{-1} and exhibits two shoulders, at 2065 cm^{-1} and 2048 cm^{-1}. Also a weak band located at 2189 cm^{-1} can be observed in these spectra.

Spent Catalyst

Following sulfidation, the next step in the hydroprocessing catalyst life cycle is the actual HDS reaction. An HDS run was interrupted after 1, 4, 8, and 12 h total reaction

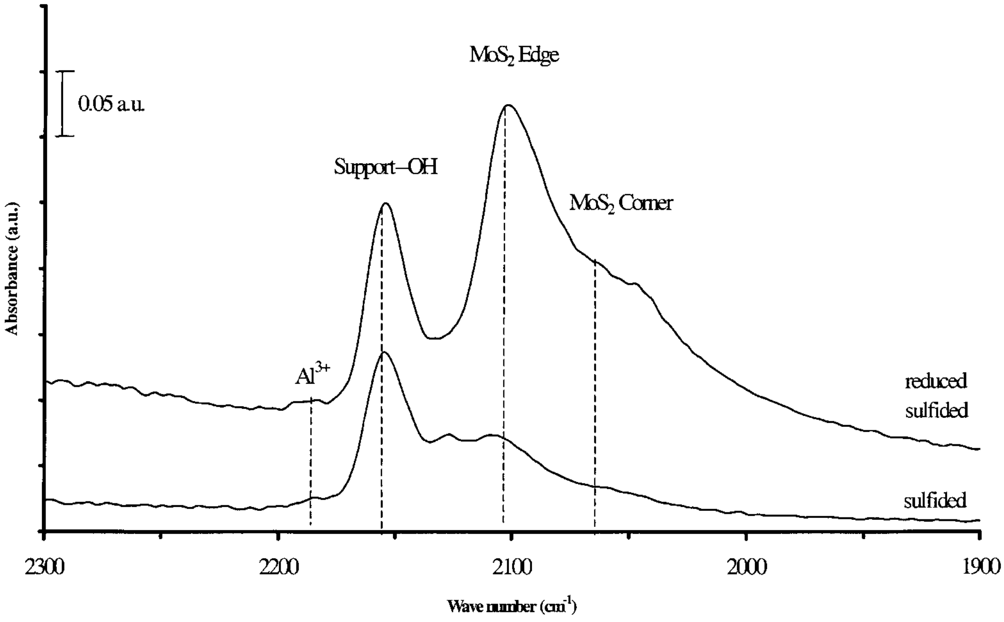

FIG. 3. Infrared spectra of a freshly sulfided sample, “sulfided,” and the same sample after hydrogen treatment at 473 K, “reduced sulfided.” All spectra were recorded at a sample temperature of 133 K under 7.5-kPa CO.

