

Comparison of the Sulfiding Rate and Mechanism of Supported NiO and Ni⁰ Particles

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The sulfiding rate and mechanism of (i) Al₂O₃-supported NiO and (ii) Al₂O₃-supported Ni⁰ particles have been studied using the temperature-programmed sulfiding technique. Both the surface and the core of Ni⁰ particles are easier to sulfide than those of NiO particles of comparable size. The Ni⁰ surface sulfides at 210 K and the inner layers sulfide between 270 and 500 K; simultaneously with the H₂S uptake H₂ is produced. The surface layer of NiO particles starts sulfiding at 300 K, while the core sulfides between 370 and 650 K. The sulfiding of NiO and Ni⁰ surface species takes place at various temperatures because of differences in the elementary steps involved in H₂S dissociation. Compared to NiO particles, the surface of Ni⁰ particles sulfides at lower temperatures due to a higher dissociation rate of H₂S on these surfaces. The sulfiding rate of the core of the particles is determined by solid-state diffusion. Sulfiding of the core of the Ni⁰ particles is determined by the diffusion rate of the Ni^{δ+} and to a lesser extent by the S^{δ-} ions, while sulfiding of the core of the NiO particles is most likely limited by diffusion of the O²⁻ ions. Surface nickel sulfide species are relatively more stable than their bulk analogues, possibly due to a relatively high entropy content of surface layers. © 1992 Academic Press, Inc.

INTRODUCTION

Reactions of metals and metal oxides with S compounds have received much attention during the last decades. Sulfiding is an important step in hydrotreating and in selective hydrogenation processes. Despite the fact that sulfiding of hydrotreating catalysts is inherent to the reactions proceeding, these catalysts are sulfided prior to the hydrotreating process. This sulfiding pretreatment is essential in obtaining a stable and active catalyst. Only a few studies have appeared concerning the sulfiding of these oxidic catalysts (1–4). Sulfiding of these catalysts generally takes place by O–S exchange reactions. With regard to sulfiding of NiO, Scheffer *et al.* (4) reported that although

sulfiding of alumina-supported catalysts started at room temperature, the major part of the sulfiding of nickel oxide took place above room temperature.

In petrochemical and refining industries reduced Ni catalysts are sulfided to obtain catalysts which can selectively hydrogenate diolefinic hydrocarbons into monoolefinic hydrocarbons (5–10). Removal of these highly olefinic hydrocarbons in pyrolysis gasoline is essential because the presence of these compounds may result in the formation of unwanted gums and resins. However, this hydrogenation reaction must be selective because hydrogenation of monoolefine results in a reduction of the octane number of the gasoline. An active and selective hydrogenation catalyst can be obtained by partial sulfiding of nickel catalysts. From Ref. (9) it can be concluded that “oversulfiding” the supported nickel catalysts results in a dramatic decrease of the activity, whereas the selectivity remains invariably

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high. When presulfiding is carried out at conditions under which thermodynamics predict bulk nickel sulfide formation (high sulfur concentration, low temperature (11)), the catalyst can only become partially sulfided in two cases. Either surface sulfiding results in one or more surface sulfide layers constituting a diffusion barrier for extensive sulfiding or a sulfur-containing hydrocarbon is used which can only be desulfurised on a metal surface under the conditions applied. Creation of a diffusion barrier could be envisaged to proceed analogously to the well-documented passivation of metallic nickel catalysts where approximately two oxide layers are found to form such a diffusion barrier against the thermodynamically highly favoured bulk oxidation by the surrounding air during storage (12, 13). Oxidation is restricted to the surface layers of the metal during passivation by carefully limiting the oxygen content in the treating gas and control of the temperature in the catalyst bed. The mechanism proposed is that nickel atoms enter the oxygen adlayer accompanied by electron transfer from Ni to O causing an increase of the oxygen radius. Nickel coming from the bulk continues to enter the oxygen adlayer until two or three NiO layers are formed, after which nickel diffusion through these NiO layers becomes extremely slow (13, 14).

