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Characterization of the Active Phase in NiW/γ-Al_2O_3 Catalysts in Various Stages of Sulfidation with FTIR(NO) and XPS

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The sulfidation of oxidic mixed metal catalysts is an important step in the activation of these catalyst precursors for hydrotreating reactions. The sulfidation of NiW/γ-Al_2O_3 catalysts is especially interesting since it is possible to study intermediate stages of sulfidation as separate, stable phases. By carrying out a systematic study, a detailed picture was obtained of the sulfiding reactions and the species formed. The major techniques used were FTIR(NO) and semiquantitative quasi *in situ* XPS. A reference catalyst was obtained by extraction of Ni from the oxidic catalysts. Four types of Ni are present in the oxidic NiW/γ-Al_2O_3 catalysts, viz., Ni in a surface aluminate, Ni in a mixed oxide with W, Ni in a mixed oxide with W and Al, and bulk Ni aluminate. No separate Ni oxide phase is present. It was found that even in dried NiW/γ-Al_2O_3 catalysts, a significant part of Ni strongly interacts with either W or the support and is present in subsurface positions. This subsurface Ni species migrates to the surface upon sulfidation below 373 K. Sulfidation below 473 K shows the development of a Ni sulfide species, which is in close interaction with an oxidic or partially sulfided W^{6+} phase. In addition, part of the W phase can be sulfided at low temperature to form WS_3 and it was established that no W^{4+} species are formed below 600 K. XPS indicated that sulfidation above 600 K results in a distinct change in the chemical environment of Ni ions, which was assigned to the formation of the so-called NiWS phase. Remarkably, FTIR(NO) showed that after sulfidation above 700 K, the gas-phase-exposed W^{4+} sites become largely inaccessible for NO. This is interpreted as a full decoration of WS_2 edges, probably with Ni sulfide, which occurs at a significantly higher temperature than the initial formation of NiWS. © 2000 Academic Press

INTRODUCTION

The sulfidation of oxidic mixed metal catalysts is an important step in the activation of these catalysts for several reactions in the oil refining industry. NiW/γ-Al_2O_3 catalysts exhibit a high activity for aromatics hydrogenation at low H_2S concentrations (1) and for the deep hydrodesulfurization of diesel fuel (2). In addition, NiW-based catalysts are commonly applied in hydrocracking reactions (3). A detailed understanding of the effect of the sulfidation procedure and temperature of the formation of active sites in this catalyst can lead to the development of more active catalysts and to more optimal start-up procedures. From a scientific point of view the sulfidation of NiW/γ-Al_2O_3 catalysts is interesting since these catalysts are more difficult to sulfide than their Mo-based counterparts (4) and, hence, intermediate stages of sulfidation can be studied as separate phases.

In a recent paper (5) it was shown by us that the combination of temperature-programmed sulfidation (TPS) and Mössbauer absorption spectrometry on ^{57}Fe (^{57}Fe-MAS) in NiW/γ-Al_2O_3 provides crucial but incomplete information about the sulfidation of Ni and W in differently calcined NiW/γ-Al_2O_3 catalysts. TPS showed that the calcination temperature strongly influences the relative contributions of the various sulfidation reactions. For instance, the formation of WS_3 which occurs at low sulfidation temperatures diminishes significantly after calcination above 673 K. Furthermore, it was deduced from ^{57}Fe-MAS that on NiW/γ-Al_2O_3 catalysts calcined at 393 K the formation of the so-called NiWS phase occurs upon sulfidation at 573 K. On catalysts calcined at 673 K and 823 K, this reaction takes place only after sulfidation at 673 K. It was suggested that this difference is related to the more difficult formation of WS_2 in catalysts calcined above 673 K. Apart from chemical information about the sulfidation of NiW/γ-Al_2O_3 catalysts, changes in the morphology upon sulfidation can also be of relevance. These changes have been studied previously with high-resolution transmission electron spectroscopy (HREM) (6). On a NiW catalyst sulfided at 613 K, HREM shows the presence of so-called subnanometer particles, which have a diameter of about 0.5 nm and are stable under practical hydrotreating conditions. It

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was proposed that these subnanometer particles consist of a partially sulfided mixed Ni(WO) or Ni(WOAl) phase. In addition, small numbers of nanometer-sized particles were observed which are believed to be intermediate species in the process of sulfidation. Finally, sulfidation above 823 K showed the presence of WS_2-like slabs, the appearance of which coincided with the disappearance of the subnanometer particles and, to a lesser extent, of the nanometer particles. It was suggested that the subnanometer particles are the nuclei for the subsequent formation of WS_2 slabs at higher sulfidation temperatures, possibly via the intermediate nanometer particles.

Because TPS mainly is a bulk characterization technique, it provides limited information about the nature of the different Ni and W species present in the various stages of sulfidation. ^{57}Fe-MAS pre-eminently gives information on the direct chemical surroundings of the different Ni species. However, a detailed interpretation of the spectra and allocation of the various spectral contributions to specific Ni species is difficult. Diffuse reflectance infrared Fourier transform spectroscopy on adsorbed NO (FTIR(NO)) will therefore be used to generate additional information on the development of specific surface sites on NiW/γ-Al_2O_3 catalysts upon sulfidation. In the literature, FTIR(NO) has been successfully applied on various NiMo- and CoMo-based sulfided catalysts (e.g., (7–11)). Some infrared analyses on oxidic and sulfided NiW/γ-Al_2O_3 catalysts have also been reported in the literature (e.g., (12–15)). The gap between quantitative techniques like TPS and MAS and essentially qualitative techniques like FTIR(NO) can possibly be bridged by X-ray photoemission spectroscopy (XPS). The binding energy position of the XPS peaks is indicative of the nature of the corresponding species while the area of the XPS peaks gives semiquantitative information on its occurrence.

In the current paper, an extensive FTIR(NO) and a quasi *in situ* XPS study on sulfided NiW/γ-Al_2O_3 catalysts will be discussed. In addition to the base NiW/γ-Al_2O_3 catalyst, a series of differently calcined catalysts was prepared, of which part of the Ni phase was removed by extraction with a diluted HCl solution. In the general discussion, the current information will be combined with the previous conclusions from TPS and ^{57}Fe-MAS (5) to develop a consistent description of the sulfidation of NiW/γ-Al_2O_3.

EXPERIMENTAL

Catalyst preparation. The base NiW/γ-Al_2O_3 catalyst was prepared by pore volume impregnation of γ-Al_2O_3 (Ketjen 000-1.5E high purity, surface area 190 $m^2\,g^{-1}$, pore volume 0.6 $ml\,g^{-1}$) with an aqueous solution of $(NH_4)_6W_{12}O_{39}\cdot xH_2O$ (Aldrich 35,897-5) and $Ni(NO_3)_2\cdot 6H_2O$ (Aldrich 20,387-4). The catalyst loading was determined by AAS: 1.2 wt% Ni (0.6 at. nm^{-2} Ni) and 15.2 wt% W (2.7 at. nm^{-2} W). After impregnation, the catalyst was dried at 393 K for 16 h in air. Calcination of the dried catalyst was done in air at various temperatures, the heating rate being 600 K h^{-1}. The maximum temperature was maintained for 1 h. The base NiW/γ-Al_2O_3 catalysts will be denoted as $NiW_{T_{calc},T_{sulf}}$, where T_{calc} stands for the calcination and T_{sulf} for the sulfidation temperature. Some catalysts were only dried in air at 393 K prior to sulfidation. In these cases, "drying" will be referred to as "calcining at 393 K." In case data of oxidic catalyst precursors are presented, the temperature of sulfidation is replaced by the subscript "ox."

The extracted catalysts were prepared from differently calcined base NiW/γ-Al_2O_3 catalysts. A batch of 4 g of dry extrudates was soaked in 10 ml of a 0.3 N HCl solution for 1 h. Afterward, the extraction liquid was analyzed for its Ni content with inductively coupled plasma (ICP) emission spectroscopy. The extracted catalyst extrudates were washed with demineralized water and dried at room temperature. The extracted NiW/γ-Al_2O_3 catalysts will be denoted as $NiW_{ex,T_{calc},T_{sulf}}$.

In situ FTIR on adsorbed NO. The FTIR(NO) measurements were done at the Shell Research and Technology Centre Amsterdam (SRTCA). All spectra were recorded at 303 K using a Biorad FTS-60A spectrometer at a resolution of 2 cm^{-1} in an *in situ* cell. First, the samples were dried *in situ* in a flowing stream of He up to 573 K with a heating rate of 600 K h^{-1} and kept at this temperature for 0.5 h. This implies that so-called dried catalysts actually have been heated to 573 K, but only under nonoxidizing conditions. Hence, we expect that, in line with previously reported data discussed in the Introduction (5), the active phase on these catalysts is still essentially representative of a dried NiW catalyst. Presulfidation of the catalysts was done in 10 vol% H_2S in H_2 at various temperatures for 0.5 h. After sulfidation, the samples were cooled to room temperature in the sulfidation mixture. Next, the H_2S was removed by flushing the cell with He for 0.5 h and a spectrum was recorded afterward. Adsorption of NO was done at 303 K by passing a stream of 4% NO in He over the catalyst for 0.5 h. It was verified that the NO partial pressure was low enough to avoid oxidation of the sulfided samples. After the gas phase NO was removed by flushing the cell with He, a spectrum of the NO-exposed sample was recorded. All FTIR(NO) spectra shown have been rescaled to comparable intensities. Hence, the absolute intensities cannot be used directly for mutual comparison.