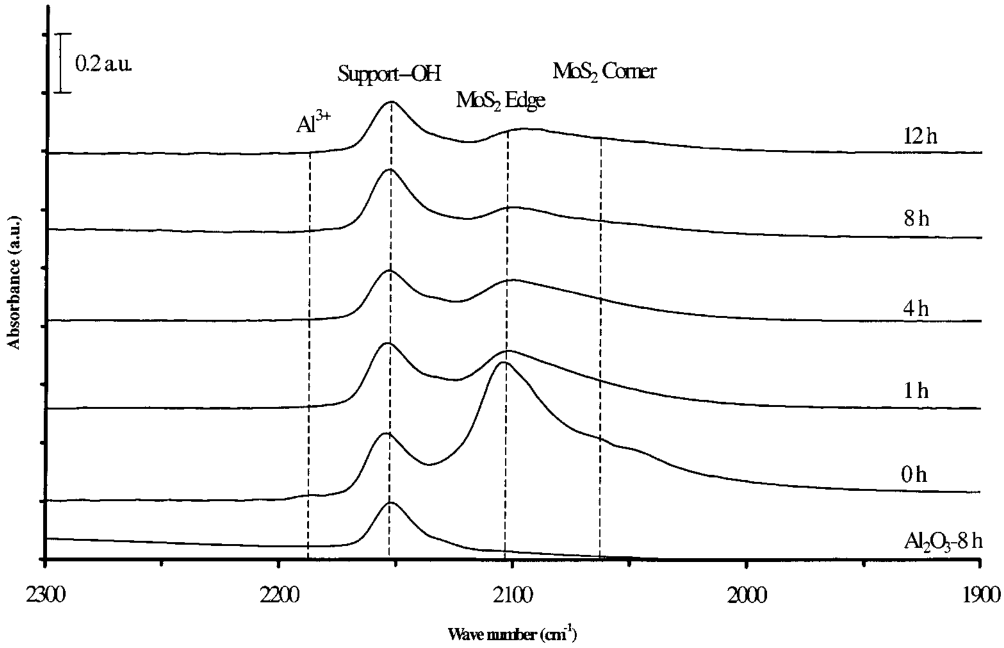

FIG. 4. Infrared spectra of a freshly sulfided catalyst, “0 h,” and after various times on-stream in thiophene HDS. The time on-stream is indicated at the various spectra. The pure alumina sample, “Al_2O_3-8 h,” was exposed to HDS reaction conditions for 8 h. All spectra were recorded at a sample temperature of 133 K under 7.5-kPa CO.

time to analyze the sample with FTIR(CO) for the nature of its deactivation. The results are collected in Fig. 4. After 12-h HDS the 2156-cm^{-1} band intensity has decreased to approximately 80% of its original value, while it slightly shifts to lower wave numbers. The band at 2106 cm^{-1} and its shoulder at 2065 cm^{-1} strongly decrease in intensity during the first hour of HDS. After that, the intensity decreases more gradually until both bands retain approximately 10% of their original value after 12-h HDS. After 12-h HDS, the 2106-cm^{-1} band is slightly shifted to a lower wave number, that is to ca. 2100 cm^{-1}.

For the sulfided alumina exposed to 8-h thiophene at 673 K, only one band can be observed at 2156 cm^{-1} and no contribution could be observed at 2189 cm^{-1}. The intensity of the 2156-cm^{-1} band is nearly equal to that of the 8-h deactivated Mo/Al_2O_3 sample.

In the 1800- to 1200-cm^{-1} region of the spent samples (0-kPa spectra) shown in Fig. 5, two absorption bands can be seen. The first is located at ca. 1575 cm^{-1} and the second at ca. 1470 cm^{-1}. The intensity of the band at 1575 cm^{-1} increases with HDS time and develops a shoulder at ca. 1560 cm^{-1} after 8-h HDS. The intensity of the 1470-cm^{-1} band stabilizes after 4-h HDS and also develops a shoulder at its low-frequency side after 8 h time on-stream. Note that the relative intensity of the 1575-cm^{-1} band increases in time compared with that at 1470 cm^{-1}. These two bands are also observed in the 0-kPa spectrum of the 8-h thiophene-exposed pure alumina sample. However, the intensities of these bands are much lower compared to the catalyst sample after 8-h thiophene HDS.

Rejuvenated Catalyst

Figure 6 presents 7.5-kPa CO spectra in the 2300- to 1900-cm^{-1} region of a sample exposed to 12-h thiophene HDS, “12 h,” followed by rejuvenation at 673 K for 2 h, “H_2/H_2S rejuvenated.” For comparison, the 7.5-kPa CO spectrum of the fresh sample, “0 h,” is also shown; the 0- and 12-h HDS spectra are the same as those in Fig. 4. Note that the band at ca. 2106 cm^{-1} strongly increases in intensity after treating the catalyst in the H_2S/H_2 mixture. Effectively, the 2106-cm^{-1} band intensity is restored to approximately 50% of its original value in the 0-h spectrum. In contrast, the intensity of the 2156-cm^{-1} band is about the same for the 12-h spent sample and the H_2/H_2S-rejuvenated sample. Note that the 2189-cm^{-1} band is not restored by this treatment.