Sulfiding of reduced nickel catalysts and films has been studied by Duyverman *et al.* (10), Saleh *et al.* (15), and Den Besten and Selwood (16). H₂S adsorption on nickel films at 200 K resulted in rapid dissociation of H₂S followed by desorption of H₂. Bulk sulfiding was observed at 270 K.

The described examples indicate that sulfiding of oxidic and metallic catalysts is of great importance in industrial processes. To understand these sulfiding reactions in more detail, fundamental knowledge about the sulfiding rate and the sulfiding mechanism is required. In this study the sulfiding rate and mechanism of alumina-supported Ni⁰ and NiO particles are compared. Sulfiding of particles is dominated by two different pro-

cesses: sulfiding of the surface is controlled by the intrinsic chemical reaction rate of the surface species and sulfiding of the core of the particles is dominated by diffusion rates. Since reaction rates of particles are affected by the particle size, catalysts that contain NiO and Ni⁰ particles of comparable size should be selected. To study the sulfiding of both the surface and the interior of the particles, catalysts with a high dispersion have been prepared. The sulfiding of these catalysts is studied with the temperature-programmed sulfiding (TPS) technique.

EXPERIMENTAL

Composition of the Catalysts

Commercial θ -Al₂O₃-supported Ni catalysts are used in this study. To vary the Ni particle sizes, the catalysts are reduced at different heating rates, flow rates, and temperatures. The most important catalyst characteristics, such as Ni⁰ surface area, particle size, dispersion, and degree of reduction, are shown in Table 1. The catalysts are denoted as Ni(x)/Al-[y], with x representing the wt% Ni and y the average Ni particle size in nanometers.

To compare the sulfiding rate of NiO and Ni⁰, it is important to know at what temperature these reactions start. In contrast with the sulfiding curves of the Ni⁰ catalysts, the start of the sulfiding reaction of the NiO catalyst cannot be deduced directly from these curves, since it is not possible to discriminate between adsorption and sulfiding. Therefore a green NiO catalyst was prepared based on α -Al₂O₃, by calcination at 970 K, which makes discrimination possible on the basis of the colour of the catalyst. Since α -Al₂O₃ is used, no nickel spinel species will be formed, even upon calcination at these high temperatures (17, 18).

Catalyst Characterisation

The nickel metal surface area was determined by H₂ chemisorption at room temperature and ca. 1×10^5 Pa. The degree of reduction was determined by measuring the amount of H₂ evolved upon dissolving the

TABLE 1
Characteristics of the Catalysts Studied

Catalyst code	Ni (wt%)	Ni _s ⁰ ^a (m ² /g Ni _{tot})	Particle size ^b (nm)	Dispersion (%)	Degree of reduction ^d (%)
Ni(6.0)/Al-[1.5]	6.0	168	1.5	43	60
Ni(12.2)/Al-[2.3]	12.2	154	2.3	29	82
Ni(12.2)/Al-[3.6]	12.2	109	3.6	19	91
Ni(10.6)/Al-[3.7]	10.6	105	3.7	18	91
Ni(10.6)/Al-[4.8]	10.6	87	4.8	14.5	96.5
Ni(10.1)/Al	10.1	—	4.0 ^c	17	0

^a Ni_s⁰, amount of Ni⁰ at the surface; calculated from H₂ chemisorption.

^b Particle size calculated on the basis of a half sphere model.

^c Determined with XRD.

^d Percentage of Ni⁰; calculated from the amount of H₂ evolved on dissolving of the reduced catalyst in acid (20).

catalyst in 2.5 M H₂SO₄ according to Ref. (19). The nickel crystallite diameter was calculated according to the method described by Coenen (20) assuming hemispherical crystallites.