Quasi in situ XPS. TPS of the samples for XPS analysis was performed in a flow reactor described in detail by Scheffer *et al.* (16). About 0.1 g of crushed catalyst was introduced in a quartz reactor. After being flushed with Ar at room temperature the catalyst was exposed to a sulfidation mixture containing H_2S, H_2, and Ar (3, 25, and 72 vol%, respectively) at a total flow rate of 33 $\mu mol\ s^{-1}$. The reactor was subjected to the same temperature program as was described for quasi *in situ* FTIR(NO), the only difference being that the maximum temperature was maintained for 1 h. After this, the sample was cooled rapidly to room temperature in the sulfidation mixture. The cooled reactor was flushed with Ar, closed, and disconnected from the TPS equipment and transferred into a glove box in which the partial pressure of O_2 and H_2O was typically less than 0.5 ppm in atmospheric Ar. The catalyst was ground and pressed into an indium foil and transported into the XPS machine under the same protective conditions. XPS analysis was performed on a Perkin-Elmer PHI 5400 ESCA system equipped with a hemispherical analyzer. Sample excitation was done by Al *Kα* X-rays (1486.6 eV). Peak shifts due to charging of the samples were corrected for by taking the Al 2*p* line of Al_2O_3 at 74.2 eV as a reference (17). Furthermore, the spectra shown in this work were corrected for satellites.

RESULTS

Ni Extraction of Catalysts Calcined at Different Temperatures

A mild extraction by diluted aqueous HCl exclusively extracts those Ni species which have a weak interaction with the support or the oxidic W phase. Figure 1 shows the relative amount of Ni, which was extracted from the differently calcined NiW catalysts. As could have been expected, the catalyst calcined at 393 K contains the largest amount of leachable Ni, about 61%. With increasing calcination temperature, the amount of leachable Ni gradually decreases.

FTIR(NO) on Oxidic Base NiW/γ-Al_2O_3

In Fig. 2 the spectra of the oxidic base catalysts, calcined at 393 K, 673 K, and 823 K, are presented. In the spectrum of $NiW_{393,ox}$, a broad band is visible which consists of two contributions at approximately 1885 and 1865 cm^{-1}. The spectrum of $NiW_{673,ox}$ shows a much sharper band at 1886 cm^{-1} and the band around 1865 cm^{-1} is present as a shoulder. The maximum of the broad band in the spectrum of $NiW_{823,ox}$ has shifted to lower frequencies as compared to $NiW_{673,ox}$, indicating that the contribution of the low-frequency band around 1865 cm^{-1} has gained importance.

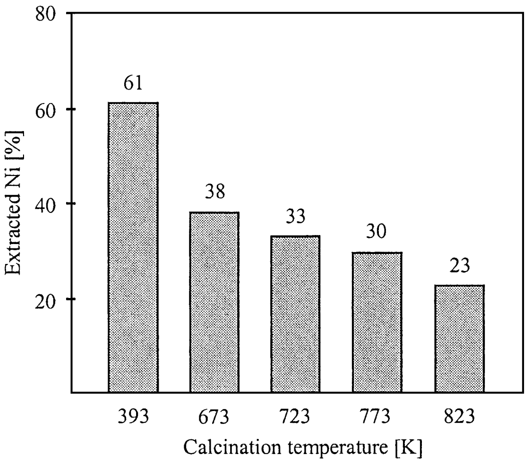

FIG. 1. Percentage of Ni that can be extracted from NiW/γ-Al_2O_3, calcined at different temperatures.

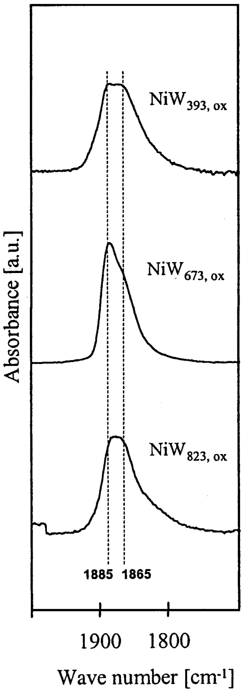

FIG. 2. Infrared spectra of NO adsorbed on oxidic $NiW_{393,ox}$, $NiW_{673,ox}$, and $NiW_{823,ox}$.

FTIR(NO) on Sulfided Base NiW/γ-Al_2O_3

The FTIR(NO) spectra of the sulfidation up to 623 K of the catalyst calcined at 393 K are shown in Fig. 3. Sulfidation at 373 K clearly changes the spectrum, as compared to that of $NiW_{393,ox}$. In particular the sharp band emerging at 1889 cm^{-1} should be noted. Furthermore, a broad band centered at about 1850 cm^{-1} is present, probably consisting of contributions of the 1865 cm^{-1} band and a newly formed band around 1840 cm^{-1}. Sulfidation at 473 K leads to a more pronounced band at 1887 cm^{-1} and the development of a shoulder at the low-frequency side of the broad band at 1790 cm^{-1}. A new band at 1690 cm^{-1} is observed in the spectrum after sulfidation at 623 K. In addition, the band at 1840 cm^{-1} and the shoulder at 1785 cm^{-1} become more pronounced as compared to $NiW_{393,473}$, while the sharp band around 1885 cm^{-1} relatively decreases in intensity.

The influence of the calcination temperature on the speciation of the active phase in NiW catalysts sulfided at 673 K is

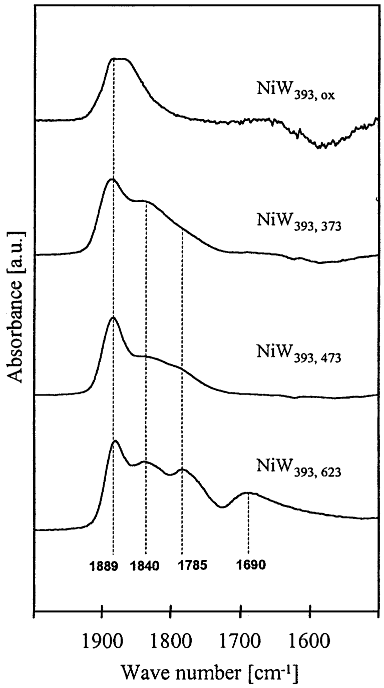

FIG. 3. Infrared spectra of NO adsorbed on oxidic $\mathrm{NiW_{393,ox}}$ and $\mathrm{NiW_{393,373...623}}$, sulfided at various temperatures from 373 to 623 K.

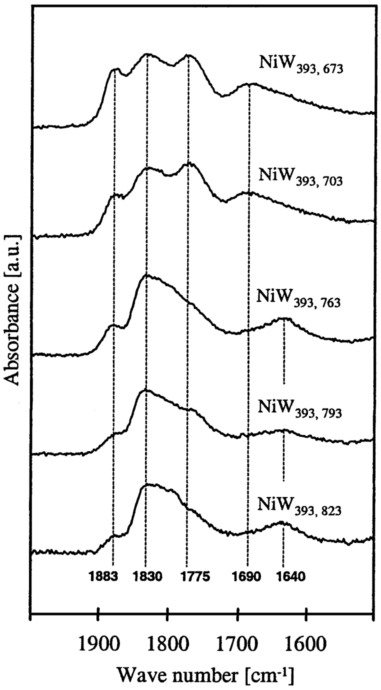

FIG. 5. Infrared spectra of NO adsorbed on $\mathrm{NiW_{393,673...823}}$, sulfided at various temperatures from 673 to 823 K.

demonstrated in Fig. 4. The general features of the spectra are similar, although some significant differences can be observed. Note that the intensity of the band at 1887 cm^{-1} increases with increasing calcination temperature. Furthermore, the bands at 1765 and 1685 cm^{-1} in the spectrum of $\mathrm{NiW_{393,673}}$ are shifted to a lower wave number as compared to the spectra of $\mathrm{NiW_{673,673}}$ and $\mathrm{NiW_{823,673}}$.

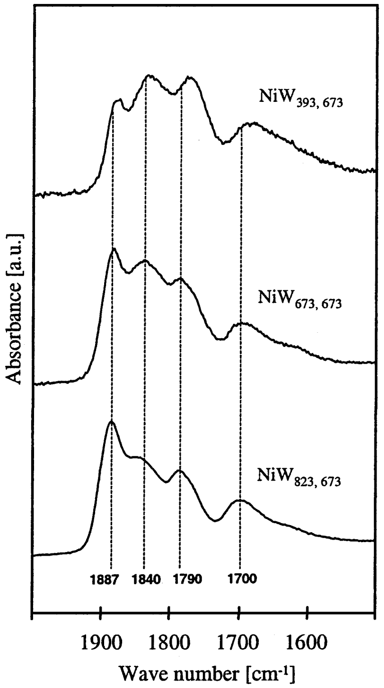

FIG. 4. Infrared spectra of NO adsorbed on $\mathrm{NiW_{393,673}}$, $\mathrm{NiW_{673,673}}$, and $\mathrm{NiW_{823,673}}$.

The evolution of the different surface species during high-temperature sulfidation has been studied in detail for the catalysts calcined at 393 K and 823 K; the results are collected in Figs. 5 and 6, respectively. While the spectrum of $\mathrm{NiW_{393,703}}$ is very similar to that of $\mathrm{NiW_{393,673}}$, sulfidation at 763 K completely changes the appearance of the spectrum. The relative intensities of the bands around 1883, 1775, and 1690 cm^{-1} decrease, while the band at 1830 cm^{-1} broadens. In addition, a broad band evolves around 1640 cm^{-1}. Sulfidation at 823 K results in a further weakening of the 1883 cm^{-1} band. In general, the developments that are observed for the high-temperature sulfided $\mathrm{NiW_{823}}$ catalysts are similar to those of the $\mathrm{NiW_{393}}$ catalysts, although the position of some bands is slightly different. A simultaneous decrease of the bands at 1885, 1785, and 1700 cm^{-1} is observed in the narrow sulfidation temperature range of 703 K to 733 K, indicating a sharp transition in the speciation of the active phase.