In Fig. 7 the 0-kPa spectra of the 1800- to 1200-cm^{-1} region are presented. It can be seen that after rejuvenation of the catalyst, both the band at 1575 cm^{-1} and the band at 1470 cm^{-1} are strongly reduced in intensity.

DISCUSSION

The band located at 2162 cm^{-1} on the oxidic catalyst precursor is attributed to hydrogen-bonded CO molecules on the alumina support, since its position and pressure dependence correspond nicely to those reported for the oxidic Mo/Al_2O_3 catalyst by Zaki *et al.* (8). The 2156-cm^{-1} contribution on the sulfided catalyst is also ascribed to H-bonded CO on the Al_2O_3 support (9, 10). Clearly, upon

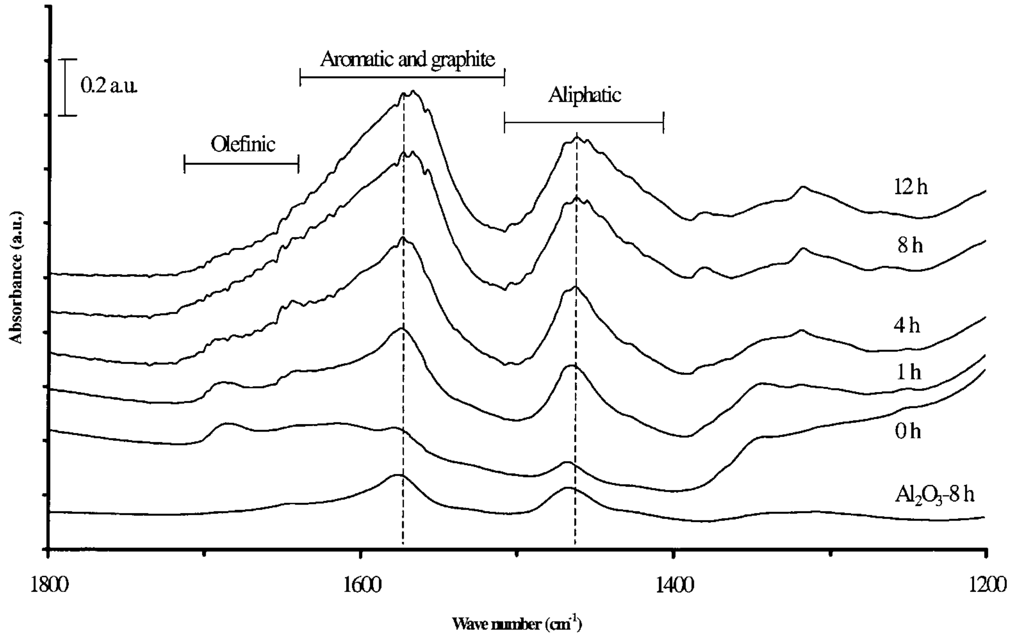

FIG. 5. Infrared spectra of carbon–carbon stretch vibration bands after various times on-stream in thiophene HDS. The time on-stream is indicated at the various spectra. The pure alumina sample, "Al_2O_3-8 h," was exposed to HDS reaction conditions for 8 h. All spectra were recorded at a sample temperature of 133 K in the absence of CO.

sulfiding the OH groups are stable, in agreement with temperature-programmed sulfiding studies (21). The band near 2140 cm^{-1}, which appears in the spectra of the oxidic and sulfided samples at high CO pressures, is attributed to fysisorbed CO (9), as it is near the gas phase CO vibration located at 2143 cm^{-1} and only appears at high CO pressures. The weak band at 2189 cm^{-1} is ascribed to CO adsorbed on octahedral Al^{3+} sites (9, 22, 23).

