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Elucidation of behavior of sulfur on nickel-based hot gas cleaning catalysts

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Abstract

A closed-loop gas-recirculation system was used to measure the isosteric heat of sulfur chemisorption on supported nickel catalysts in hot gas cleaning conditions of gasification gas. During sulfur adsorption, reconstruction of the catalysts occurred. In addition, probably the enormous increase in surface diffusion due to sulfur adsorption on some nickel catalysts with high flow rates resulted in melt formation of adsorbed species on the surfaces of catalyst particles. Heat of sulfur adsorption on nickel decreased when sulfur coverage was increased. However, the enthalpy of adsorption decreased even below the heat of formation of bulk Ni_3S_2 , indicating most likely multi-layer or subsurface sulfur formation on catalyst surfaces. The structural properties of the catalysts had a great influence on sulfur adsorption behavior. The effect of sulfur on ammonia decomposition in synthetic gasification gas tests was explained by the change of heat of sulfur chemisorption on nickel. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

It was observed [1,2] that sulfur affected quite unexpectedly the nickel-based hot gas cleaning catalyst performance in a simulated gasification gas mixture. The ammonia conversion seemed to be enhanced by a high H_2S concentration in gas compared to a low H_2S concentration. On the other hand, the enhanced effect of low temperature and high total pressure on sulfur poisoning of nickel catalysts in ammonia and tar decomposition could be accounted for the increased

amount of sulfur, probably as a mode of multi-layer sulfur, adsorbed on the catalysts. Although the sulfur adsorption on nickel catalysts has been studied in different conditions using different kinds of methods for decades, the thermodynamic aspects of sulfur chemisorption on supported metal (nickel) catalysts have not been determined in the conditions comparable to the hot gas cleaning of gasification gas, where the $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratios can be as high as 3×10^{-4} – 3×10^{-3} at 1073–1223 K.

There are rather few studies where thermodynamics of sulfur adsorption on nickel has been reported. Rostrup-Nielsen [3] studied H_2S chemisorption on the $\text{Ni/MgAl}_2\text{O}_4$ catalyst. He measured sulfur chemi-

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sorption isotherms with ($P_{\text{H}_2\text{S}}/P_{\text{H}_2}$) ratios of the order of $<10 \times 10^{-6}$ at 823–918 K. Oliphant et al. [4] published H_2S desorption isotherms measured at 723 K ($P_{\text{H}_2\text{S}}/P_{\text{H}_2} < 30 \times 10^{-6}$) for several supported nickel catalysts. McCarty and Wise [5] made an extensive study of the thermodynamics of H_2S chemisorption on $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts. They determined isosteres for $\text{Ni}/\text{Al}_2\text{O}_3$ catalysts in the very low $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratios from 0.001×10^{-6} to 0.1×10^{-6} at 477–863 K. A plot of $\log(P_{\text{H}_2\text{S}}/P_{\text{H}_2})$ vs $1/T$ gave straight-line isosteres with heats of chemisorption varying from 160 to 90 kJ/mol. All these studies suggested that the free energy of formation of chemisorbed sulfur was much more negative than the most stable bulk sulfide Ni_3S_2 . Alstrup et al. [6] studied the chemisorption of H_2S on $\text{Ni}/\text{MgAl}_2\text{O}_4$ catalyst at much higher $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratios (7–50 ppm) and higher temperatures (773–1023 K) than McCarty and Wise. They were able to fit their own data and the part of the data of McCarty and Wise up to about 90% of saturation to a Temkin-like isotherm, which contains an entropy, being independent of coverage, and an enthalpy, which depends linearly on coverage.

The present study deals with chemisorption of H_2S on Ni-based catalysts with a H_2S detection technique similar to that used by McCarty and Wise [5] but far higher $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratios and temperatures than even in the studies of Alstrup et al. [6]. The data are of practical interest in connection with the catalytic hot gas cleaning conditions of gasification gas.

2. Experimental

2.1. Test facility and procedure

A closed-loop gas-recirculation system was used to measure isosteric heats of sulfur chemisorption on nickel-based catalyst samples. Fig. 1 shows a schematic diagram of the apparatus. The essential parts in the apparatus are an electrically heated quartz micro-reactor where the catalyst sample is placed; three metal rotary valves: one for gas analysis and the others for gas flow control; and a metal bellows pump with a glass bulb to damp pressure fluctuations. Metal tubings were used instead of teflon in order to prevent leaks. It was experienced that teflon tubing was not tight enough with rotary valves. On the other hand, it is

known that teflon is more inert to H_2S adsorption than metal. However, because the H_2S concentration level in the gas phase was high in the present tests, the H_2S adsorption in the system reached a steady-state relatively fast. This was ascertained by several tests with an empty reactor. Hence, the results were not affected by the materials of construction. High-purity gases of H_2 , He and $\text{H}_2\text{S}/\text{H}_2$ ($\pm 3\%$) were used in the experiments. The H_2S concentration of the gas was measured by a gas chromatograph equipped with a packed column of Chromosil 310 and a PID-detector (HNU Model PI-52) with a 10.2 eV hydrogen lamp.

The test runs were started by placing a weighed sample (0.5–2 g) of nickel catalyst onto the quartz grid of the quartz reactor tube. The reactor was closed and flushed with hydrogen to remove the remaining air from the system. The reactor was heated up to the desired temperature 1223 K (1073 K) in H_2 flow (about $0.3 \text{ dm}^3/\text{min}$, 50 K/min). The catalyst was reduced at this temperature under H_2 flow for an hour. The $\text{H}_2\text{S}/\text{H}_2$ gas was mixed with hydrogen by calibrated mass controllers and fed into the reactor until the reactor inlet and outlet H_2S concentrations were equal. The H_2S concentration in the gas was monitored at one-minute intervals. After that the gas-recirculation loop was closed and the circulation of the gas through the catalyst bed was started with GC analysis. The axial temperature difference in the catalyst bed was monitored to be within less than ± 10 K.