FTIR(NO) on Oxidic Extracted NiW/γ-Al_2O_3

In Fig. 7, the FTIR (NO) spectra of the oxidic, extracted NiW catalysts are shown. The spectrum of $\mathrm{NiW_{ex,393,ox}}$ reveals that after extraction no Ni species are available at the surface of the catalyst for NO adsorption. In contrast, in the spectrum of $\mathrm{NiW_{ex,673,ox}}$, a sharp band is observed at

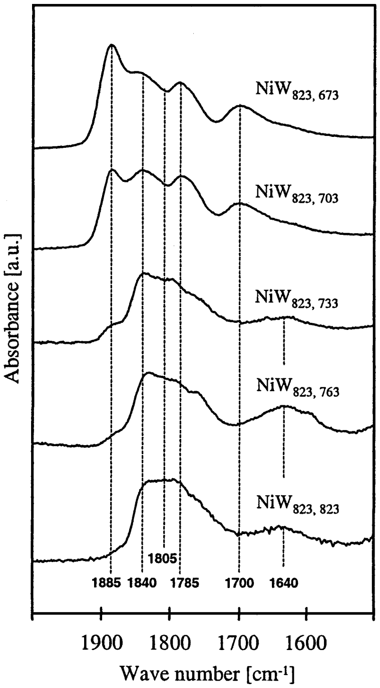

FIG. 6. Infrared spectra of NO adsorbed on $NiW_{823,673...823}$, sulfided at various temperatures from 673 to 823 K.

1892 cm^{-1}. On the low-frequency side of this band a broad shoulder is present. The spectrum of $NiW_{ex,823,ox}$ shows a relatively well-defined band around 1865 cm^{-1} with a weak shoulder at 1885 cm^{-1}.

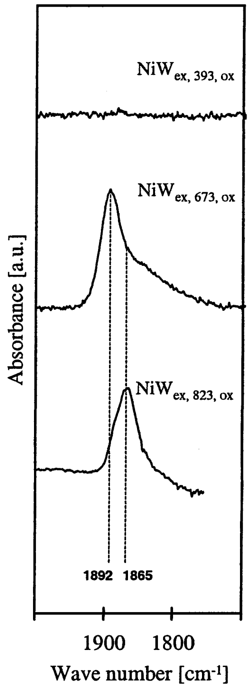

FIG. 7. Infrared spectra of NO adsorbed on oxidic $NiW_{ex,393,ox}$, $NiW_{ex,673,ox}$, and $NiW_{ex,823,ox}$.

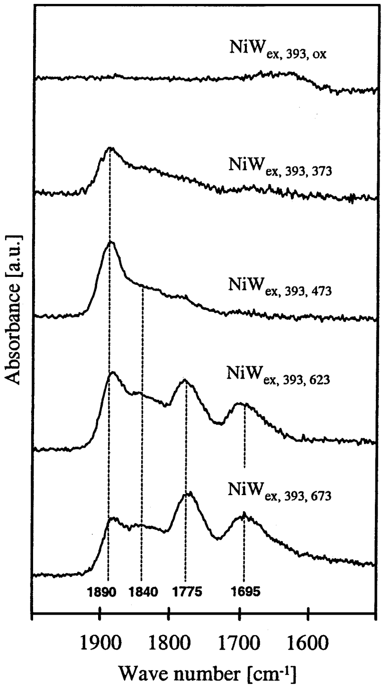

FIG. 8. Infrared spectra of NO adsorbed on oxidic $NiW_{ex,393,\,ox}$ and $NiW_{ex,393,373...673}$, sulfided at various temperatures from 373 to 673 K.

FTIR(NO) on Sulfided Extracted NiW/γ-Al_2O_3

Figure 8 shows the FTIR(NO) spectra of $NiW_{ex,393,ox}$ and $NiW_{ex,393,373...673}$, sulfided at various temperatures up to 673 K. In contrast to that of the oxidic precursor, the spectrum of $NiW_{ex,393,373}$ shows that after sulfiding no accessible Ni species are present at the catalyst surface. A band at about 1890 cm^{-1} with a broad shoulder on the low-frequency side can be seen. Sulfidation at 473 K results in a more intense band at 1890 cm^{-1} whereas after sulfidation at 623 K a strong band around 1775 cm^{-1} becomes visible. The spectra of $NiW_{ex,393,623}$ and $NiW_{ex,393,623}$ strongly resemble those of the base 393 K calcined catalysts shown in Fig. 6, except for the fact that on the extracted catalyst the band at 1840 cm^{-1} does not shift to 1830 cm^{-1}.

In Fig. 9, one can see that the development of the various species is very similar to that shown in Fig. 8, notwithstanding the fact that for the catalyst shown in Fig. 8 a significant part of the Ni has been leached, as can be seen in Fig. 1.

XP Spectra of the W 4f Emission Line Region

The XP spectra of the W 4*f* emission line region of four $NiW_{823,298...773}$ catalysts, sulfided at various increasing temperatures, are shown in Fig. 10. The spectra of $NiW_{823,298}$ and $NiW_{823,540}$ show a doublet peak of W $4f_{5/2}$ and W $4f_{7/2}$ electrons at a binding energy (BE) position of 38.0 and 35.9 eV, respectively. These peaks have been assigned to W^{6+} species, in this case most likely $W^{6+}O_3$ (17, 18). After sulfidation at 613 K a second doublet peak, typical for

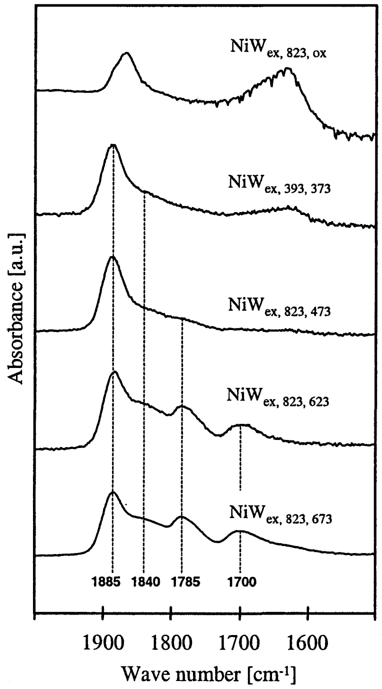

FIG. 9. Infrared spectra of NO adsorbed on oxidic NiW$_{ex,823,ox}$ and NiW$_{ex,823,373...673}$, sulfided at various temperatures from 373 to 673 K.

$W^{4+}S_2$, emerges at 34.4 and 32.5 eV (17, 18). The contribution of the $W^{4+}S_2$ peaks strongly increases after sulfidation at 773 K.

Decomposition of the Ni 2p Emission Line Region in the XP Spectra

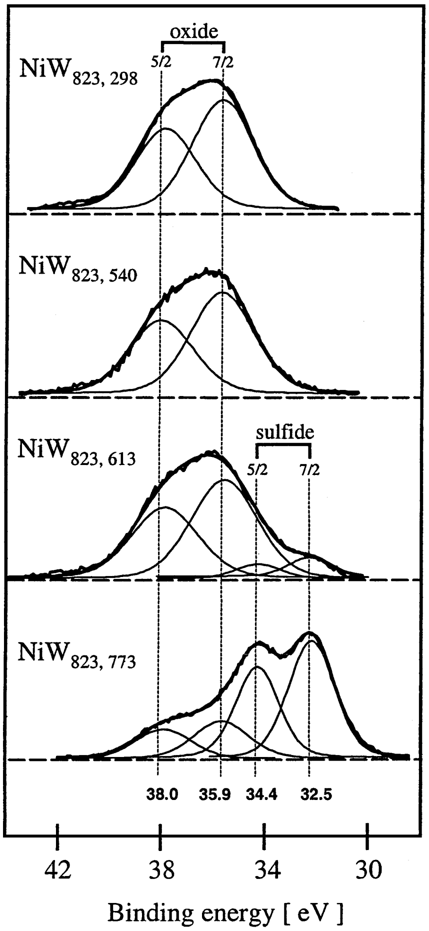

FIG. 10. XP spectra of the W 4*f* emission line region of NiW$_{823,298...773}$, sulfided at various temperatures from 298 to 773 K.

The XP spectra of the Ni 2*p* emission line region of NiW$_{673}$ and NiW$_{823}$ have been measured at various stages of sulfidation. As a result, the XP spectra of two successive samples altered only gradually and subtle changes can be distinguished. Moreover, since additional knowledge about the presence of the various Ni species in the catalysts was available from the complementary techniques (TPS, FTIR(NO), and ^{57}Fe-MAS), an attempt was made to relate the presence of different Ni species to the subtle changes in the Ni $2p_{3/2}$ emission lines. The results do not allow a direct quantitative interpretation in terms of the various Ni species for the following reasons. First, in the absence of detailed information on the exact morpholgy of the active phase, attenuation effects due to, for instance, the dissolution of Ni in the alumina have been neglected. Second, the relative intensity of the shake-up peak of the various oxidic Ni species is unknown; consequently, the contributions of the shakeup satellites were not taken into account in the decomposition procedure. Hence, when comparing the relative peak areas in Figs. 11, 12, and 13, the contribution of the various oxidic Ni species will be underestimated, especially in the catalysts sulfided up to 473 K. As a consequence, the data in Table 1 only reflect changes in the

TABLE 1

	High *BE* Ni oxide		Low *BE* Ni oxide		Ni inter		Ni sulfide	
Catalyst	*BE* (eV)	%	*BE* (eV)	%	*BE* (eV)	%	*BE* (eV)	%
NiW$_{ex,393, ox}$	856.9	100	—	0	—	0	—	0
NiW$_{ex,393, 373}$	856.9	64	—	0	855.2	14	853.5	22
NiW$_{ex,823,ox}$	856.9	58	856.2	42	—	0	—	0
NiW$_{ex,823,373}$	856.9	55	856.1	16	855.2	12	853.5	17