Temperature-Programmed Sulfiding

A detailed description of the TPS apparatus is given elsewhere (1, 21). The sulfiding mixture used consisted of 3.8% H₂S, 22.9% H₂, and 73.3% Ar. The flow rate was 10.2×10^{-6} mol/s; the pressure was 1.05 bar. The sample size varied between 100 and 150 mg depending on the Ni content of the catalyst. The experiments were started at a reactor temperature of 210 K; the reactor was kept at this temperature for 1800 s. Subsequently, the reactor temperature was increased with a heating rate of 0.167 K/s to 1270 K, except in the temperature region from 210 to 290 K. Between 210 K and room temperature, the reactor temperature was increased by pulling the reactor out of the dry ice/acetone cooling bath and exposing it to ambient temperature. Above 1270 K, the reactor was cooled to ambient temperature. A UV spectrophotometer and a mass spectrometer were used to measure the H₂S concentration. Changes in the H₂ concentration were measured with a thermal conduc-

tivity detector (TCD). In all patterns shown, a peak in the positive direction indicates a production peak while a peak in the negative direction indicates a consumption.

RESULTS

Reduced Catalysts

Table 1 shows the Ni⁰ surface area, the Ni⁰ particle size, the degree of dispersion, and the degree of reduction of all catalysts investigated, including the oxidic catalyst. The Ni⁰ surface area increases of course with decreasing average particle size. A lower degree of reduction corresponds with smaller Ni⁰ particles. The TPS patterns of reduced Ni/Al catalysts are shown in Fig. 1. The quantitative data are given in Table 2. All data in this table are normalised to a total standard quantity of 100 mol of nickel.

All reduced catalysts show a H₂S uptake at 210 K. The H₂S/Ni ratio at this temperature decreases with increasing Ni particle size. Immediately after raising the reactor temperature, a part of the H₂S desorbs. This amount decreases with increasing particle size and increasing degree of reduction. Between 270 and 450 K, three H₂S consumption peaks are observed at 270, 300, and 380 K, respectively. The relative height of the peak at 380 K increases, whereas that

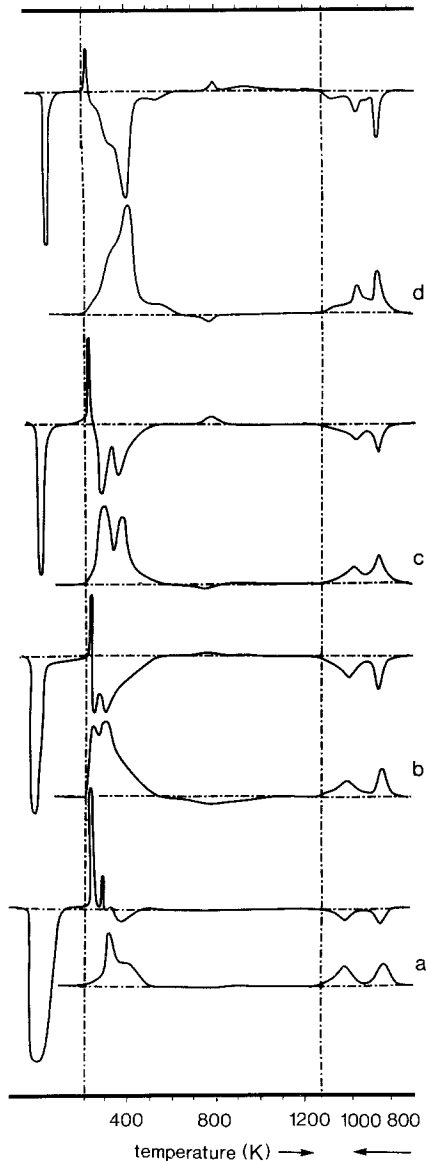


FIG. 1. TPS patterns (H_2S signal upper curve, H_2 signal lower curve) of reduced Ni catalysts. (a) Ni(6.0)/Al-[1.5], (b) Ni(12.2)/Al-[2.3], (c) Ni(10.6)/Al-[3.7], (d) Ni(10.6)/Al-[4.8].