Adsorption isosteres for the nickel–sulfur system were determined by re-circulating the gas through the catalyst bed until the steady-state was reached. After the steady-state was attained at the highest temperature examined (1223 K) for the coverage, isosteres were measured by decreasing (50 K), then increasing the catalyst temperature and monitoring the $\text{H}_2\text{S}/\text{H}_2$ ratio while the gas circulated over the catalyst. The circulation pump was switched off before sampling the gas H_2S content. The coverage was considered to be uniform when the isosteric data points agreed with decreasing and increasing temperature. After the tests the catalyst bed was flushed with helium at the test temperature until all H_2S was removed from the gas. Then the reactor was let to cool down under helium flow.

In the sulfur adsorption tests we used H_2S exposure levels of 150, 500, 2000, 3750 ppmv and gas flow rates of about 0.3 and $1 \text{ dm}^3/\text{min}$. The higher flow rate was

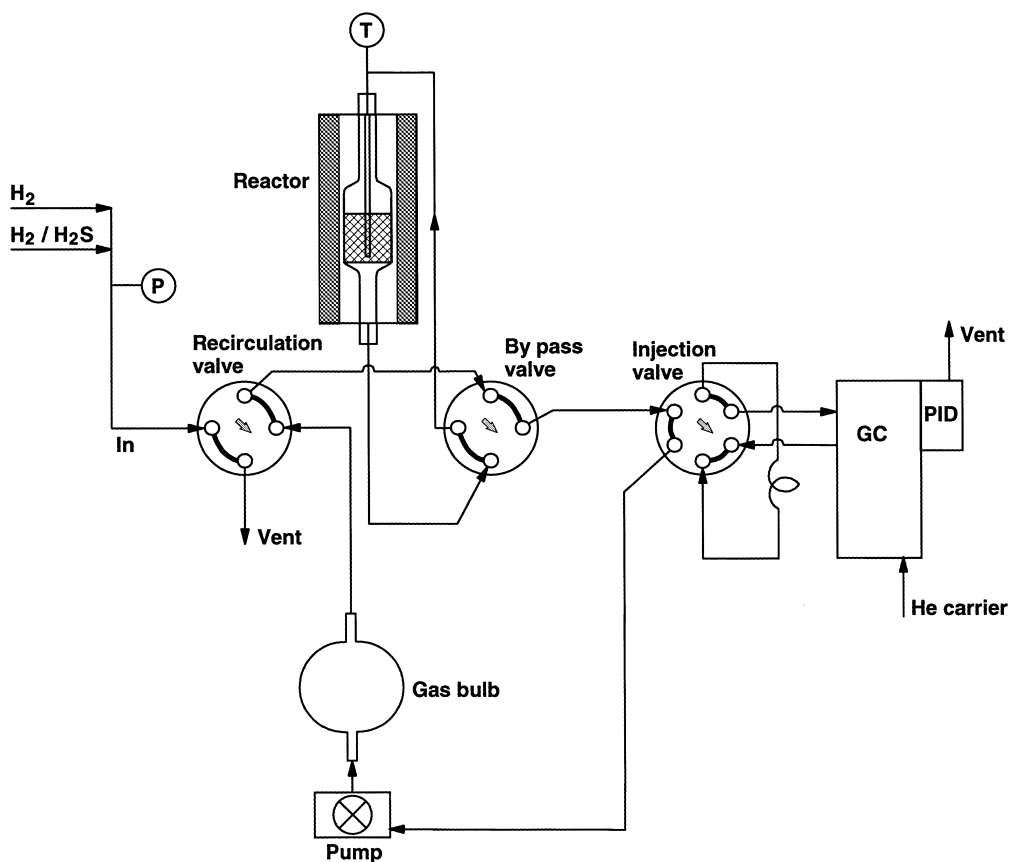


Fig. 1. Sulfur chemisorption equipment for nickel catalysts.

employed only with low sulfur levels of 150 and 500 ppm. In recirculation the flow rate through the catalyst bed was measured to be about $0.57 \text{ dm}^3/\text{min}$ (total volume of recirculation loop was 0.113 dm^3). During adsorption the overpressure before the catalyst bed varied from 40 to 180 mbar depending on the flow rate and the catalyst used. During recirculation the overpressure decreased to near zero.

Due to the unexpected behavior of sulfur during the tests compared to the test with very low H₂S concentrations [5], we had to make several extra adsorption and re-circulation tests with the catalysts to ascertain the results obtained.

2.2. Materials and analysis

Sulfur chemisorption isosteres were measured for three nickel samples. The first one was the nickel

catalyst (A), 13.3% Ni supported on α -alumina (particle size 0.3–0.4 mm), used in our earlier tests [1,2]. The second sample (B) was a 23% Ni catalyst supported on alumina/zirconium (particle size 0.5–1.2 mm). Both of these catalysts were obtained from the catalyst manufacturers for research purposes. The third sample (C) was very fine powder of Ni (7.4%) supported on LaAl₁₁O₁₈ [7]. The support was impregnated with an aqueous solution of Ni(NO₃)₂ by incipient wetness technique. The sample was calcined in air at 500°C for 60 min. Support materials Al₂O₃ (α) and LaAl₁₁O₁₈ were used as reference materials in sulfur adsorption tests.

The nickel surface area of these catalysts was measured by static volumetric hydrogen chemisorption (accuracy $\pm 10\%$ based on repeated measurements). Before the measurements the samples were in situ reduced in pure hydrogen atmosphere by rais-

Table 1
Properties of nickel catalysts

Catalyst	Support	Specific surface area BET (m ² /g)	Specific surface area metal ^a (m ² /g)
A	Al ₂ O ₃ (α)	5.9	1.6
		5.2	
B	Al ₂ O ₃ /ZrO ₂	52.6	5.7
C	LaAl ₁₁ O ₁₈	40.1	3.7
		36.5	

^aBased on total H₂ uptake at 303 K and the assumption of H/Ni=1 and 6.5×10⁻² nm²/Ni atom.

ing the temperature up to 1223 K and keeping at that temperature for an hour (like in the sulfur adsorption tests). The samples were cooled in Helium flow and measurements were performed at 303 K. The BET surface area of the materials was measured by the nitrogen adsorption method. The sulfur contents (accuracy ±5%) of the catalyst beds were analyzed. Some X-ray diffraction analyses for some selected catalyst beds were also carried out. Table 1 summarizes the properties of the three nickel samples used in this study.