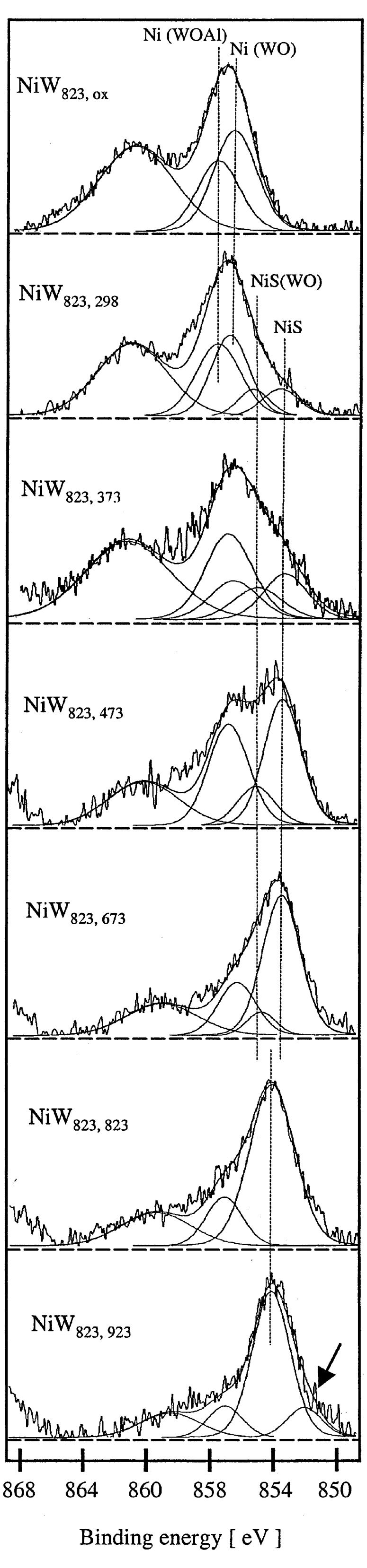

FIG. 11. Decomposition of the Ni $2p_{3/2}$ XPS emission line of oxidic $NiW_{823,ox}$ and $NiW_{823,298...923}$, sulfided at various temperatures from 298 to 923 K.

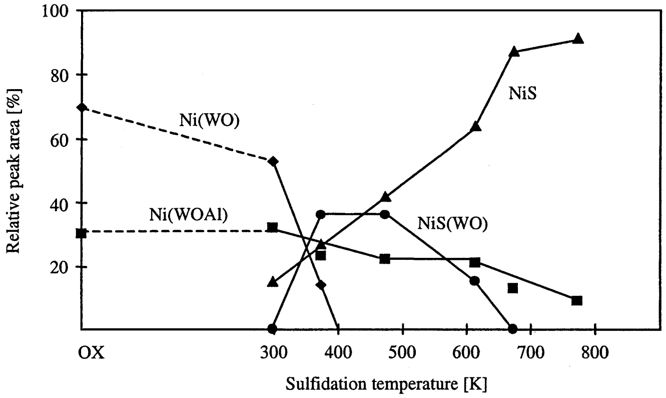

FIG. 12. Relative peak area related to different Ni species as derived from the decomposition of the Ni $2p_{3/2}$ XPS emission line of oxidic $NiW_{673,ox}$, indicated as "OX" on the horizontal axis, and $NiW_{673,298...773}$, sulfided at various temperatures from 298 to 773 K.

relative peak areas in the main Ni $2p_{3/2}$ emission line, and should be considered only as a semiquantitative trend for the transformation in the Ni speciation upon sulfiding.

A preliminary evaluation of the Ni $2p_{3/2}$ emission line of the sulfided catalysts indicated that two contributions, an oxidic and a sulfidic, could be identified. However, from the work of Scheffer *et al.* (4), it was deduced that oxidic Ni species in NiW/γ-Al_2O_3 can be divided into two groups on the basis of their sulfidability: species that are sulfided below 600 K and species that are only sulfided above 600 K. Therefore, the overall oxidic contribution was fitted with two separate contributions.

The first step was a decomposition of the spectra of $NiW_{673,ox}$ and $NiW_{823,ox}$ in order to assess the binding energy positions of the two Ni oxidic contributions. Next, an attempt was made to fit the series of spectra of $NiW_{823,298...613}$ with two Ni oxides and a single Ni sulfide contribution. In line with the assumptions based on the work of Scheffer *et al.* (4), the relative intensity of one of the

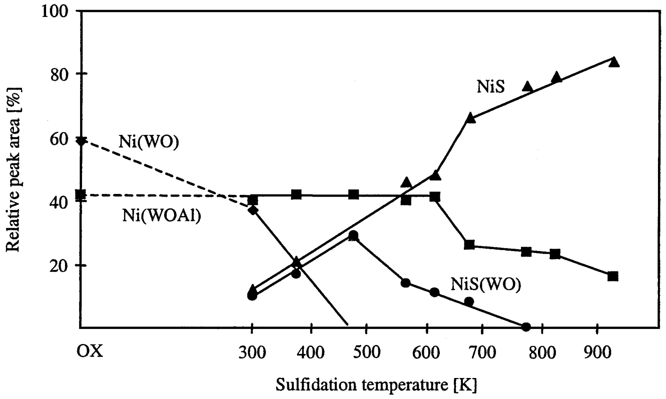

FIG. 13. Relative peak area related to different Ni species as derived from the decomposition of the Ni $2p_{3/2}$ XPS emission line of oxidic $NiW_{823,ox}$, indicated as "OX" on the horizontal axis, and $NiW_{823,298...923}$, sulfided at various temperatures from 298 to 923 K.

Ni oxide contributions indeed remained constant during sulfidation up to 613 K. Moreover, especially in the spectra of $NiW_{823,373}$ and $NiW_{823,473}$, it was inevitable that a fourth contribution was introduced. Therefore, an additional contribution was defined of which the binding energy position was kept constant in all spectra. This approach did lead to a consistent fit of the spectra of the complete series of the sulfided NiW_{823} and sulfided NiW_{673} catalysts. Figure 11 shows the decomposed spectra of the Ni $2p_{3/2}$ emission line of the sulfided $NiW_{823,298...923}$ catalysts. From these decomposed spectra, the binding energy position and the relative area related to the four Ni species (based on integrated areas) were determined as a function of the sulfidation temperature. The relative accuracy of the decomposition is estimated to be 10%.

Quasi in Situ XPS on Base NiW/γ-Al_2O_3

The relative peak areas, related to the four Ni species in the two sets of catalysts calcined at 673 and 823 K, are presented in Figs. 12 and 13, respectively.

In $NiW_{673,ox,}$ a low and a high binding energy Ni oxide species are present at respectively about 856.3 and 857.2 eV in a 3 : 1 ratio. Upon sulfidation to 473 K, the contribution of the low binding energy Ni oxide species rapidly decreases (Fig. 12). In the same temperature range, a so-called intermediate Ni species, NiS(WO), and a Ni sulfide species, NiS, develop. Sulfidation above 613 K results in the disappearance of the NiS(WO) and a gradual increase of the NiS. Moreover, a slow decrease of the high binding energy Ni oxide species, Ni(WOAl), is observed. At the highest sulfidation temperature (773 K), about 90% of the Ni is present in the form of the NiS, balanced with the Ni(WOAl).

In $NiW_{823,ox}$, the same two Ni oxide species as in $NiW_{673,ox}$ are present but now in a 3 : 2 ratio, as can be seen in Fig. 13. Similar to NiW_{673}, the contribution of the low binding energy Ni oxide species disappears upon sulfidation at 473 K. The Ni intermediate species formed on NiW_{823} is more stable than that formed on NiW_{673} since it remains present up to sulfidation at 673 K. The contribution of the Ni sulfide species gradually increases and reaches about 85% after sulfidation at 923 K. As discussed in the previous paragraph, the contribution of high binding energy oxide Ni species was kept as a fixed contribution up to a sulfidation temperature of 613 K. At higher sulfidation temperatures its contribution slowly decreases to about 15% in $NiW_{823,923}$. In addition, for $NiW_{823,923}$ a small additional band, which is indicated by an arrow in Fig. 11, was found at about 852.5 eV.

In Figs. 14 and 15, the binding energy positions of the various Ni species are shown for the sulfided catalysts series calcined at 673 K and 823 K, respectively. The binding energy position of the Ni intermediate species was kept constant at 855.0 ± 0.1 eV. On NiW_{673} the binding energy position of the high binding energy oxide Ni species tends to shift about −0.6 eV upon sulfidation between 298 K and 613 K and remains constant at higher sulfidation temperatures. In NiW_{823} the binding energy position of the high binding energy oxide Ni species at high sulfidation temperatures is the same as for that in the 673 K calcined series. The binding energy position of the Ni sulfide species in the NiW_{673} series is fairly constant up to sulfidation at 613 K. However, in $NiW_{673,673}$ a shift in the binding energy position of +0.5 eV is observed which is preserved after sulfidation at 773 K, as can be seen from Fig. 14. Interestingly, the same phenomenon is observed for the NiW_{823} series.

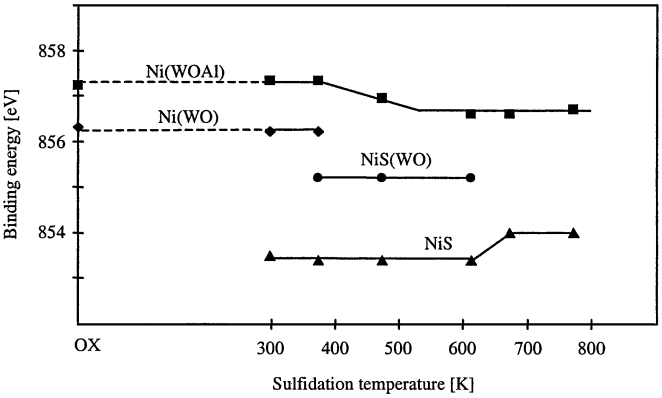

FIG. 14. Binding energy positions in electronvolts of different Ni species as derived from decomposition of the Ni $2p_{3/2}$ XPS emission line of oxidic $NiW_{673,ox}$, indicated as "OX" on the horizontal axis, and $NiW_{673,298...773}$, sulfided at various temperatures from 298 to 773 K.