at 300 K decreases with increasing particle size. The peak at 270 K is only clearly observed for the Ni(12.2)/Al-[2.3] catalyst. Simultaneously with the H_2S consumption, H_2 is produced. For the catalysts with the largest nickel particles the amount of H_2 produced is almost equal to the amount of H_2S consumed. For the catalysts with the small-

est nickel particles this H_2/H_2S ratio is slightly higher. The amount of H_2 produced between 270 and 500 K increases with increasing metal-particle size. All catalysts were completely sulfided at 500 K. In the TPS patterns of the catalysts containing Ni particles larger than 2.3 nm, a H_2S production coupled to a H_2 consumption is observed around 730 K. At the end of the temperature program the total amount of H_2S consumed results in a S/Ni ratio of 0.79–0.84 for the various catalysts. During cooling, H_2S consumption peaks, coinciding with H_2 production peaks, are observed at 720 and 890 K.

Oxidic Catalyst

The TPS pattern of an oxidic Ni/Al catalyst is shown in Fig. 2. Despite the uptake of a small amount of H_2S at 210 K, the green colour of the catalyst did not change. Upon increasing the temperature of the reactor, the major part of the H_2S consumed desorbed. Between 340 and 370 K, a minor H_2S uptake which resulted in a colour change of the catalyst from green to black is observed. The major part of the H_2S consumption took place in a sharp peak around 560 K. Up to 600 K no significant change in the H_2 concentration is observed. At ca. 730 K, equal amounts of H_2S and H_2 are produced and consumed, respectively. In the temperature region from 750 to 1000 K,

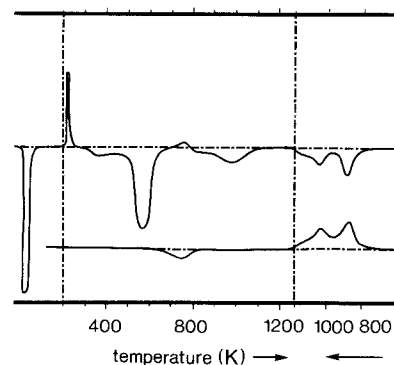


FIG. 2. TPS pattern of Ni(10.1)/Al (H_2S signal upper curve, H_2 lower curve).

TABLE 2
 Quantitative Data (in mol)

Catalyst code	Ni _s ^a	Ni _b ^b	Ni _{ox} ^c	H ₂ S _{upt} ^d (210 K)	H ₂ S _{prod} (273–300 K)	H ₂ S _{upt} (300–1270 K)	H ₂ _{prod} (270–1270 K)	H ₂ S _{upt} ^d (Total)	H ₂ S _{upt} ^e (1270–300 K)	θ _s ^f
Ni(6.0)/Al-[1.5]	25.8	34.2	40.0	108.8	39.6	14.0	36	83.2	16.7	0.27
Ni(12.2)/Al-[2.3]	23.8	58.2	18.0	36.7	4.9	50.3	58.6	82.1	14.4	0.23
Ni(12.2)/Al-[3.6]	17.2	73.7	9.0	30.2	3.9	57.6	63.0	83.9	15.8	0.70
Ni(10.6)/Al-[3.7]	16.4	74.6	9.0	30.9	7.1	57.2	59.7	81.0	15.8	0.75
Ni(10.6)/Al-[4.8]	14.0	83.5	3.5	13.2	2.6	68.4	68.8	79.1	19.8	0.50
Ni(10.1)/Al	—	—	100	13.1	10.5	79.8	—	82.5	21.6	—

^a Amount of Ni⁰ exposed on the surface.

^b Amount of Ni⁰ in the bulk.

^c Amount NiO.

^d Total H₂S uptake between 210 and 1270 K.

^e H₂S uptake during cooling.

^f θ_s = sulfur coverage on Ni_s, calculated according to: θ_s = (A - B - C)/D; A = total H₂S_{upt}, B = H₂_{prod} between 270 and 1270 K, C = NiO (total amount of oxidic Ni), D = Ni_s (total amount of surface Ni⁰).

a broad H₂S consumption is observed. Analogous to the reduced catalysts, H₂S consumption and H₂ production peaks are observed during cooling.

