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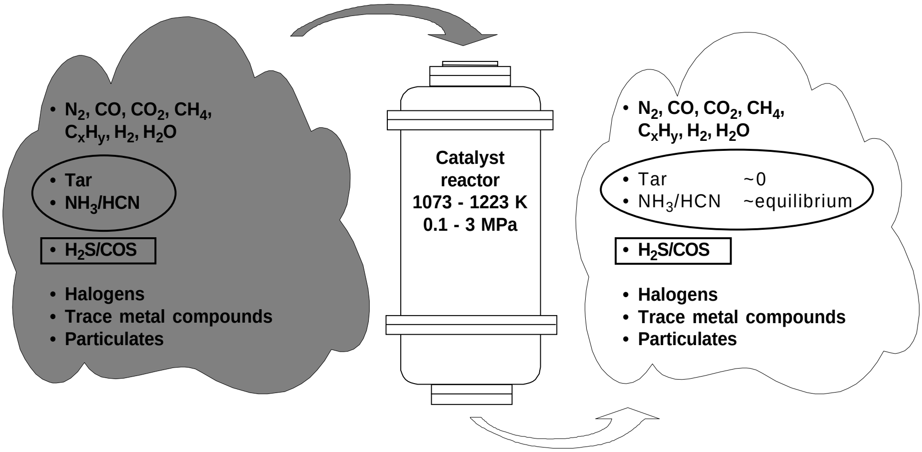
Sulfur transformations in catalytic hot-gas cleaning of gasification gas



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Sulfur transformations in catalytic hot-gas cleaning of gasification gas

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Abstract

The aim of the present work was to obtain new knowledge on the poisoning effects of sulfur on nickel catalysts used for tar and ammonia decomposition in gasification gas. Catalyst performance tests and sulfur poisoning tests were carried out in atmospheric and pressurized fixed-bed tube reactors and in a pressurized honeycomb reactor. The desorption behavior of chemisorbed sulfur from the bed materials was monitored using temperature-programmed hydrogenation. A closed-loop gas-recirculation system was used to measure the isosteric heat of sulfur chemisorption on supported nickel catalysts under hot-gas cleaning conditions.

Under the same conditions, sulfur affected the hydrocarbon (tar, methane)-decomposing activity less than the ammonia decomposing activity. When the temperature was increased or the total pressure decreased, the effect of sulfur poisoning likewise decreased. To prevent sulfur poisoning of nickel catalysts in tar and ammonia decomposition, the catalytic process should operate at temperatures above 1173 K. It turned out that bulk nickel sulfide was active in decomposing ammonia under high-temperature gasification gas-cleaning conditions. The methane decomposing activity of the catalyst, however, was not affected by bulk nickel sulfide formation under pressurized conditions, but that of toluene clearly decreased. The activity of the catalyst in ammonia decomposing already increased before the H_2S concentration in the gas phase reached the bulk nickel sulfide formation limit. This activity change caused by adsorbed sulfur species, therefore, was not related to the phase change only but was explained by the decrease in enthalpy resulting from sulfur chemisorption on nickel. The dissociative adsorption of ammonia is probably facilitated on the nickel surfaces when the binding energy of sulfur on nickel decreases.

Sulfur was adsorbed on nickel catalysts in different chemical states, depending on the process conditions applied. In high-temperature gasification gas

(T>1 173 K) the sulfur adsorbed on the catalyst formed an irreversible monolayer on the catalyst surfaces, while at lower temperatures (T< 1 173 K) the adsorbed sulfur, probably composed of multilayer sulfur, was desorbed from the catalyst in a sulfur-free hydrogen-containing atmosphere. A monolayer of sulfur, however, still remained on the catalyst after desorption. The enhanced effect of high total pressure on sulfur poisoning of nickel catalysts could be accounted for by the increased amount of sulfur adsorbed on the catalyst.

During sulfur adsorption in an H_2S/H_2 atmosphere, reconstruction (sintering) of the catalysts occurred and probably under some conditions, melt formation on the catalyst surfaces. High surface area and high basicity of support materials favored H_2S adsorption on these materials. Under steady-state conditions, the strong sulfur adsorption on a catalyst could be facilitated due to smaller crystallites of nickel.

Preface

The research work was carried out during 1992 - 1998 in the Gasification and Gas Cleaning Group of VTT Energy at the Technical Research Center of Finland (VTT). The sponsors and collaboration partners of this work are gratefully acknowledged: financing for the work has been channeled through projects included in the VTT Research Program CREAM, JOULE-THERMIE Program of the European Commission, and the Finnish National Research Program LIEKKI financed partly by the National Technology Agency of Finland (Tekes). The work was also supported financially by the A. Ahlstrom Corporation, Enviropower Ltd., Fortum Power and Heat (former Imatran Voima), and BASF AG. The sulfur chemisorption measurements in 1997 were performed in collaboration with SRI International, Menlo Park, CA, USA. The financial support from VTT Energy and a grant received from the Imatran Voima Foundation in 1997 helped me essentially to carry out the experimental work in the United States.