Quasi in Situ XPS on Extracted Calcined NiW/γ-Al_2O_3

$NiW_{ex,393,ox}$, $NiW_{ex,393,373}$, $NiW_{ex,823}$, and $NiW_{ex,823,373}$ were also studied with XPS and are shown in Fig. 16. In Table 1, the relative peak areas, related to the different Ni species and their corresponding binding energy positions, are presented. In general, the binding energy positions are

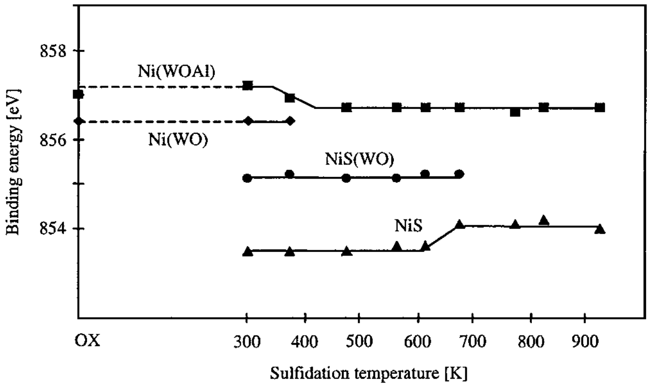

FIG. 15. Binding energy positions in electronvolts of different Ni species as derived from the decomposition of the Ni $2p_{3/2}$ XPS emission line of oxidic $NiW_{823,ox}$, indicated as "OX" on the horizontal axis, and $NiW_{823,298...823}$, sulfided at various temperatures from 298 to 823 K.

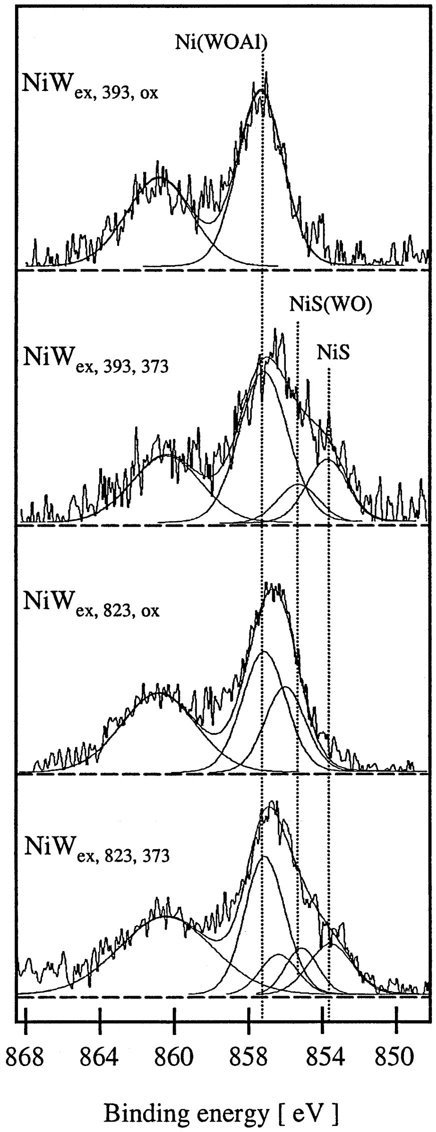

FIG. 16. Decomposition of the Ni $2p_{3/2}$ XPS emission line of $NiW_{ex,393,ox}$, $NiW_{ex,393,373}$, $NiW_{ex,823,ox}$, and $NiW_{ex,823,373}$.

close to those observed for the base NiW catalysts, but the relative contribution of the different Ni species is quite different. The Ni $2p_{3/2}$ emission lines of $NiW_{ex,393,ox}$ could be fitted satisfactorily with a single band at a binding energy position close to that of the high binding energy Ni oxide species. In contrast, for $NiW_{ex,823,ox}$ a contribution of the low binding energy Ni oxide species was also present, although the ratio of the two species (2 : 3) was different from that of the base $NiW_{823,ox}$ (3 : 2).

For $NiW_{ex,393,ox}$ the high binding energy Ni oxide species is partially sulfided, thus forming the Ni intermediate and Ni sulfide species in $NiW_{ex,393,373}$. In contrast, upon sulfidation of $NiW_{ex,823,ox}$ into $NiW_{ex,823,373}$, the Ni intermediate species and Ni sulfide species are formed exclusively from sulfidation of the low binding energy Ni oxide species, whereas sulfiding of the high binding energy oxide species does not occur.

DISCUSSION

An extensive characterization of oxidic and sulfided NiW/γ-Al_2O_3 catalysts has been presented in the previous sections. In this section, the results of FTIR(NO) and XPS will be discussed first and the main conclusions will be integrated with previous TPS and ^{57}Fe-MAS (5) and HREM (6) results.

FTIR(NO) on Oxidic Catalysts

Various W and Ni species can be expected in oxidic NiW/γ-Al_2O_3 of which the relative occurrence depends on the calcination temperature. A schematic representation of the various Ni and W species is given in Fig. 17. A highly disperse WO_3 phase, WO_3, may be present (19), whereas the presence of a separate NiO phase is not expected in view of the low Ni loading of the catalysts (19, 20). However, Ni ions may be present in the alumina surface as so-called surface Ni aluminate, Ni(Al) (20, 21). At calcination temperatures above 800 K, stable bulk Ni aluminates, Ni–Al, are formed due to the diffusion of Ni ions into the support (21, 22). Finally, the presence of a mixed NiWOAl phase has been reported (19). In view of the heterogeneous nature of the oxidic phase on NiW/γ-Al_2O_3, the presence of a well-defined NiWOAl phase is unlikely. It can be expected that, dependent on the calcination temperature, Ni^{2+} species with different W, Al, and O coordination are present, of which the reactivity toward sulfidation decreases with increasing number of W–O–Al bonds (4). Based on this, the mixed oxides are divided into two categories. The first contains mixed oxides with a low number of W–O–Al bonds and a relatively high Ni concentration and, hence, a weak interaction with the support, Ni(WO). The second consists of mixed oxides with more W–O–Al bonds and a relatively low Ni concentration and has a strong interaction with the support, Ni(WOAl). Although the 393 K calcined catalyst has a structure different from the others because the tungsten in it is largely present in the molecular complex of

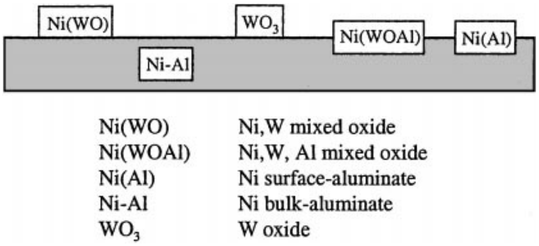

FIG. 17. Schematic representation of the various Ni species in oxidic NiW/γ-Al_2O_3.

the precursor, all catalysts will be discussed in terms of the species indicated in Fig. 17.

The broad band in the FTIR(NO) spectra consists of a contribution around 1865 and 1885 cm^{-1} (Fig. 2) and can be assigned as follows. For NO adsorbed on oxidic Ni/Al_2O_3 catalysts with a low metal loading (11, 23), an absorption band around 1865 cm^{-1} has been reported. It was suggested that this band can be related to an oxidic Ni^{2+} species in defect octahedral sites of the support (Ni(Al)). Furthermore, for oxidic CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 a band around 1885 cm^{-1} has been reported (11, 24). As this band was not observed on Co/-, Ni/-, or Mo/γ-Al_2O_3 catalysts, it must be attributed to NO adsorbed on Ni^{2+} (Co^{2+}) in a mixed oxide of Ni–Mo or Co–Mo. In analogy, the band around 1885 cm^{-1} in our samples is assigned to the adsorption of NO on Ni^{2+} ions in Ni(WO) or Ni(WOAl).

No infrared absorption bands are observed which can be attributed to oxidic W^{6+}. This can be understood from the fact that analogously to Mo^{6+}, W^{6+} has a d^0 structure which allows only a weak adsorption of NO (24, 25). Moreover, W^{6+} is octahedrally coordinated and, hence, is sterically screened.

Based on previous assignments, the presence of a band around 1868 cm^{-1} in $NiW_{393,ox}$ is notable, since a surface Ni aluminate will be formed only upon calcination at sufficiently high temperature. Indeed, the chemical stability of this Ni species in $NiW_{393,ox}$ is low, since it can be removed completely by extraction. Its formation can be understood by leaching of the alumina in the impregnation step, as reported previously by Sacconi (26). In the presence of hydrolyzable salts like $Ni(NO_3)_2$, Al^{3+} can be leached from the alumina, followed by re-adsorption upon drying, during which Ni ions can be incorporated in an amorphous and weakly interacting Al phase (27). Since 60% of the Ni on $NiW_{393,ox}$ can be removed by extraction and no surface Ni is found on $NiW_{ex,393,ox}$ (Fig. 7), it is estimated that 40% of the Ni is present in subsurface positions, probably in a mixed phase with W surface complexes.

In the spectrum of $NiW_{673,ox}$, a band is found at 1886 cm^{-1}, indicating that after calcination at 673 K most of the Ni is present in the form of Ni(WO) or Ni(WOAl). One would expect that after extraction the contribution of the shoulder at 1868 cm^{-1} increases in relative intensity. However, from the spectrum of $NiW_{ex,673,ox}$ this is not obvious. In $NiW_{823,ox}$, the band at 1868 cm^{-1} is relatively more important as compared to the one in $NiW_{673,ox}$. This confirms that more Ni surface aluminate is formed at higher calcination temperatures. Clearly the 1868 cm^{-1} band must be correlated to the most stable species.

Summarizing, two absorption bands have been observed in oxidic NiW catalysts. In calcined catalysts, the band at 1868 cm^{-1} can be ascribed to a Ni surface aluminate (Ni(Al)), the amount of which increases upon calcination. The band close to 1885 cm^{-1} can probably be attributed to Ni^{2+} in W oxide (Ni(WO)) or a mixed W/Al oxide (Ni(WOAl)).