DISCUSSION

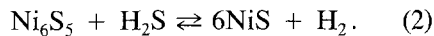
Reduced Catalysts

For clarity, the overall result is treated first. According to the Ni–S phase diagram (11), all Ni should be present as Ni₃S₂ at 1270 K in a gas phase with a $p_{\text{H}_2\text{S}}/p_{\text{H}_2}$ ratio of about 0.1. Based on this, a total H₂S uptake of 67 mol per 100 mol of Ni should have been observed. However, the total amount of H₂S consumed is higher for all catalysts, indicating that nickel sulfides with a S content higher than that in Ni₃S₂ are present. One could suggest that this is caused by H₂S decomposition over the alumina support. In fact some H₂S decomposition is observed during TPS of the nonimpregnated alumina supports. However, from the amount of H₂S consumed during cooling and from the overall sulfur balance, one can deduce that H₂S decomposition on the carrier does not have to be taken into consideration on these catalysts. This can be understood as follows. Under the assumption that all Ni would have been present as Ni₃S₂ after sulfiding up to 1270 K, a H₂S consumption of about 33 mol should have been observed during cooling (Ni₃S₂ → NiS). However, during cooling to room temperature only 15–20 mol H₂S is

consumed, resulting in a S/Ni ratio of about 1, which is the expected value based on thermodynamics. Therefore, it is highly unlikely that the sulfur balance is disturbed by H₂S decomposition. Of course, the rate of decomposition might well be higher than on the pure support due to the catalytic sites present, but also the hydrogenation will be accelerated. In conclusion, decomposition is not reflected in our patterns. Hence, we can safely conclude that after TPS, Ni is present with a stoichiometry of about Ni₃S_{2.5}.

The part of the particles which cannot be described by bulk thermodynamics is that comprising the surface layers. In the high-temperature region the main driving force for transformations becomes the entropy, and as a consequence phases with relatively high structural disorder, such as Ni₃S₂, will be relatively stable (11). NiS_{1+x} (0 < x < 0.06) and Ni₆S₅, which have less structural disorder as compared to Ni₃S₂, become more disordered when exposed to the surface. Hence it is conceivable that surface layers of NiS_{1+x} and Ni₆S₅ are stable compared to Ni₃S₂ up to temperatures higher than bulk thermodynamics predict. The sulfur content most likely decreases gradually from the outside to the inside of the particles until the structure can be described by the Ni₃S₂ structure. During cooling, Ni₃S₂ and nickel sulfide layers with a higher S content

react to Ni_6S_5 and subsequently to NiS_{1+x} , according to reaction equations (1) and (2). For convenience, NiS_{1+x} is further indicated as NiS.



Since in the temperature-programmed sulfiding pattern no further H_2S uptake is observed above 500 K, it is clear that both NiO and Ni^0 species are completely sulfided below this temperature. The shape of the H_2S and H_2 signals and the amount of H_2S and H_2 consumed and produced, respectively, are almost equal between 270 and 500 K, indicating that the main reaction taking place is the sulfiding of the Ni^0 atoms according to



The different peak maxima observed at 270, 300, and 380 K are most likely due to sulfiding of different Ni layers. Obviously the peak at the highest temperature represents the sulfiding of the core of the metal particles. This is corroborated by the observation that the high-temperature peak is more predominant, the larger the Ni^0 particle size. The outer surface layers are sulfided to NiS below 300 K. Due to the high density of the NiS layer, ionic diffusion will become the rate-limiting step. Due to the change in the density of the various layers, two sulfiding peaks are observed. An explanation for the peak at 270 K, which is only observed for the NiO(12.2)/Al-[2.3] catalyst, is not obvious. The reason could be a different morphology of the Ni^0 particles. It is plausible to assume that the surface of metal particles of ca. 2.0 nm is nearly completely stepped. Incorporation of sulfur in surface and sub-surface layers is probably more easy in the case of highly stepped surfaces. On the basis of this explanation the peak at 270 K was also expected to be present in the sulfiding pattern of the catalyst with the smallest Ni^0 particles. However, it is conceivable that these Ni^0 particles are not

present as hemispheres but more likely as "pancakes," which results in a sulfiding behaviour more similar to the large Ni^0 particles.