The 2106-cm^{-1} band in the spectra is attributed to CO adsorbed on Mo^{2+} cus sites located at the edges of MoS_2 slabs (8–11, 24). Upon sulfidation these Mo^{2+} cus sites are covered with chemisorbed sulfur (9). To obtain an "IR-active"

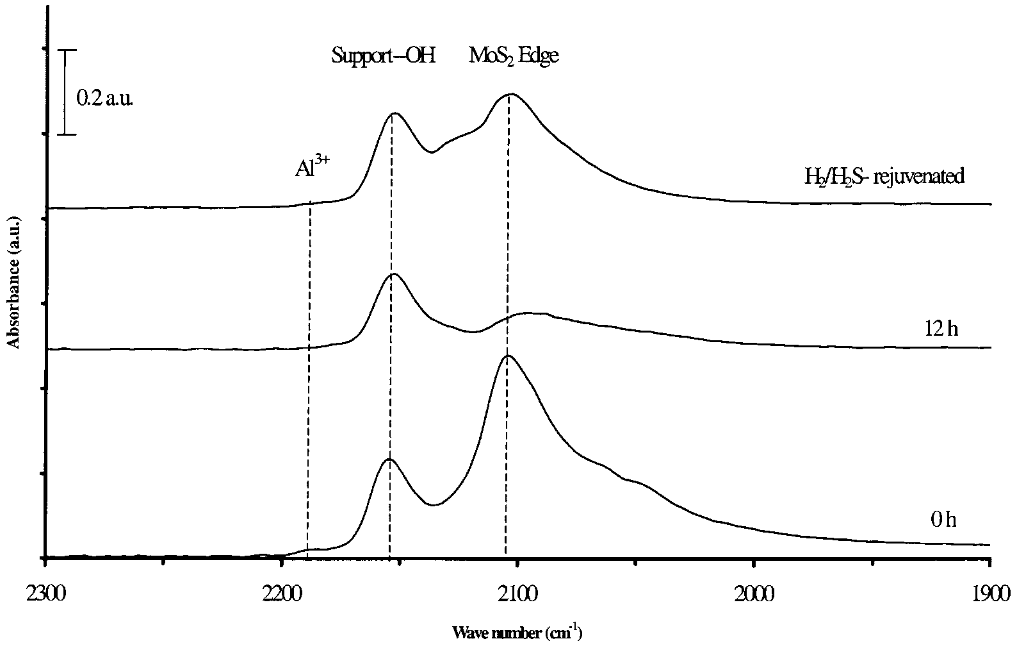

FIG. 6. Infrared spectra of a freshly sulfided catalyst, "0 h," after 12-h thiophene HDS, "12 h," and after H_2/H_2S rejuvenation, "H_2/H_2S-rejuvenated." All spectra were recorded at a sample temperature of 133 K under 7.5-kPa CO.