3. Results

3.1. Sulfur adsorption/desorption

Fig. 2 shows typical breakthrough curves of H₂S with catalyst A at 1223 K. The breakthrough seemed to occur in a few minutes depending on the gas flow rate, catalyst amount and H₂S concentration. In the case of catalysts B and C the breakthrough took a longer time (breakthrough curves 1–3 h) because of a different nickel content or differences in catalyst structural properties. After this adsorption period the system was closed and the circulation of the gas through the catalyst bed was started in order to reach the steady-state at this temperature by monitoring the H₂S content of the gas. However, we observed that the H₂S content in the circulation gas started to increase. Nevertheless, after hours (1–21 h) depending on the catalyst, test temperature and the H₂S concentration used in adsorption, the system reached the steady-state. This kind of sulfur desorption from the catalyst bed during circulation was not expected on the basis of previous experiments of similar type with a low sulfur content [5]. During those tests it was observed that the

content of H₂S in the circulation gas decreased a little, not increased, during equilibration. Due to the desorption of sulfur from the catalyst bed, several tests were carried out in order to better understand the behavior of this “labile” sulfur.

Fig. 3 shows the effect of $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratio, used in adsorption, on sulfur desorption from catalyst beds. It can be seen that the amount of desorbed sulfur decreased as the $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratio increased. This can be seen more clearly in the case of catalyst C, because the amount of desorbed sulfur from this catalyst was much higher than that from both the other catalysts. However, when the H₂S content during adsorption was high enough (in these tests 3750 ppm) at 1223 K, there was no sulfur desorption from the catalyst bed anymore. Meanwhile, the sulfur content in the gas decreased a little. According to the test results with catalyst A, it seems that at 1073 K the respective limit for non-sulfur desorption during gas circulation after adsorption is lower than at 1223 K. On the other hand, the amount of desorbed sulfur is higher at 1073 K than at 1223 K with low sulfur levels. It is worth mentioning that catalyst A contained trace amounts of zinc (7.3 μg/g catalyst) that during gas circulation for reaching the steady-state vaporized from the catalyst bed and condensed with sulfur on the cool quartz tube downstream of the catalyst bed. This sulfur, measured to be about 25–50 μg S/g catalyst, likely decreased slightly the measured amount of desorbed sulfur from this catalyst. The tests with the support (LaAl₁₁O₁₈) of catalyst C showed that the amount of adsorbed (Section 3.2) and desorbed sulfur even from this material was rather high. On the other hand, the support material of catalyst A (α-Al₂O₃) adsorbed (Section 3.2) and desorbed very small amounts of sulfur (below 10 ppm(w)/g Al₂O₃). The support material of catalyst B was not available.

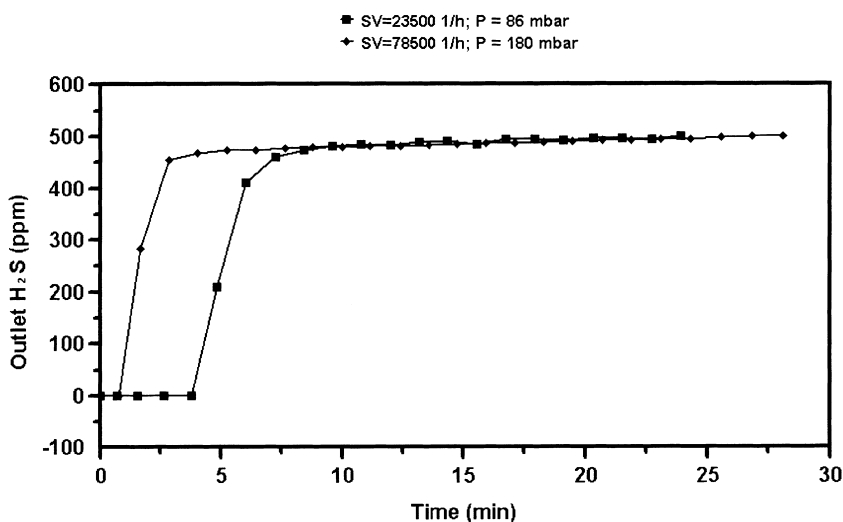


Fig. 2. Sulfur adsorption on catalyst A at 1223 K. SV=space velocity, P=overpressure before catalyst bed.

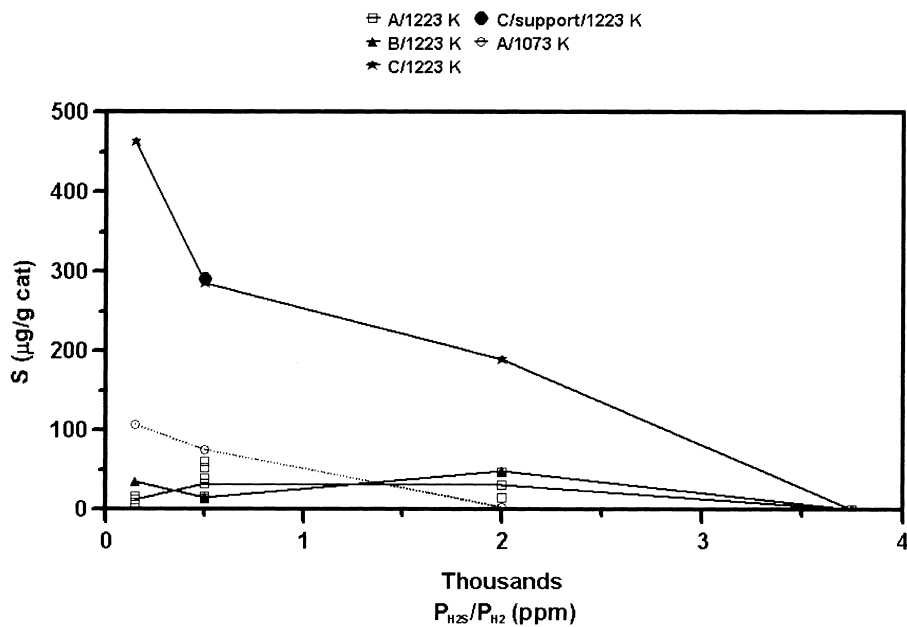


Fig. 3. Effect of P_{H_2S}/P_{H_2} -ratio in adsorption on sulfur desorption from catalyst beds.