FTIR(NO) on Sulfided Catalysts

At first sight it is remarkable that all catalysts, except for those which were calcined and sulfided at the highest temperature, show a large band near 1890 cm^{-1}. The position of this band is in the proximity of that attributed to Ni^{2+} in Ni(WO) or Ni(WOAl). However, there are indications that another Ni species is responsible for this band. First, the 1890 cm^{-1} band in the spectra of NiW_{393} intensifies up to a sulfidation temperature of 473 K and remains present after sulfidation up to 700 K. Such a behavior is not likely to be related to an oxidic Ni species. Moreover, the spectrum of $NiW_{ex,393,ox}$ indicates that no Ni species are present in the catalyst surface. After a mild sulfidation at 373 K, however, the band at 1890 cm^{-1} develops. Finally, the stability of the 1885 cm^{-1} band on oxidic catalysts in a flow of He is much lower than that of the 1890 cm^{-1} band on sulfided catalysts. This clearly indicates that both bands must be attributed to different Ni species.

The nature of the Ni species related to the 1890 cm^{-1} band is not obvious a priori. In the literature, a band around 1890 cm^{-1} has been reported before on sulfided and fluorinated NiW/γ-Al_2O_3 catalysts (15). Benitez *et al.* (15) attributed this band to NO adsorbed on Ni^{2+} ions in an oxygen surrounding. Atanasova *et al.* (7) observed a band at 1880–1886 cm^{-1} in subsequently reduced and sulfided NiMo(P)/γ-Al_2O_3 catalysts. They attributed the band to dispersed Ni ions with a low reactivity toward reduction and/or sulfidation. Since the 1890 cm^{-1} band was not observed in sulfided Ni/γ-Al_2O_3 catalysts (11), the interaction with W or Mo must play an important role. Scheffer *et al.* (4) proposed that Ni ions, present in a mixed W/Al phase, remain in the vicinity of W, which is still essentially oxidic after low-temperature sulfidation. The role of oxidic W in the formation of the 1890 cm^{-1} band can also be inferred from the fact that the stability of the 1890 cm^{-1} band increases with increasing calcination temperature and thus with a decreasing reactivity toward sulfidation of WO_3 as can be seen in Fig. 4. Therefore, it is proposed that the 1890 cm^{-1} adsorption band can be attributed to partially sulfided Ni species in close interaction with an oxidic W phase.

The band around 1840 cm^{-1} has been assigned to a highly disperse Ni sulfide species in sulfided NiW/A_2O_3 and NiMo/Al_2O_3 catalysts (11, 28, 29). The decrease of the 1890 cm^{-1} band and the formation of disperse Ni sulfide species as observed for the mildly sulfided catalysts is in line with the sulfidation of W in a mixed oxide and the formation of WS_2 above 600 K. With increasing calcination temperature, the shift of the 1840 cm^{-1} band to 1830 cm^{-1} occurs at higher sulfidation temperature. Apparently, the species related to the 1840 cm^{-1} band is stabilized by the tungstate upon higher calcination temperatures. Topsøe and Topsøe (11) and López Agudo *et al.*(30) reported a band at 1830 cm^{-1} on sulfided Ni/Al_2O_3 catalysts. Based on these considerations, the band around 1830 cm^{-1} is assigned to a less disperse Ni sulfide species. Additional support for this assignment is found in the spectrum of $NiW_{ex,393,673}$. In contrast to the base $NiW_{393,673}$ catalyst there is no shift of the 1840 cm^{-1} band to 1830 cm^{-1}. Since the remaining Ni species on $NiW_{ex,ox}$ have a stronger interaction with W on the support, the tendency toward sintering will be lower.

Another obvious change in the active phase at sulfidation temperatures between 473 and 673 K is the formation of bands around 1785 and 1695 cm^{-1}. In literature, there is agreement that these bands are related to the coupled vibration of two absorbed NO molecules on W^{4+} in WS_2 and are due to the symmetric and asymmetric stretching vibration of the NO dimer, respectively (25). A similar phenomenon has been observed for sulfided Mo- and NiMo/Al_2O_3 catalysts (7, 25). Independent of the calcination temperature, a weak band around 1785 cm^{-1} is already observed upon sulfidation at 473 K (Figs. 3, 8, and 9). The formation of the band at about 1695 cm^{-1}, however, is exclusively observed after sulfidation above 623 K, in line with the temperature of W^{4+} formation as inferred from XPS and TPS (5). Based on these findings, it can be concluded that the onset temperature for the formation of WS_2 is well above 573 K. The shoulder around 1785 cm^{-1} in the low-temperature sulfided samples is therefore probably not related to W^{4+} species but may be attributed to the presence of W^{5+} oxysulfides.

When comparing the spectra of $NiW_{ex,393,673}$ and $NiW_{ex,823,673}$ with those of $NiW_{393,673}$ and $NiW_{823,673}$ one sees that they are very similar. Apparently, the various surface species formed on the base catalysts after sulfidation at 673 K are also formed on the extracted catalysts, although in a different ratio. This is especially remarkable in case of $NiW_{ex,393}$ since weakly interacting Ni species, comprising about 60% of the total amount, have been removed by the extraction. Therefore, it can be concluded that the chemical nature of the oxidic precursor is indeed important for the relative contribution of the various Ni species in sulfided catalysts, but at sufficiently high sulfidation temperature in all catalysts similar species will be formed.

Finally, the high-temperature sulfidation behavior of the catalysts calcined at 393 and 823 K will be discussed. As can be seen for NiW_{393}, no significant change is observed upon sulfidation in the temperature range of 673 to 703 K. However, after sulfidation at 763 K, a simultaneous decrease of the intensity of the 1885, 1775, and 1690 cm^{-1} bands is observed. The disappearance of the two bands at 1775 and 1690 cm^{-1} is an indication that the WS_2 edges have become largely inaccessible for NO. Since extensive sintering of WS_2 in this temperature range is not expected, it is assumed that the disappearance of absorption bands of NO absorbed on WS_2 is most likely due to the saturation of the WS_2 edges with NiS. Simultaneously, a weak additional band appears in the spectrum between the 1830 cm^{-1} and the 1780 cm^{-1} bands. The nature of the broad band that evolves around 1640 cm^{-1} is not clear at present. A further increase of the sulfidation temperature to 823 K does not cause significant changes in the presence of the surface species. Similar phenomena are observed for high-temperature sulfided NiW_{823}, where edge decoration of WS_2 occurs between 703 and 733 K. Remarkably, the contribution of the asymmetric stretch vibration of NO on W^{4+} at 1695 cm^{-1} completely disappears whereas that of the symmetric vibration remains present as a shoulder at 1785 cm^{-1}. Although the FTIR(NO) results indicate that a NiWS interaction phase is being formed in this temperature range, except for a weak contribution around 1805 cm^{-1} no evident new contribution is found in the FTIR(NO) spectrum. In the literature, no definite assignments have been reported for adsorption of NO on Ni in either NiWS or NiMoS. From a close inspection of the spectra, which have been reported by Atanasova *et al.* (7), it can be deduced that a band due to Ni in the NiWS phase should be close to 1805 cm^{-1}. Moreover, Topsøe and Topsøe (11) have compared the FTIR(NO) spectrum of a sulfided CoMo/$A1_2O_3$ catalyst to the computed sum of the FTIR(NO) spectra of a sulfided Co- and Mo/$A1_2O_3$ catalyst. It was assumed that differences between the spectra should be due to specific Co–Mo interaction phases. Although the differences are small, the spectrum of the sulfided CoMo/$A1_2O_3$ catalysts shows a shoulder around 1800 cm^{-1}, which is absent in the simulated spectrum. Based on these observations and our findings it is tentatively concluded that on NiW/γ-$A1_2O_3$ catalysts, a specific NiWS interaction phase is formed in the sulfidation temperature range of 703 and 733 K which shows a weak FTIR(NO) absorption band around 1805 cm^{-1}.

Quasi in Situ XPS

As mentioned above, the contribution of the shake-up peak of the oxidic Ni species has been neglected in the evaluation. Hence, the XPS analysis provides only semiquantitative information on the occurrence of the different species in oxidic and sulfided NiW/γ-Al_2O_3. Upon sulfidation, we observe a gradual shift of the peak maximum of the Ni $2p_{3/2}$ line of the 823 K calcined catalysts toward lower binding energy. This is in line with XPS analysis by Breysse *et al.* on sulfided NiW catalysts (31, 32) and can be attributed to the replacement of oxygen by the larger sulfur anion. As was found from the decomposition of the XP spectra, four different Ni contributions can be discerned over the range of sulfidation temperatures. The nature of the four Ni species may be clarified on the basis of their binding energy position and their reactivity toward sulfidation.

For the oxidic catalyst precursors, the emission line of Ni $2p_{3/2}$ can be fitted with two contributions, one at about 857.0 eV and the other at about 856.4 eV. The contribution of the high binding energy Ni oxide species is about 60% for the extrated catalyst against only 40% in the base catalyst. Apparently, the band at 857.0 eV is related to a more strongly interacting Ni species formed at higher calcination temperatures. The Ni $2p_{3/2}$ emission line in the spectrum of $NiW_{ex,393,ox}$ could be fitted well with a single contribution at 856.9 eV, confirming that the low binding energy oxide Ni species at 856.4 eV has a weaker interaction (Table 1). It has to be noted that the Ni(WO) and Ni(WOAl) may consist of a few species which are very similar in their chemical nature and their reactivity. The low binding energy Ni oxide species is weakly coordinated by the support and the WO_3 phase, since it can be partially removed by extraction and is completely sulfided below 473 K. As stated before, the presence of a separate NiO phase on these catalysts it is not expected. In accordance, the binding energy position of the low binding energy Ni oxide species is about 856.3 eV, which is significantly higher than that of NiO, which has been reported at 854.5 eV (33). The binding energy of Ni in $NiAl_2O_4$ and $NiWO_4$ is 857.2 and 857.4 eV, respectively (17), which suggests that the low binding energy Ni oxide species is in the vicinity of W and/or Al. Scheffer *et al.* (4) proposed that the sulfidation of a mixed NiWOAl phase occurs below 610 K, in line with the sulfidation temperature of the low binding energy Ni oxide species. It is proposed that the low binding energy Ni oxide species is related to Ni ions in the Ni(WO) phase.