Since all Ni^0 atoms are sulfided below 500 K, the total amount of H_2 produced can be estimated. Assuming that NiO sulfides to NiS, the total H_2 production can be estimated by subtracting the amount of NiO from the total amount of H_2S consumed. All values calculated are higher than the H_2 production observed, indicating that a part of the H_2 is already desorbed at 210 K. It is therefore concluded that H_2 is directly produced from H_2S after dissociation on the Ni^0 surface at 210 K. At first sight it might be surprising that H_2 is desorbed at such low temperatures but due to the high H_2S concentration, H_2 is removed by the more strongly adsorbing H_2S . Because of the experimental setup, we were unable to measure this H_2 production at 210 K. Dissociation of H_2S at 210 K and subsequent desorption of H_2 has also been reported by others (15, 16, 22).

The amount of H_2S consumed at 210 K increases with decreasing Ni^0 particle size, obviously due to the larger number of exposed Ni^0 and NiO species. The large amount of H_2S consumed indicates that nearly all the NiO species were accessible for H_2S . Since the H_2S consumption exceeds the total amount of Ni_s^0 and NiO, multilayer adsorption must have taken place. Due to the interaction of the well-dispersed NiO species with the alumina support, Ni^{2+} ions become polarised by the Al^{3+} ions, resulting in a higher effective charge of the Ni ions. This change of the surface properties results in physisorption of larger amounts of H_2S . As soon as the reactor temperature is increased, a part of the H_2S is desorbed. Determination of the exact amount of physisorbed H_2S is rather difficult because, simultaneously with desorption of H_2S , sulfiding takes place. In addition to the sulfiding of Ni^0 , part of the H_2S is used to sulfide the NiO species. Consequently, it is not clear from the present

results at what temperature the actual sulfiding takes place.

Despite these uncertainties we are able to calculate the S coverage (θ_s) on the Ni⁰ surfaces. To calculate these values, we assumed that all NiO species were accessible for H₂S at 210 K and subsequently were sulfided to NiS during the temperature program. The total amount of H₂S consumed is divided between the Ni⁰ surface, Ni⁰ bulk, and NiO species. The amount of H₂S used to sulfide the bulk can be calculated from the H₂ production above 270 K. The surface coverage with sulfur, θ_s , is calculated by subtracting the amount of H₂ produced above 270 K and the total amount of NiO from the amount of H₂S consumed during the temperature program and subsequently dividing this value by the amount of surface exposed Ni⁰ (Ni_s). The values calculated in this way are given in Table 2. Due to the assumption in our calculations of complete sulfiding of NiO to NiS, instead of partly to Ni₃S₂, the θ_s values for the catalysts with the smallest Ni⁰ particles, which contain the highest amount of oxidic Ni, will most likely be too low. The θ_s values for the catalyst with the largest Ni particles agree very well with those reported in the literature, viz. 0.5–0.8 (22–25).

Oxidic Catalyst

In contrast with the sulfiding of the Ni⁰ atoms which starts already at 210 K, sulfiding of the surface layer of the NiO particles starts at 340 K. Scheffer *et al.* (4), however, reported that a part of a γ -Al₂O₃-supported NiO species were already sulfided at room temperature. In that study NiO was well dispersed and relatively strongly bound on the γ -Al₂O₃ support. The NiO/ α -Al₂O₃ catalyst contained NiO particles with an average size of about 4.0 nm. Under the assumption that weakly bound NiO is sulfided more easily than strongly bound NiO species, one would expect that the surface layer of the NiO/ α -Al₂O₃ particles was sulfided at a lower temperature than the γ -Al₂O₃-supported NiO species. Arnoldy *et al.* (1) sug-

gested that sulfiding reactions of surface species were not dominated by the bond strength of the metal oxides with the support but by the amount of anion vacancies on the oxidic catalyst which can adsorb H₂S. Therefore the difference between the present results and those of Scheffer *et al.* (4) can most likely be explained by the difference in the number of anion vacancies between both NiO catalysts. The green colour of the α -alumina-supported NiO catalyst suggests that NiO particles that contain at most a few defects are present, which supports this explanation.