The effect of sulfur adsorption time on the amount of desorbed sulfur from the catalyst beds was studied with catalyst A by increasing the sulfur exposure time. In these tests the flow rate through the catalyst bed (overpressure before catalyst bed) was equal. Fig. 4

shows that extending the adsorption time decreased the desorbed sulfur amount from the bed. After 5 h no labile sulfur existed. Fig. 5 shows the result when we repeated the exposure of the catalyst to sulfur and equilibrated the system three times. Between the

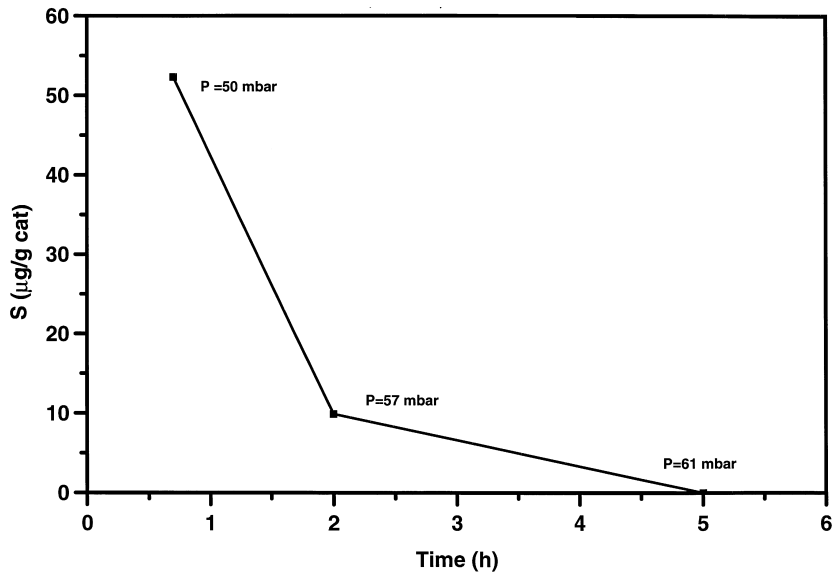


Fig. 4. Effect of adsorption time on sulfur desorption from catalyst beds. Catalyst A, $T=1223$ K, $P_{\text{H}_2\text{S}}/P_{\text{H}_2} = 500$ ppm H_2S , P =overpressure before catalyst bed.

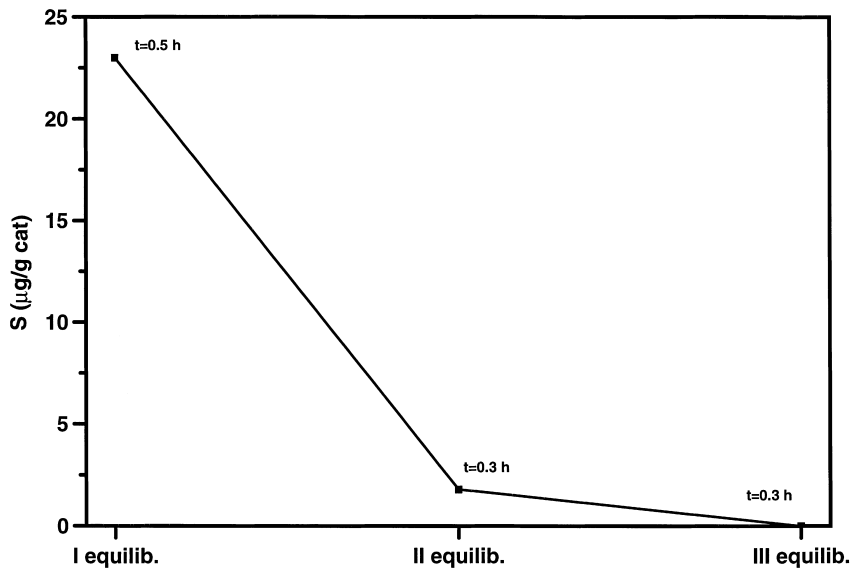


Fig. 5. Effect of repeated sulfur adsorption/equilibration on sulfur desorption from catalyst beds. Catalyst A, $T=1223$ K, $P_{\text{H}_2\text{S}}/P_{\text{H}_2} = 500$ ppm, $P=50$ mbar, t =time of exposure.

phases the catalyst bed was flushed with helium to remove all remaining sulfur from the gas before new sulfur exposure. It was observed that after having reached the steady-state, i.e. the catalyst was no more

able to adsorb sulfur and therefore the existence of “labile” sulfur disappeared. These results most probably indicated that, due to sulfur adsorption, the structure of metallic substrate is rearranged and this

complex change in the structure requires quite a long time even at as high a temperature as 1223 K.

The effect of the gas flow rate, applied in sulfur adsorption, on the desorption of sulfur was carried out by varying the sulfur exposure flow rates through the catalyst bed. The experiments with increased flow rates were made only with 500 ppm H₂S levels (Fig. 2). These experiments were performed only with catalyst A because with catalysts B and C the high flow rate increased the pressure drop in the catalyst bed too much. Although we did not notice any visible blocking of the catalyst bed after cooling we believe after repeated tests that the reason for this behavior is most probably the increased adsorption of sulfur on the catalyst. Fig. 6 shows the amount of desorbed sulfur from the bed in the case of catalyst A as a function of the exposure (over)pressure before the catalyst bed. The adsorption times in the experiments were comparable to each other. It can be seen that when the overpressure (flow rate) is raised the amount of desorbed sulfur from the catalyst bed is increased.