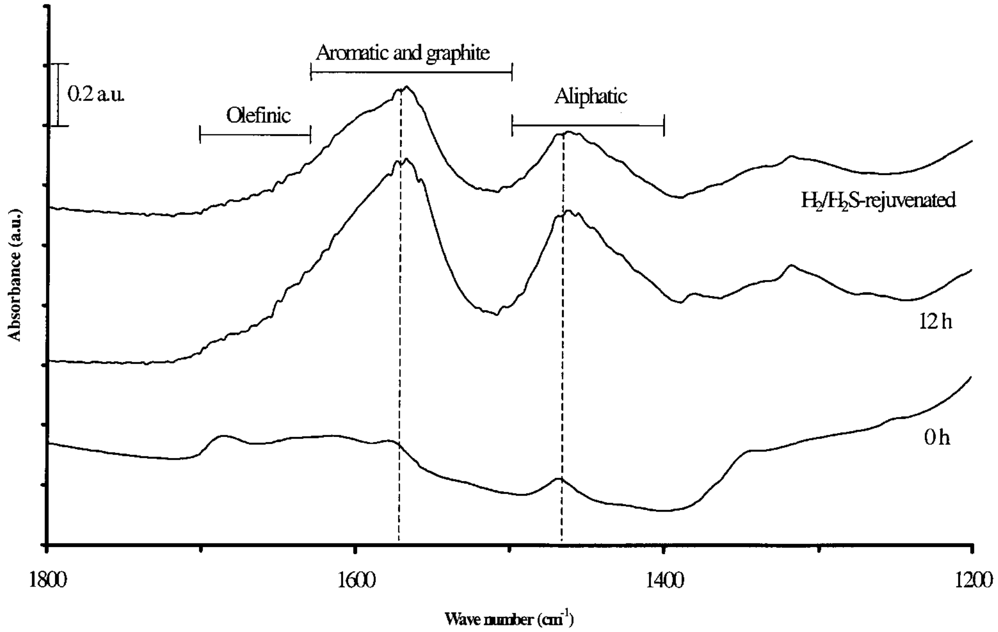

FIG. 7. Infrared spectra of carbon–carbon stretch vibration bands on a freshly sulfided catalyst, "0 h," after 12-h thiophene HDS, "12 h," and after H_2/H_2S rejuvenation, "H_2/H_2S-rejuvenated." All spectra were recorded at a sample temperature of 133 K in the absence of CO.

sample, this sulfur has to be removed by treatment with H_2 at 473 K. Müller *et al.* (9) observed a band located at about 2060 cm^{-1} on a sulfided catalyst reduced in H_2 at 453 K. It is suggested that the band at 2065 cm^{-1} originates from corner Mo cus sites, which have a stronger π-back donation because of their more unsaturated nature than the edge sites (9, 23). The presence of a shoulder 2048 cm^{-1} suggests the existence of even more unsaturated and protruding corner sites, associated with the MoS_2 slabs. The higher degree of unsaturation of these sites is suggested to enhance the π-back donation, thus shifting the CO vibration to a lower wave number. However, additional research will be a prerequisite for a further clarification on this point.

Figure 8 is introduced to provide a better insight into the deactivation of the catalyst sample and indicates the presence of a relationship between the amount of coke on the sample and the number of active sites. In this figure, the peak height of various bands, characteristic for the changes

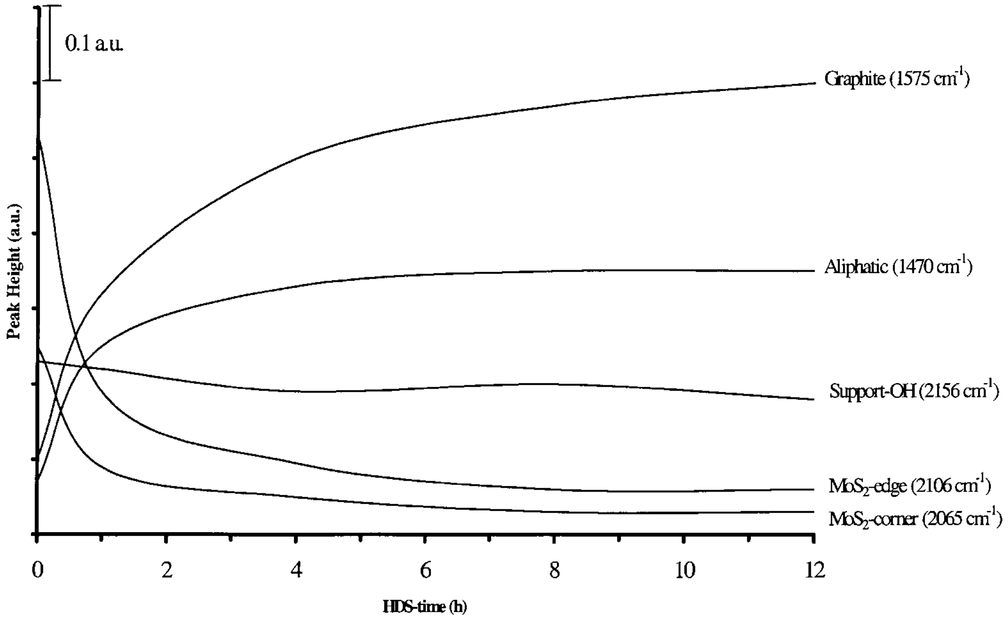

FIG. 8. Peak height of the various bands, characteristic for the changes in the catalyst surface as function of HDS time.