I am grateful to my supervisor, Professor Outi Krause for providing the guidance and support I needed to complete this thesis. I would also like to express my gratitude to the management of VTT Energy for their flexibility during the preparation of this thesis and for a positive attitude toward increasing scientific know-how by supporting applied research at VTT.

I wish to thank my colleagues in the research group and the other personnel at VTT who have contributed to this work. Special thanks are due to my co-authors Esa Kurkela, Pekka Simell, Yrjö Solantausta, and Pekka Ståhlberg for successful collaboration. For technical assistance I wish to thank Katja Heiskanen and Tom Gustafsson, who carried out much of the work on fixed-bed reactors. I am also grateful to Maija Korhonen for editing this thesis and my previous papers.

I wish to express my gratitude to the personnel of SRI International for their help during my experimental work, and to my co-authors Jon McCarty and Victor Wong of Catalytica Inc., Mountain View, CA, USA, and Gopala Krishnan of SRI International for their valuable contribution to the sulfur chemisorption part of this thesis.

Finally I wish to thank my wife Helena and our children Mikko, Janne and Aino-Maija for their patience, understanding, and support during my extended research efforts.

Espoo, March 2000

Jouko Hepola

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APPENDICES I - VI

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List of symbols

B	adsorption coefficient, mol S/mol H_2S in particle void, $B = s_\infty 10^{-6} \rho / 32(\varepsilon p_{H2S} /(RT))^{-1}$
C_i	concentration of component i in gas phase, mol/m^3
D_{eff}	effective diffusion coefficient, m^2/s
F_o	molar flow rate of gas, mol/h
ΔH	enthalpy change of adsorption, kJ/mol
k	apparent rate constant of reaction, $m^3/(kg_{cat}\ h)$
k_c	theoretical mass transfer coefficient, m/s
n, m, x, y	numbers in equation 5 and in Figure 2
P_{H_2}	partial pressure of H_2 in the gas phase, bar
P_{H_2S}	partial pressure of H_2S in the gas phase, bar
R	universal gas constant, J/(mol K)
R_{eq}	equivalent particle radius, m
ΔS	entropy change of adsorption, J/(mol K)
SV	space velocity, 1/h
s_t	sulfur uptake after a period of t, wt. ppm
s_∞	sulfur uptake at equilibrium, wt. ppm
T	temperature, K
t	time, s
w_{cat}	weight of catalyst, kg
X_i	fractional conversion of component i

Greek symbols

α	parameter defined by equation 10
β	parameter in equation 7
ε	catalyst porosity
θ	sulfur coverage
ρ	catalyst density, kg/m^3

Abbreviations

BET	specific surface area (Brunauer-Emmett-Teller method)
EDX	energy-dispersive X-ray analysis
ESCA	Electron spectroscopy for chemical analysis
FPD	flame photometric detector
GC	gas chromatography
IGCC	integrated gasification combined cycle process
LEED	low-energy electron diffraction
M	bivalent metal ion (Ca^{2+}, Mg^{2+}or Fe^{2+})
PDU	pilot demonstration unit
PID	photoionization detector
SEM	scanning electron microscopy
SIMS	secondary ion mass spectrometry
TPH	temperature-programmed hydrogenation

List of publications

This thesis is based on the following publications which are referred to by their Roman numerals. The supplementary publications by the author of this thesis are provided in the references Kurkela et al. (1991), Hepola (1993), and Hepola (1996).

I Hepola, J., Simell, P., Kurkela, E. & Ståhlberg, P. 1994. Sulfur poisoning of nickel catalysts in catalytic hot-gas cleaning conditions of biomass gasification. In: Delmon, B. & Froment, G. F. (eds.). Catalyst deactivation 1994. Amsterdam: Elsevier Science Publishers B. V. Pp. 499 - 506.

II Simell, P., Ståhlberg, P., Solantausta, Y., Hepola, J. & Kurkela, E. 1996. Gasification gas cleaning with nickel monolith catalyst. In: Bridgwater, A.V. & Boocock, D. G. B. (eds.). Developments in thermochemical biomass conversion. Vol. 2. Banff, Canada, 20 - 24 May 1996. Glasgow: Blackie Academic & Professional. Pp. 1103 - 1116.

III Simell, P., Hepola, J. & Krause, O. 1997. Effect of gasification gas components on tar and ammonia decomposition over hot gas cleaning catalysts. Fuel, Vol. 76, No. 12, pp. 1117 - 1127.

IV Hepola, J. & Simell, P. 1997. Sulfur poisoning of nickel-based hot gas cleaning catalysts in synthetic gasification gas. I. Effect of different process parameters. Appl. Catal. B, vol. 14, pp. 287 - 303.