The hypothesis of reconstruction of the nickel surface by adsorbed sulfur finds considerable support in the literature [8,9,10]. It has been reported that surfaces of various solids undergo faceting, i.e. changes of surface structure in the presence of impurities at the

surface. During faceting new crystal planes are formed on the surface. These planes have crystallographic orientations that are different from those present in the absence of the surface impurities [9]. In different studies of sulfur on nickel it has been found that faceting is favored by high surface coverages at which the catalyst is completely deactivated. Such an effect would be expected to prevail because in high adatom densities the surface energy is reduced significantly [8]. The rearrangement of surface structure is, in general, a rapid surface diffusion process. It has been found [11–13] that sulfur and other impurities (halogens) can increase the surface diffusion rates of silver and copper enormously. According to the results with the Ag–S system at 1173 K, it was suggested that the surface compound can melt to form a two-dimensional liquid. This was based on the obtained high values of diffusion coefficients ($3 \times 10^{-4} \text{ cm}^2/\text{s}$), which were comparable to the value obtained for a clean metal close to the melting point [13].

It can be well suggested according to the information mentioned above that the desorption of H₂S during circulation into the gas phase was due to a reconstruction (probably also due to slight sintering of nickel crystal sizes) of the catalyst as a consequence of sulfur adsorption. However, this desorption of sulfur

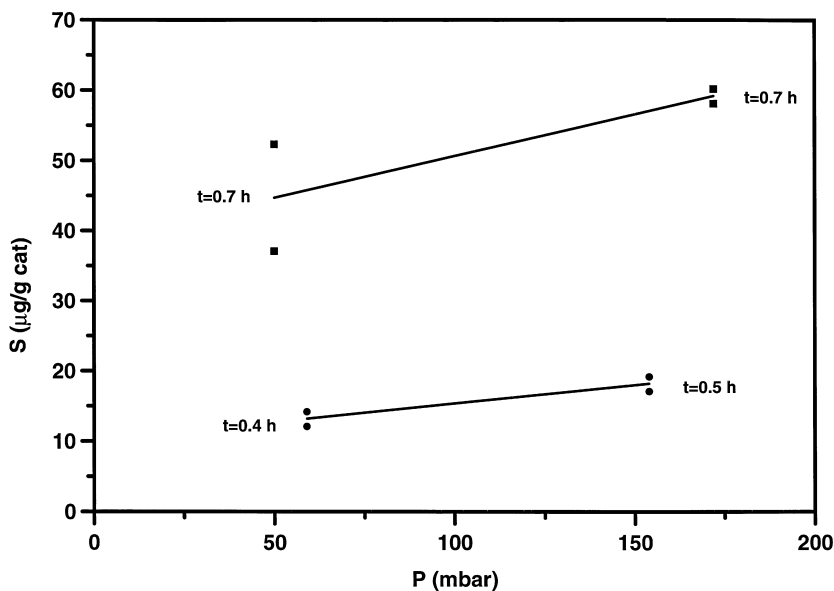


Fig. 6. Effect of exposure pressure (P) during adsorption on sulfur desorption from catalyst beds. Catalyst A, $T=1223 \text{ K}$, $P_{\text{H}_2\text{S}}/P_{\text{H}_2} = 500 \text{ ppm}$, t =time of exposure.

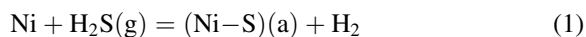
(reconstruction) from the catalyst was not observed in flow through mode, i.e. without the small volume of the circulation loop of the experimental system. Pressure increase is known to increase the mobility of the adsorbed species on the surface of catalysts [1]. This increased mobility and therefore the increased adsorption capability of sulfur is probably the reason for the increased amount of sulfur desorbed from the catalyst when the bed was exposed to high gas flow rates, i.e. overpressures. The total pressure reduction (40–180 mbar) before the catalyst bed during gas circulation was also expected to have some effect on the amount of desorbed sulfur from the bed. Probably in these tests the pressure reduction could facilitate the desorption of sulfur from the catalyst to the gas phase because reduction in total pressure should decrease the H_2S concentration in gas.

The strange behavior of increased pressure drop in catalyst bed, during high flow rates in sulfur adsorption with catalysts B and C, can most probably be explained according to melting of the surface phase. Because it is known that bulk nickel sulfide forms a liquid sulfide product at temperatures above 908 K [2], it can be expected that the Ni–S system is capable of forming a similar kind of two-dimensional liquid as was suggested with the Ag–S system. In the present study the increased amount of sulfur adsorption probably increased the self-diffusion rate of nickel on the catalyst surfaces so much that the sticky liquid-like solution formed blocked the catalyst bed/sinter under the bed, resulting in an increased pressure drop. As such a behavior did not occur with catalyst A, the reason is probably dependent on the catalyst properties. The nickel content of catalyst B and dispersions of catalysts B and C were higher than those of catalyst A. Accordingly the nickel crystal sizes were smaller with catalysts B and C than with catalyst A. A LEED study by Demuth et al. [14] has shown that sulfur atoms reside on high coordination sites, in four-fold coordinated sites on the (1 1 0) and (0 0 1) surfaces and in the three-fold coordinated sites on the (1 1 1) surface. Therefore it is also reasonable to expect that the layered sulfur adsorption would be facilitated by small crystallites having a large fraction of high-coordination sites. This assumption may also be supported by studies of CO adsorption on alumina-supported Ni and Rh catalysts [15]. The catalysts with a low metal loading of small crystallites have shown

evidence for adsorption of subcarbonyl species. However, this does apparently not occur with poorly dispersed nickel. It is also evidently possible to relate the layered sulfur adsorption to metal–support interactions like in the case of subcarbonyl adsorption [15], since if a large fraction of small metal particles are in intimate contact with the support their geometrical shape and electronic properties may be markedly influenced by the strong metal–support interaction. This could result in a relatively weaker bond between sulfur and nickel, which could enhance layered sulfur formation.

3.2. Chemisorption isosteres

The chemisorption isosteres of the three nickel catalysts were determined by measuring the gaseous sulfur (expressed as the fraction of H_2S in atmospheric H_2) as a function of temperature for several values of sulfur coverage (Fig. 7). The enthalpy and entropy for dissociative sulfur adsorption



were calculated from the least-squares analysis of the logarithm of sulfur chemical potential vs reciprocal temperature (Eq. (2), Table 2)

$$\Delta G^0 = RT \ln(P_{H_2S}/P_{H_2}) = \Delta H - T\Delta S, \quad (2)$$

where ΔH and ΔS are relative to gaseous H_2S and H_2 . The parameter θ represents the fractional surface coverage by sulfur relative to H_2 adsorption.