in the catalyst surface, is presented as a function of HDS time on-stream. This figure clearly shows that the band at 2106 cm^{-1}, indicative of gas-phase exposed Mo^{2+} cus sites in MoS_2, is strongly reduced in intensity during the first hours of the HDS reaction. This means that fewer Mo^{2+} cus sites are available for CO adsorption. At the same time, the amount of coke on the catalyst sample increases, as indicated by the increased intensity of the bands centered at 1575 and 1470 cm^{-1}. These results clearly indicate that the Mo^{2+} cus sites are preferentially blocked by coke. This is further supported by the observation that on pure alumina exposed to thiophene at 673 K for 8 h, some coke is deposited, but not nearly as much as on the 8-h spent catalyst sample. The carbonaceous deposits on the Mo^{2+} cus sites are also suggested to be the cause of the shift of the 2106-cm^{-1} band to 2100 cm^{-1} after 12 h of HDS.

From Fig. 8 it can be observed that the decrease in intensity for both the 2106-cm^{-1} and the 2065-cm^{-1} band after 12-h HDS is ca. 90%. The intensity ratio of these bands (edge/corner sites) varies in the range of 2.0–2.1 throughout the 12 h of thiophene HDS. Based on the current results it is concluded that there are no differences in the coke deposition rate on edge and corner sites. The loss of active sites is highest during the first hour of HDS. After that, the intensity of the 2106-cm^{-1} band decreases only slowly, until after 4 h the number of active sites seems to be at equilibrium, suggesting that the HDS activity will be nearly constant. These results correlate well with the work of Ledoux *et al.* (25), who observed a rapid activity loss during first 3 h of HDS, followed by a long period of relatively constant activity. Furthermore, commercial hydrotreating catalysts exhibit the same behavior albeit on a much larger time scale (1).

Absorption bands in the 1800- to 1200-cm^{-1} region can be identified as C–C stretch and C–H bending vibrations of the carbonaceous deposits on the catalyst sample. Several authors (26–28) studied coke formation by means of Raman spectroscopy, which is a vibrational spectroscopy analogous to infrared analysis. They observed bands at a Raman shift of 1575–1580 cm^{-1} and approximately 1350 cm^{-1} (26–28). This second band is also visible in Fig. 5, although at a slightly lower wave number, i.e., ca. 1340 cm^{-1}.

All spectra of the spent sample contain two small contributions, one at ca. 1691 cm^{-1} and the other at 1643 cm^{-1}. These bands are located in the olefinic stretch region, indicating that the coke also contains unsaturated components. The contribution at 1691 cm^{-1} can be ascribed to a *trans*-C=C vibration (29), which also gives rise to a weak band at ca. 1420 cm^{-1}. The latter is present as a small shoulder in the peak centered at 1470 cm^{-1}. The band located at 1643 cm^{-1} is ascribed to a *cis*-C=C vibration (29). This leads to the conclusion that the coke contains both *trans*- and *cis*-butene-like species, which is a product of thiophene HDS. Brenner and Thompson (30) obtained similar results with thiophene adsorption on a CoMo catalyst and attributed bands to (a precursor of) 1-butene.

Vibrations in the 1500- to 1400-cm^{-1} region can be associated with CH_2 and CH_3 groups. Wang and Griffiths (31) have attributed bands located at approximately 1470 and 1375 cm^{-1} to C–H bending modes of methylene groups in long aliphatic chains. The first was ascribed to the asymmetrical bending mode and the second to the symmetrical bending mode of a methyl/methylene group. The number of methyl groups seems to stabilize after 4-h HDS, as the peak intensity at 1470 cm^{-1} remains constant after that time. Figure 8 shows that the relative contribution of the 1575-cm^{-1} peak compared to the 1470 cm^{-1} peak increases with reaction time, indicating that the composition of the coke changes with time. The varying intensity ratio after 1-h deactivation also leads to the conclusion that these bands cannot be attributed to the formation a single species, like a carboxylate group as reported by Datka *et al.* (32). To summarize, with increasing time on-stream, the carbonaceous deposit contains less hydrogen and becomes more graphitic.