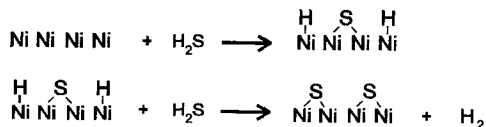
After sulfiding of the outer surface layer, between 340 and 380 K, the core is sulfided at about 560 K. Compared with the Ni⁰ particles, sulfiding of the core of the NiO particles takes place at a temperature which is about 160 K higher. A lower sulfiding rate of the oxidic particles has also been reported elsewhere (26). The difference in the sulfiding rate of the core of metallic and oxidic particles is most likely caused by a difference in the sulfiding mechanisms (see below). The H₂S consumption in the high-temperature region indicates that a small amount of the NiO was present in the surface octahedral or tetrahedral sites of the alumina. Despite the fact that no spinel structures are expected on α -Al₂O₃, it is likely that some occupation of surface octahedral or tetrahedral sites is possible. Analogous to the reduced catalysts, sulfide transformations were observed during cooling.

To understand the differences in sulfiding behaviour of metallic and oxidic particles, the sulfiding mechanisms are discussed in detail.

SULFIDING MECHANISM

Surface Layer

The sulfiding of the surface layers is controlled by their ability to adsorb H₂S and by their intrinsic reactivity towards H₂S dissociation. As observed in this study and by others (15–17), sulfiding of Ni⁰ surface atoms takes place by dissociative adsorption of H₂S. The number of sites involved is

FIG. 3. Sulfiding scheme of Ni⁰ surface layers.

most likely to depend on the reaction temperature, crystal surface plane exposed, and the S coverage. A LEED study by Demuth *et al.* (27), on low index faces of nickel, has shown that S atoms reside on high coordination sites, i.e., a fourfold coordinated site on the (110) and (001) surfaces and in a threefold coordinated site on the (111) surface. At high S coverages the number of unoccupied sites decreases and consequently the number of sites involved will also decrease. A sulfiding scheme of a Ni⁰ surface layer is given in Fig. 3. We focus only on the dissociative chemisorption of H₂S and the subsequent desorption of H₂; the number of sites involved is an arbitrary choice. When the S coverage becomes higher, a part of the sulfiding might also take place by adsorption of H₂S without dissociative adsorption. The θ_s values of 0.5–0.8 suggest that the major part of the H₂ is removed at 210 K.

Sulfiding of NiO starts at a higher temperature than that of reduced Ni species. This difference can be explained by a difference in dissociation rate of H₂S on the metallic and oxidic sites, respectively. After adsorption of H₂S, the sulfiding of the NiO species probably takes place according to the mechanism proposed by Arnoldy *et al.* (2). A scheme of this sulfiding reaction is shown in Fig. 4. After H₂S adsorption on an anion vacancy, sulfiding takes place by intermolecular proton transfer from the S to the O.

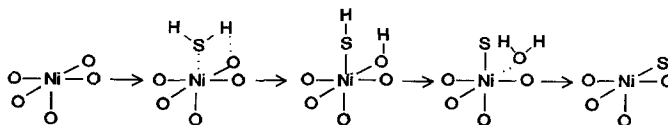
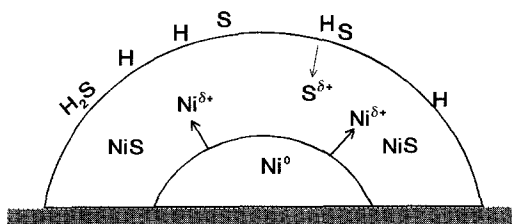


FIG. 4. Sulfiding scheme of NiO surface species.

FIG. 5. Sulfiding scheme of the core of the Ni⁰ particles; indication of the rate-determining diffusion steps.