As mentioned earlier it took a rather long time to reach the steady-state due to desorption of sulfur from the catalyst even at 1223 K. Depending on the catalyst and on the H_2S level in adsorption, the equilibration took 1–21 h. According to the few tests at 1073 K the respective equilibration time was longer than at 1223 K. Especially with catalysts B and C the slow diffusion through the porous catalyst particles in low H_2S concentrations was most likely responsible for the long time required to reach uniform coverage. However, at other temperatures (after steady-state at 1223 K) the reach of steady-state was relatively fast. It took less than an hour to reach the steady-state. When the temperature was elevated from 1073 K the steady-state H_2S values were reached in the same timescale as at decreasing temperatures. The H_2S levels obtained at rising temperatures were then fairly

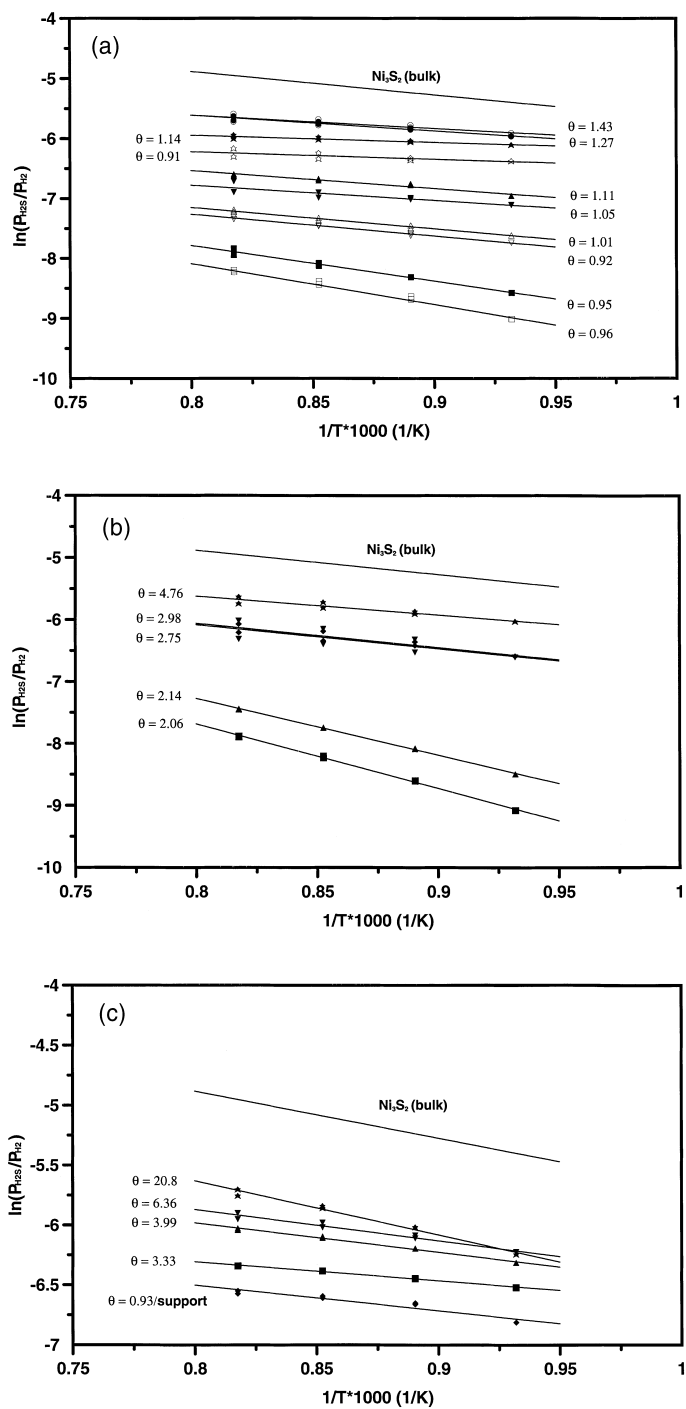


Fig. 7. Sulfur chemisorption isotherms on nickel catalysts. Catalyst A [a], catalyst B [b], catalyst C [c]. Coverage θ normalized to total H_2 uptake at 303 K.

Table 2
 H_2S/H_2 isosteres on different nickel catalysts (least-squares analysis, seven data points, P_{H_2S}/P_{H_2} and coverage at $T_{avg}=1148$ K)

P_{H_2S}/P_{H_2}	Coverage ^a	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol K)	R^{2b}
<i>Catalyst A</i>				
195	0.96	-56.9±2.3	21.7±2.3	0.995
277	0.95	-49.6±4.1	25.0±3.7	0.999
541	0.92	-30.5±1.6	36.0±1.4	0.999
609	1.01	-29.8±1.2	35.6±1.2	0.998
949	1.05	-21.3±6.6	39.3±6.0	0.971
1172	1.11	-25.1±0.8	34.3±0.7	0.962
1807	0.91	-10.6±5.2	43.2±4.8	0.982
2393	1.14	-10.1±2.3	41.4±2.2	0.981
3062	1.43	-21.9±2.4	29.0±2.2	0.995
3139	1.27	-18.5±4.9	31.8±4.6	0.990
<i>Catalyst B</i>				
238	2.06	-86.5±0.8	-5.35±0.7	0.998
381	2.14	-76.2±0.2	-0.43±0.3	0.999
1739	2.75	-32.3±10.1	24.8±9.6	0.995
1766	2.98	-32.6±5.5	24.4±5.2	0.992
2924	4.76	-25.4±4.2	26.4±3.9	0.993
<i>Catalyst C</i>				
1300 ^c	0.93	-17.7±0.8	39.8±0.8	0.995
1619	3.33	-13.2±0.0	41.9±0.0	0.993
2107	3.99	-20.5±0.5	33.4±0.5	0.993
2331	6.36	-21.8±1.8	31.4±1.7	0.990
2610	20.8	-37.6±1.9	16.8±1.7	0.922

^aBased on total H_2 uptake at 303 K and on the assumption of $H/Ni=1$ and 6.5×10^{-2} nm²/Ni atom, mono-layer sulfur content: 445 $\mu\text{gS}/\text{m}^2$ Ni, $S/Ni=0.5$ [18].