The stability of the high binding energy Ni oxide species toward extraction is higher, in line with its low sulfidability. The binding energy at 857.0 eV is close to the values reported for bulk $NiAl_2O_4$ or $NiWO_4$ (17). It is, however, unlikely that a large part of Ni is present as either bulk $NiAl_2O_4$ or $NiWO_4$ since these species are especially formed at calcination temperatures above 850 K (22). On the other hand, it was deduced from FTIR(NO) that part of the Ni is present in a Ni surface aluminate (Ni(Al)) which may be sulfided above 600 K (4). In addition, Ni ions, present in a mixed oxide phase with a large number of W–O–Al bonds and low Ni concentration (Ni(WOAl)), will also have a low reactivity toward sulfidation. Based on the small difference in the binding energy of Ni^{2+} in $NiAl_2O_4$ and $NiWO_4$, it is expected that the binding energy of Ni in respectively Ni(Al) and Ni(WOAl) will be similar. In NiW_{823}, a refractory Ni species is present, which is not sulfided even at 923 K. From the work of Scheffer *et al.* (22), it can be deduced that in NiW_{823} about 20% of the Ni will be tetrahedrally coordinated, probably in the bulk of the support (Ni–Al) and, hence, is highly refractory toward sulfidation. From Fig. 13 it can be seen that this nicely fits with the decomposition results. It is proposed that the contribution of the high binding energy Ni oxide species in the XP spectra consists of the sum of three types of oxidic Ni, viz., Ni(WOAl), Ni(Al), and Ni–Al. In $NiW_{673,ox}$, the contribution of Ni–Al is very low.

During low-temperature sulfidation, mainly Ni in Ni(WO) is gradually converted into a Ni sulfide species, NiS, and a so-called intermediate Ni species. A significant part of the Ni in NiW_{673} and NiW_{823} K calcined catalysts is likely present as Ni(Al), Ni–Al, and Ni(WOAl), and is not sulfided below 600 K.

After room temperature sulfidation, a small Ni sulfide contribution is observed, in line with work of Breysse *et al.* (32). For catalysts sulfided below 613 K, the *BE* of the Ni sulfide species is constant and close to 853.5 eV. Shepelin (34) has reported a *BE* of 853.4 eV for Ni ions in ultradisperse Ni sulfide on SiO_2 which was prepared by decomposition of organometallic complexes in H_2S. In addition, a *BE* for Ni in bulk NiS of 852.9 has been reported by Zaikovskii *et al.* (35). Consequently, the Ni species at 853.5 eV is assigned to a highly disperse Ni sulfide, probably formed from Ni(WO). After sulfidation of the base catalysts above 673 K, a shift of +0.5 eV to 854.0 eV in the *BE* of the Ni sulfide species is observed. The *BE* of 854.0 eV is close to values reported in the literature for Ni sulfide on unsupported WS_2 (35), for NiWS on SiO_2 (34) and NiWS on Al_2O_3 (36). A shift of 0.5–0.9 eV to higher binding energies upon formation of the bimetallic sulfided interaction (CoMoS) phase was reported for alumina-supported NiW by Blanchard *et al.* (36), alumina supported NiMo by Houssenbay *et al.* (37), and alumina-supported CoMo by Alstrup *et al.* (38). Apparently, after sulfidation at 673 K, a major part of the highly disperse Ni sulfide starts to interact with WS_2 which can be explained in terms of the formation of the so-called NiWS phase. In the case of $NiW_{823,923}$, a small contribution is found with a *BE* of about 852.5 eV, close to the *BE* for bulk NiS as reported by Zaikovskii *et al.* (35). Since at a sulfidation temperature of 923 K sintering of the active phase can be expected, the contribution at 852.5 eV is assigned to larger Ni sulfide particles.

Finally, the decomposed spectra of the catalysts sulfided between 298 and 673 K indicate the presence of a fourth Ni species (Fig. 12). The contribution of this so-called intermediate Ni species reaches a maximum at a sulfidation temperature of ca. 450 K. The Ni $2p_{3/2}$ *BE* of this species is 855.0 eV, which is too high to be related to a Ni sulfide species. Furthermore, the stability of this species is higher in NiW_{823} than in NiW_{673}, indicating that the sulfidability of W plays a role in its presence. This suggests that the intermediate Ni species is converted into a Ni sulfide when the neighboring W phase becomes sulfided. On the basis of these considerations it is proposed that the intermediate Ni species is a partially sulfided Ni in close interaction with an oxidic or partially sulfided W phase, NiS(WO), and is mainly formed from the sulfidation of Ni in Ni(WO).

General Discussion on the Sulfidation of NiW/γ-Al_2O_3

A combined TPS and ^{57}Fe-MAS study (5) and a HREM study (6) of the sulfidation of NiW/γ-Al_2O_3 catalysts were recently presented elsewhere by us. In the present paper, additional information about the various stages of sulfidation of NiW/γ-Al_2O_3 catalysts was obtained from *in situ* FTIR(NO) and quasi *in situ* XPS. Since the nature of these various techniques is different, it is worthwhile to evaluate possible analogies and differences. The most important transitions in the course of sulfidation on NiW/γ-Al_2O_3 catalysts as derived from the different characterization techniques are schematically presented in Fig. 18. Furthermore, the various oxidic and sulfidic Ni and W species that are concluded to be present at different stages of sulfidation are schematically presented in Fig. 19.

Figure 17 gives the species present in the oxidic catalyst, the occurrence of which depends on the preceding treatments. The evidence for this picture is the following. By FTIR(NO), two types of Ni could be discerned. Upon mild calcination Ni is partly present as surface aluminate (Ni(Al)) and partly as a mixed oxide phase which contains W or W and Al. The XPS data support these conclusions. After calcination at 673 K, most of the Ni is present in a phase which is referred to as Ni(WO) and can be sulfided below 600 K. After calcination at 823 K, a larger part of the Ni is present in relatively stable phases such as Ni(WOAl) and Ni(Al) and about 15% of the Ni is present as Ni–Al.

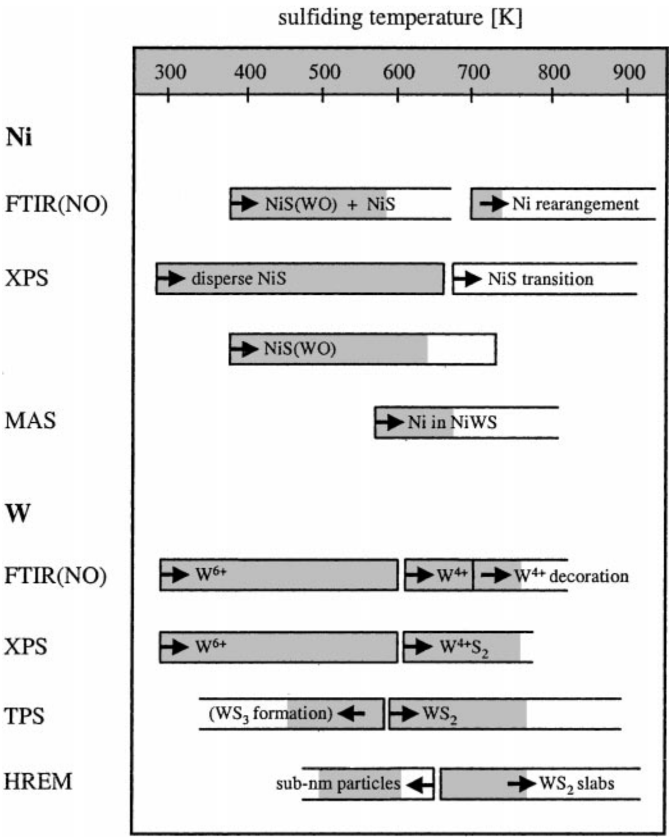

FIG. 18. Schematic representation of the most important transitions in NiW/γ-Al_2O_3 as a function of sulfidation temperature as derived from various characterization techniques.

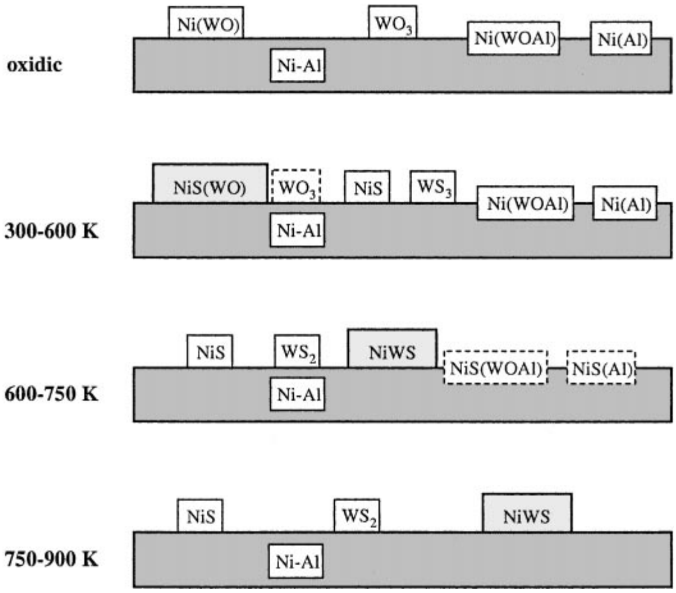

FIG. 19. Schematic representation of the various Ni species in oxidic NiW/γ-Al_2O_3 and NiW/γ-Al_2O_3 catalysts at different stages of sulfidation.

The reactivity of NiW/γ-Al_2O_3 toward sulfidation strongly depends on its preceeding calcination temperature. With increasing calcination temperature, the sulfidation shifts toward higher temperatures as is confirmed by XPS and HREM. For catalysts calcined below 673 K it was concluded from quantitative TPS that a significant part of the tungsten is sulfided into WS_3 (5) during sulfidation up to ca. 600 K. After calcination at 673 K, the formation of WS_3 was very limited, and after sulfidation at 613 K so-called subnanometer particles were observed with HREM. These species were suggested to consist of a partially sulfided Ni(WO) or Ni(WOAl) phase, which may be the nuclei for WS_2 slab formation at higher sulfidation temperatures (6).