After substitution of the H₂O for S, adsorption of H₂S can take place again. Hence it is not surprising that sulfiding of Ni⁰ and NiO surfaces takes place at different temperatures since reaction takes place by fundamentally different steps.

The Core of the Particles

Due to the high density of the structures before and after sulfiding, the sulfiding reaction is not controlled by molecular diffusion (H₂S, H₂O) but by ionic diffusion. Despite the fact that we are dealing with Ni⁰ and NiO particles of comparable size, the reaction of the core of NiO particles is slower than that of Ni⁰ particles. A more detailed understanding of the parameters that control the diffusion rate might shed more light on this difference. Sulfiding of the Ni⁰ particles is visualised in Fig. 5. A driving force for diffusion exists for both Ni and S atoms. In the literature, it is proposed that diffusion of Ni²⁺ is faster than that of S²⁻ ions (16). This assumption was based on a difference in ionic radii of Ni²⁺ [0.07 nm] and S²⁻ [0.175 nm] (15). However, the small difference in electronegativity between Ni [1.8] and S [2.5] suggests that the NiS bond is mainly covalent and therefore the difference in

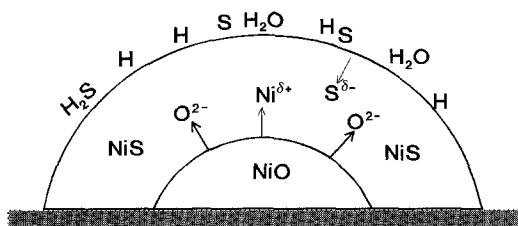


FIG. 6. Sulfiding scheme of the core of NiO particles; indication of the rate-determining diffusion steps.

ionic radii is much smaller than suggested. As a consequence, a contribution of diffusion of $S^{\delta-}$ cannot be ruled out.

The sulfiding of NiO particles is shown in Fig. 6. The difference in sulfiding of Ni^0 and NiO particles is that in the latter case oxygen ions must be removed. The lower sulfiding rate of the NiO particles can be ascribed to the relatively slow diffusion rate of the O^{2-} ions compared to the $Ni^{\delta+}$ and $S^{\delta-}$ ions. The O^{2-} ions are slightly larger than the $Ni^{\delta+}$ ions in a NiS compound; hence this difference in radii will contribute to the differences in sulfiding rate. Since diffusion can be considered as a continuous process of making and breaking of bonds, the energy of the bonds will be of importance too. In consequence, the difference in bonding strength between NiS and NiO will be of influence on the diffusion rate. The greater bond strength of NiO [392 kJ/mol] compared to NiS [360 kJ/mol] will result in a lower diffusion rate constant for O^{2-} (28). The sulfiding rate of NiO and Ni^0 is most likely to be dominated by the diffusion of O^{2-} and $Ni^{\delta+}$, respectively.

CONCLUSIONS

—Both the surface and the core of the Ni^0 are easier to sulfide than NiO particles of comparable size. Sulfiding of Ni^0 surface atoms takes place at 210 K, whereas the sulfiding of the NiO surface layer occurs between 370 and 650 K. Sulfiding of the surface NiO species takes place at slightly higher temperatures because of its inability to dissociate H_2S at this temperature.

—Sulfiding of the core of the nickel particles takes place between 270 and 500 K, whereas the core of the NiO particles is sulfided between 370 and 650 K. Sulfiding of the inside of the Ni^0 particles is mainly controlled by diffusion of $Ni^{\delta+}$ and probably to some extent by $S^{\delta-}$. The rate-limiting step in the sulfiding of the core of the NiO particles is the diffusion of O^{2-} .

—Sulfiding of Ni^0 particles takes place by simultaneous H_2S consumption and H_2 production.

—The outer layers of the sulfided particles contain more sulfur than expected on the basis of bulk thermodynamics. Due to a higher entropy of surface-exposed NiS, these species remain stable up to higher temperatures than expected on the basis of bulk thermodynamic calculations.

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