^bCorrelation coefficient for $\ln(P_{H_2S}/P_{H_2})$ vs $1000 K/T$.

^cData for support (LaAl₁₁O₁₈).

close to the steady-state values of decreasing temperatures (Fig. 7). The small difference in the values may be explained by the sintering phenomenon of nickel during the experiments. X-ray diffraction analysis of some samples of catalyst A indicated that a slight increase in nickel crystal size had occurred during the tests.

The heat of adsorption calculated from the isosteres (Table 2 and Fig. 7) shows that the adsorption energy decreased as the sulfur content in the gas phase (or coverage) increased. This is consistent with the data obtained from literature [5,6]. Only with catalyst C such a decrease of ΔH_{ads} cannot be seen, because the sulfur content, due to a high amount of desorbed sulfur (Fig. 3), in these tests was high compared to that with other catalysts. At low sulfur coverages the adsorbed sulfur is very strongly bound to the surface of nickel. Bulk Ni₃S₂ has a heat of formation per mole sulfur of

-32.6 kJ/mol at 1148 K. In the present study the chemisorbed sulfur is hence, at the maximum, from 24 (catalyst A) to 54 kJ/mol (catalyst B) energetically more stable than the sulfur in bulk Ni₃S₂. A significant phenomenon, seen especially with catalyst A, is that the adsorption energy decreases even to a lower level than the enthalpy of formation of bulk Ni₃S₂ at 1073–1223 K. However, the ΔH_{ads} level is increased again with a high gas H₂S content, near to the enthalpy value of bulk Ni₃S₂ formation. The adsorption entropies (ΔS_{ads}) remain nearly constant, at the level of the entropy of formation of bulk Ni₃S₂ (14.6 J/mol K), changing only slightly coincidentally with ΔH_{ads} .

The decrease of ΔH_{ads} with increased sulfur coverage can probably be explained by repulsive interaction between adjacent chemisorbed sulfur atoms [5]. However, the adsorption energy decrease to the lower value than the enthalpy of bulk Ni₃S₂ formation can likely

be explained by the “multi-layer” or subsurface sulfur formation on nickel before the bulk sulfide (Ni_3S_2 , $\text{S/Ni}=0.67$) development at higher ratios of $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$. Although an evidence of the formation of multi-layer or subsurface sulfides has been reported [2], the nature of these sulfides is not well-known in different conditions. However, it is quite reasonable to expect that when accumulation of multi-layers occurs, likely after completion of mono-layer, the binding energy of layered sulfur on nickel could then be even smaller than the enthalpy of formation of bulk nickel sulfide. This assumption is supported by studies of Buckley et al. [16] and our previous studies [2]. Buckley et al. observed with gold in aqueous acid medium, that multi-layers of sulfur had a lower volatility and a smaller electron binding energy than bulk elemental sulfur. In our research the sulfur species adsorbed on nickel were desorbed at much lower temperature than the sulfur from bulk nickel sulfide.

Comparing the values of adsorption energies of sulfur with catalysts A and B, it can be seen that the values are much higher with catalyst B than with catalyst A. Probably the phenomenon can be explained by different structural properties of the catalyst materials, which have an effect on the sulfur adsorption behavior. In comparison with the supported nickel catalysts with unsupported nickel catalysts Oliphant et al. [4] observed that mono-layer coverage of sulfur was completed at a lower partial pressure of H_2S on supported nickel, indicating that small, supported crystallites of nickel adsorb sulfur more strongly, because of catalyst support and extent of reduction effects. The results of the present study support this finding due to the fact that the smaller crystal size of catalyst B (larger dispersion) and therefore a more efficient contact of nickel with the support, could favor the stronger sulfur adsorption.

The calculated sulfur coverages with different catalysts differed from each other significantly. The support of catalyst C adsorbed quite an abundance of sulfur (Table 2, Fig. 3). On the other hand, according to tests of this study and previous [2] studies, the support material ($\alpha\text{-Al}_2\text{O}_3$) of catalyst A adsorbed sulfur in very small amounts, i.e. <0.02 wt%. Because the support material of catalyst B was not available, we could not test the sulfur adsorption capability of this catalyst. However, it can be expected, based on the high surface area of catalyst B (Table 1) and its more

basic nature than Al_2O_3 [17] that it will adsorb more sulfur than the low surface area α -alumina. Probably the differences of sulfur adsorption on supports, interactions of support with metal, metal dispersions and nickel crystal sizes have affected the obtained large differences in coverages.

In the present study we calculated the sulfur coverage (Table 2, Fig. 7) based on the common agreement [18,19] of the composition of the saturation layer of single-crystal planes (two-dimensional sulfide). The sulfur content is close to $445 \mu\text{g S/m}^2 \text{Ni}$. This value, which does not vary significantly from face to face, corresponds to 0.5 sulfur atom per nickel atom ($\text{S/Ni}=0.5$). The sulfur capacity correlates with hydrogen capacity by $\text{H/Ni}=1$ [18] and by assumption of $6.5 \times 10^{-2} \text{ nm}^2/\text{Ni}$ atom. However, with polycrystalline and supported nickel there is only a fair agreement about the stoichiometry at saturation of H_2S adsorption. The saturation stoichiometry depends apparently on $P_{\text{H}_2\text{S}}$ and varies with temperature. According to different adsorption studies of polycrystalline or supported Ni, the S/Ni values have ranged from 0.25 to 1.3 [19]. The near unity values of S/Ni observed by Oliphant et al. [4] for supported and unsupported Ni obtained by desorption after saturation at 25–30 ppm $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ could be best explained by surface reconstruction leading to new surface phases. The results by Erekson [20] suggest that the value of S/Ni ratio increased with increasing $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ between 0.2 and 30 ppm. Moreover, it was suggested [19] that Ni–S surfaces vary from well-defined structures ($\theta=0.5$) at low H_2S concentrations to reconstructed surfaces of Ni_3S_2 and NiS stoichiometries in intermediate conditions to multi-layer sulfides for high H_2S concentrations. Although surface structures consistent with Ni_3S_2 and NiS stoichiometry and multi-layer surface sulfides have been reported, all studies have been conducted at partial pressures of H_2S and temperatures significantly lower than the conditions of the present study. In this research the stoichiometry of H_2S adsorption on nickel can be best discussed (without sulfur adsorption too much on catalyst support) with the data of catalyst A. It can be seen (Table 2) that the values of $\text{S/Ni}=0.63\text{--}0.72$, obtained for the highest H_2S concentrations used in the tests, are near to the stoichiometry of Ni_3S_2 ($\text{S/Ni}=0.67$). This approach of the sulfur adsorption stoichiometry on nickel to the stoichiometry of bulk Ni_3S_2 is consistent with the