Sulfidation of NiW/γ-Al_2O_3 at temperatures below 473 K shows a number of interesting reactions. At first, sulfidation of $NiW_{ex,393}$ reveals that a surface-exposed Ni species is formed from Ni which is located in subsurface positions on the oxidic precursor, probably in a mixed W oxide phase. This observation suggests that in the presence of H_2S, Ni ions are mobile even at low temperatures. FTIR(NO) shows that after sulfidation at 373 K, a Ni species is formed with an oxidic character. However, since this species is not present in oxidic catalysts and is formed in the course of sulfidation, it has been assigned to a sulfided Ni species in close interaction with an essentially oxidic W phase (NiS(WO)). XPS confirms this and suggests that it is formed from Ni(WO).

From XPS it could be inferred that Ni sulfide species are already formed after sulfidation at 298 K. XPS shows that a significant part of the Ni in catalyst calcined at 673 K and especially that calcined at 823 K is not sulfided below 600 K.

From XPS and FTIR(NO) it was inferred that the formation of $W^{4+}S_2$ species occurs only after sulfidation above 600 K. In the same temperature range, both XPS and ^{57}Fe-MAS (5) show a distinct change in the chemical environment of Ni sulfide. By ^{57}Fe-MAS it was established that in calcined samples the so-called NiWS phase, analogous to the well-known CoMoS phase, was formed after sulfidation at 673 K. It was inferred from TPS and HREM that the NiWS formation is related to the formation of WS_2 slabs. This is supported by the observation that on catalysts calcined at 393 K both WS_2 and NiWS formation occurs upon sulfidation at 573 K. Moreover, at a sulfidation temperature above 600 K, the more stable Ni species, such as Ni(WOAl) and Ni(Al), also start to sulfide.

After sulfidation at 700 K and higher, both TPS and HREM indicate a progressive formation of WS_2. Interestingly, FTIR(NO) indicates that a decoration of the WS_2 edges occurs only upon sulfidation above 700 K. This suggests that the formation of WS_2 is a prerequisite for its decoration by Ni. ^{57}Fe-MAS showed, however, that NiWS formation occurs upon sulfidation at about 600 K for NiW_{393} and about 650 K for NiW_{823}. It is therefore concluded that the edge decoration as inferred from FTIR(NO) may not be identical with the formation of the NiWS phase as observed with ^{57}Fe-MAS. The degree of sulfidation depends on the amount of bulk aluminate present: at about 800 K, almost all Ni species in the 673 K calcined catalysts are sulfided, whereas in the 823 K calcined catalysts about 15% of the Ni is present as a bulk aluminate. As a consequence, this catalyst is not fully sulfided, even at 923 K.

CONCLUSIONS

The speciation of Ni in oxidic NiW/γ-Al_2O_3 depends on its preceeding calcination temperature. In the catalyst precursors two types of Ni are present, Ni in a surface aluminate and Ni in a mixed oxide, with W and Al. No separate Ni oxide phase was present. After calcination at 823 K, a minority fraction of the Ni is present as a bulk aluminate.

After sulfidation at room temperature a small amount of Ni sulfide is formed. Sulfidation below 473 K shows the development of a Ni sulfide species in close interaction with an oxidic or partially sulfided W phase. In addition, part of the W phase may be sulfided at low temperature to form WS_3; reduction to W^{4+} species occurs only above 600 K. It was found that a significant part of the Ni strongly interacts with either the tungstate or the alumina and is present in subsurface positions. Upon low-temperature sulfidation these species migrate to the surface.

After sulfidation above 600 K, a distinct change in the chemical environment of Ni sulfide was observed, which was correlated to the formation of the so-called NiWS phase. The formation of NiWS could be related to the formation of WS_2-like slabs. Remarkably, a complete decoration of the WS_2 edges with Ni sulfide occurs only upon sulfidation above 700 K.

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REFERENCES

1. Stanislaus, A., and Cooper, B. H., *Catal. Rev.-Sci. Eng.* **36**, 75 (1994).
2. Reinhoudt, H. R., Troost, R., Van Langeveld, A. D., Sie, S. T., Van Veen, J. A. R., and Moulijn, J. A., *Fuel Processing Technol.* **61**, 133 (1999).
3. Topsøe, H., Clausen, B. S., and Massoth, F. E., *in* “Hydrotreating Catalysis,” Catalysis, Science and Technology, Vol. 11 (J. R. Anderson and M. Boudart, Eds.), Springer, Berlin, 1996.
4. Scheffer, B., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 18 (1990).
5. Reinhoudt, H. R., Van der Meer, Y., Van der Kraan, A. M., Van Langeveld, A. D., and Moulijn, J. A., *Fuel Processing Technol.* **61**, 43 (1999).
6. Reinhoudt, H. R., Van Langeveld, A. D., Kooyman, P. J., Stockmann, R. M., Prins, R., Zandbergen, H. W., and Moulijn, J. A., *J. Catal.* **179**, 443 (1998).
7. Atanasova, P., and Lopez Agudo, A., *Appl. Catal. B* **5**, 329 (1995).
8. Topsøe, H., and Clausen, B. S., *Appl. Catal.* **25**, 273 (1986).
9. Kung, M. C., and Kung, H. H., *Catal. Rev.-Sci. Eng.* **27**, 425 (1985).
10. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **77**, 293 (1982).
11. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **84**, 386 (1983).
12. Park, Y.-C., Oh, E.-S., and Rhee, H.-K., *Ind. Eng. Chem. Res.* **36**, 5083 (1997).
13. Koizumi, N., Yamazaki, Y., Ijima, M., and Yamada, M., *Appl. Surf. Sci.* **121/122**, 429 (1997).
14. Atanasova, P., Tabakova, T., Vladov, Ch., Halachev, T., and Lopez Agudo, A., *Appl. Catal.* **161**, 105 (1997).
15. Benitez, A., Ramirez, J., Fierro, J. L. G., and Lopez Agudo, A., *Appl. Catal.* **144**, 343 (1996).
16. Scheffer, B., Dekker, N. J. J., Mangnus, P. J., and Moulijn, J. A., *J. Catal.* **121**, 31 (1990).
17. Ng, K. T., and Hercules, D. M., *J. Phys. Chem.* **80**, 2094 (1976).
18. Salvati, L., Jr., Makovsky, L. E., Stencel, J. M., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **85**, 3700 (1981).
19. Scheffer, B., Molhoek, P., and Moulijn, J. A., *Appl. Catal.* **46**, 11 (1989).
20. De Bokx, P. K., Wassenberg, W. B. A., and Geus, J. W., *J. Catal.* **104**, 86 (1987).
21. Puxley, D. C., Kitchener, I. J., Komodromos, C., and Parkyns, N. D., *Stud. Surf. Sci. Catal.* **16**, 237 (1983).
22. Scheffer, B., Heijeinga, J. J., and Moulijn, J. A., *J. Phys. Chem.* **91**, 4752 (1987).

23. Peri, J. B., *J. Catal.* **86**, 84 (1984).
24. Topsøe, N.-Y., and Topsøe, H., *J. Catal.* **75**, 354 (1982).
25. Portela, L., Grange, P., and Delmon, B., *J. Catal.* **156**, 243 (1995).
26. Sacconi, L., *Discuss. Faraday Soc.* **7**, 173 (1949).
27. Tsai, W., Schwarz, J. A., and Driscoll, C. T., *J. Catal.* **78**, 88 (1982).
28. Ouafi, D., Mauge, F., Lavalley, J. C., Payen, E., Kasztelan, S., Houari, M., Grimblot, J., and Bonnelle, J. P., *Catal. Today* **4**, 23 (1988).
29. Halachev, T., Atanasova, P., Lopez Agudo, A., Arias, P. L., and Ramirez, J., *Appl. Catal.* **136**, 161 (1996).
30. López Agudo, A., Gil Llambias, F. J., Tascon, J. M. D., and Fierro, J. L. G., *Bull. Soc. Chim. Belg.* **93**, 719 (1984).
31. Breysse, M., Cattenot, M., Decamp, T., Frety, R., Gachet, C., Lacroix, M., Leclercq, C., De Mourgues, L., Portefaix, J. L., Vrinat, M., Houari, M., Grimblot, J., Kasztelan, S., Bonnelle, J. P., Housni, S., Bachelier, J., and Duchet, J. C., *Catal. Today* **4**, 39 (1988).
32. Breysse, M., Bachelier, J., Bonnelle, J. P., Cattenot, M., Cornet, D., Decamp, T., Duchet, J. C., Engelhard, P., Frety, R., Gachet, C., Geneste, P., Grimblot, J., Gueguen, C., Kasztelan, S., Lacroix, M., Lavalley, J. C., Leclercq, C., Moreau, C., De Mourgues, L., Olive, J. L., Payen, E., Portefaix, J. L., Toulhoat, H., and Vrinat, M., *Bull. Soc. Chim. Belg.* **96**, 829 (1987).
33. Matienzo, L., Yin, L. I., Grim, S. O., and Wartz, W. E., Jr., *Inorg. Chem.* **12**, 2762 (1973).
34. Shepelin, A. P., *Appl. Catal.* **11**, 29 (1984).
35. Zaikovskii, V. I., Shepelin, A. P., Burmistrov, V. A., Startsev, A. N., and Yermakov, Y. I., *React. Kinet. Catal. Lett.* **25**, 17 (1984).
36. Blanchard, L., Grimblot, J., and Bonnelle, J. P., *J. Catal.* **98**, 229 (1986).
37. Houssenbay, S., Kasztelan, S., Toulhoat, H., Bonnelle, J. P., and Grimblot, J., *J. Phys. Chem.* **93**, 7176 (1989).
38. Alstrup, I., Chorkendorf, I., Candia, R., Clausen, B. S., and Topsøe, H., *J. Catal.* **77**, 397 (1982).