Furthermore, the broad shoulder on the low-frequency side of 1470-cm^{-1} band indicates that, apparently, different methyl groups are present in the coke. Possibly, reorganization of the carbonaceous deposits occurs, that is, branching and/or chain length growth of the adsorbed hydrocarbons. Simultaneously, the 1643-cm^{-1} contribution increases, indicating that the aliphatic chains are dehydrogenated into olefinic components.

This is confirmed by the appearance of a distinct shoulder of the graphite contribution located at ca. 1560 cm^{-1}, which was attributed to conjugated olefins by Li and Stair (26). This indicates that, under the experimental conditions applied, the degree of unsaturation increases with HDS time. Li and Stair qualified these conjugated olefins as precursors of aromatics. According to these authors, aromatic components give rise to absorption bands at ca. 1610 cm^{-1} and polyaromatics at 1595 cm^{-1}. As can be seen in Fig. 5, these contributions increase with HDS time. This leads to the conclusion that the coke increases in aromaticity with catalyst age, in accord with the earlier work of Fonseca *et al.* (33, 34).

In conclusion, the coking mechanism on $MoS_2/\gamma\text{-}Al_2O_3$ under thiophene HDS conditions seems to consist of several steps which were also reported by Li and Stair (26). The first step is the adsorption of aliphatic and olefinic species and dehydrogenation of the adsorbed components, leading to a rather olefinic coke. This step is possibly followed by an increase in chain length, while conjugation of olefinic groups leads to the formation of (poly)aromatics. The last step is the formation of a (pre)graphitic structure on the sample.

Upon rejuvenation, the CO spectrum changes toward that of the fresh catalyst: the intensity of the peak at 2106 cm^{-1} increases to approximately 50% of the fresh catalyst. This is accompanied by a decrease in intensity of bands located in the 1800- to 1200-cm^{-1} region, indicating that a smaller amount of coke is present on the H_2S/H_2-rejuvenated sample compared to the 12-h spent sample. This indicates that active sites are freed from coke. Apparently, the aromatic/graphitic (1630–1550 cm^{-1}) and the aliphatic (1500–1400 cm^{-1}) components are equally removed from the sample. It is interesting that the peak representing the OH groups does not change within limits of accuracy.

These results are in accordance with those of Ledoux *et al.* (25), who observed that the catalyst activity returned to its initial value upon treatment with the sulfiding mixture at 500 K. They ascribed the deactivation of the catalyst to reduction of the active phase. However, the reaction temperature of 500 K applied is much too low for the reduction of molybdenum into inactive Mo^0 to take place, as can be inferred from results of Arnoldy (35). Furthermore, it was shown that the reductive treatment at 473 K of freshly sulfided catalyst results in the further enhancement of the active phase, due to the formation of active edge/corner sites as shown in Fig. 3.

CONCLUSIONS

FTIR(CO) is a suitable technique to obtain qualitative information on the deactivation behavior of MoO_3/Al_2O_3 catalysts under thiophene HDS. For the freshly sulfided samples, bands located at ca. 2106 and 2065 cm^{-1} were attributed to HDS active edge and corner sites of the MoS_2 slabs, respectively. The intensity of these bands decreases with increasing reaction time. Simultaneously, contributions in the carbon–carbon stretch region at 1800–1200 cm^{-1} increase, leading to the conclusion that coke deposits preferentially block the active sites. Within limits of accuracy, no differences were observed in the coking behavior of edge and corner sites.

It was found that both the amount and the chemical nature of the coke changes with increasing HDS time. Apart from aliphatic and olefinic components, the coke deposits also contain graphite structures already after a short time on-stream. The coking mechanism eventually leads to the formation of a highly aromatic and graphitic type of coke. This coke can be removed from the catalyst by a rejuvenation step under H_2S/H_2 and it was concluded that aliphatic and aromatic/graphitic components are equally removed.

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