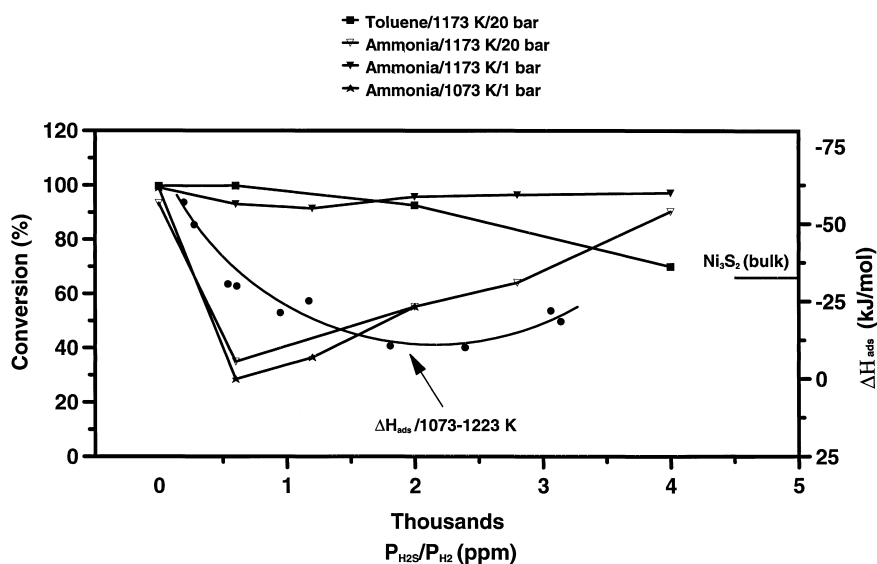


Fig. 8. Effect of sulfur on the conversion of ammonia and toluene with catalyst A in synthetic gasification gas [2]. ΔH_{ads} values from the present study in P_{H_2S}/P_{H_2} atmosphere.

thermodynamics. However, the stoichiometry may not be the same at lower levels of P_{H_2S}/P_{H_2} used in this study.

Previously [1,2] we studied the effect of sulfur on the performance of nickel-based hot gas cleaning catalysts in a simulated gasification gas mixture. Fig. 8 shows the conversion of ammonia and toluene (tar model compound) as a function of P_{H_2S}/P_{H_2} in those tests (catalyst A, temperature 1073–1173 K, pressure 1 and 20 bar). In the same plot, data on heat of adsorption of sulfur on nickel are presented in P_{H_2S}/P_{H_2} atmosphere of the present study. The unexpected behavior in the conversion of ammonia (i.e. increase of conversion when the H_2S concentration is increased), observed especially in the pressurized test, can most likely be explained by the obtained ΔH_{ads} values. The conversion of ammonia is increased due to the decreased binding energy of sulfur on nickel. Probably the dissociative adsorption of ammonia is facilitated on the nickel surfaces when the binding energy of sulfur on nickel is decreased. When the H_2S concentration in the gas is increased close to the level of bulk sulfide formation, the sulfur adsorption energy approaches the formation energy of nickel bulk sulfide. On the other hand, bulk nickel sulfide has been observed to be active in ammonia decomposition [2]. Hydrocarbon (methane, higher hydrocarbons) decom-

position is known to be possible in partially sulfur-poisoned nickel [2,18]. However, when sulfur coverage (P_{H_2S}/P_{H_2}) is increased too much or a bulk nickel sulfide phase is formed, the conversion of toluene is decreased (Fig. 8).

4. Conclusions

Sulfur chemisorption on supported nickel catalysts was studied in hot gas cleaning conditions of gasification gas, i.e. at higher temperatures (1073–1223 K) and at higher P_{H_2S}/P_{H_2} levels (150×10^{-6} – 3750×10^{-6}) than in previous comparable studies. The conclusions from these studies are as follows:

- Due to the sulfur adsorption on the catalyst, a reconstructing of catalyst surfaces occurred. This reconstructing of surfaces took several hours depending on the material and structural properties of catalysts, temperature and H_2S concentration in the gas. Temperature and H_2S concentration increase decreased the equilibration period.
- When the catalyst was exposed to a high gas flow rate of low H_2S content, the pressure drop in the catalyst bed increased so that the tests had to be suspended. The reason for this phenomenon was

probably melt formation as a consequence of very high surface diffusion (due to sulfur adsorption) rates of surface species. The phenomenon could be also attributed to the structural properties of the catalysts.

- Heat of sulfur adsorption on nickel decreased with increasing sulfur coverage (or $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratio) consistently with literature data. However, the heat of adsorption decreased below the limit of the formation enthalpy of bulk nickel sulfide. This phenomenon reflected likely the multi-layer or subsurface nature of the sulfur adsorption. At $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ ratios near the bulk sulfide formation limit, S/Ni stoichiometry was consistent with Ni_3S_2 . The properties of the catalysts used, i.e. support, nickel content, metal dispersion and crystal size, affected significantly the sulfur adsorption behavior.
- Earlier behavior of sulfur on ammonia decomposition with nickel in synthetic gasification gas could be explained by the heat of sulfur chemisorption on nickel. Due to the decreased sulfur adsorption energy with increased H_2S concentration, dissociative ammonia adsorption on nickel could probably be facilitated. Therefore a high concentration of H_2S favors ammonia decomposition on nickel.

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