V Hepola, J. & Simell, P. 1997. Sulfur poisoning of nickel-based hot gas cleaning catalysts in synthetic gasification gas. II. Chemisorption of hydrogen sulfide. Appl. Catal. B, vol. 14, pp. 305 - 321.

VI Hepola, J., McCarty, J., Krishnan, G. & Wong, V. 1999. Elucidation of behavior of sulfur on nickel-based hot gas cleaning catalysts. Appl. Catal. B, vol. 20, pp. 191 - 203.

Author's contribution

The contributions of the author to the publications used in this thesis are as follows:

He participated in the planning and carrying out of the experiments reported in publications I, II, III, IV, V and VI. He analyzed and interpreted the results of papers I, IV, V and VI. The author also contributed to the evaluation of the results reported in publication III. He wrote papers I, IV, V and VI, and contributed to the writing of publications II and III.

1. Background

1.1 Hot-gas desulfurization of gasification gas

Purification is an essential step prior to utilization of combustible gases from coal and biomass conversion. In this respect the particulate matter and corrosive components must be removed to avoid detrimental effects on materials and environment. For example, a great deal of attention has been focused on sulfur-containing species, of which H_2S is usually the most abundant and the most stable compound. Under reducing conditions, such as those usually applied in moving-bed and fluidized-bed gasification, a substantial portion of the sulfur present in the feedstock is converted to H_2S and only minor amounts of COS are present. The H_2S removal is essential prior to utilization of gasification products either as fuel (using gas turbines or fuel cells) or as synthesis gas. In the former, the use in combined-cycle power generation has been investigated over the past two decades. In an Integrated Gasification Combined Cycle (IGCC) process the system feedstock (coal, peat, biomass, etc.) is gasified at elevated pressures, typically 2 - 3 MPa, to produce a low-volume fuel gas that is desulfurized prior to burning in a combustion turbine to produce electricity. Higher efficiency and lower costs (Gangwal 1996) are achieved using efficient air and steam integration, modular design of the gasification, hot-gas cleanup, and turbine subsystems. The present status of the gas-cleaning route indicates that purification at high temperature (> 623 K, Gangwal 1996) is required to make it economically viable, especially in small-scale power production. On the other hand (Kurkela et al. 1993), processes based on oxygen gasification and cold-gas cleanup are becoming commercially available and offer an environmentally acceptable alternative for coal utilization in large-scale power production.

Continuous efforts have been made to develop purification technology for removing H_2S at high temperatures. This would avoid energy losses associated with cooling the gas prior to purification when employing current cold-gas cleanup technologies. The pioneering work described by Swisher and Schwerdtfeger (1992) provided both the foundation and the stimulation for continuing research and development of hot-gas cleaning from the early 1900s to the present. Research on hot-gas desulfurization methods for fuel gas in IGCC systems has focused on the use of metal oxide sorbents. A number of solid materials have been tested and patented as potential adsorbents for H_2S

removal from hot gas. These solids can be divided into two main groups (Furimsky & Yumura, 1986), i.e. the adsorbents containing alkaline-earth metals and those containing transition metals. Among the former, calcium oxide and naturally occurring materials such as limestone, dolomite, and calcium silicate have attracted a great deal of attention. With these low-cost disposable sorbents the bulk of the sulfur can be removed in the gasifier at 973 - 1 373 K (Goyal et al. 1990, Kurkela et al. 1991). The adsorbents of the second group include iron oxide alone or in combination with some supports such as zinc oxide, zinc ferrite, zinc titanate, and manganese oxide. These materials can be used in a separate polishing reactor - downstream gasifier with sorbent regeneration to reduce the gas-sulfur content to low levels. The materials containing both the alkaline-earth metals and transition metals, e.g., manganese nodules, fly ash, and rejects from the aluminum industry have also been evaluated (Furimsky & Yumura, 1986). The problem with alkali-earth metal sorbents is mainly disposal following sulfidation. Sorbents based on zinc and iron have reached the pilot-to-demonstration scale testing stage, whereas development of sorbents based on other transition metals is in the laboratory stage. This does not imply (Gangwal 1996) that all problems with zinc- and iron-based sorbents have been resolved. A number of problems still exist in design of appropriate sorbents to ensure a high number of utilization-regeneration cycles and the recovery of the absorbed sulfur.

Since the late 1980s, the focus of Finnish gasification R & D has been on the development of simplified IGCC processes based on pressurized fluidized-bed air gasification followed by dry-gas cleaning. This development is mainly concentrated on the utilization of different biomasses. However, since the economical competitiveness of simplified IGCC plants can be achieved only on relatively large scales (30 - 150 MW_e), it may often be difficult to base the power plant on the use of biomass only (Kurkela et al. 1995). IGCC plants, therefore, should be able to use different fuels in separate and in cofeeding modes. In Finland, various wood wastes, domestic peat, and imported coals are the most potential feedstocks of the simplified IGCC power plants. Due to the low sulfur content of biomass, probably no separate sulfur removal unit is needed. In the case of cofeeding mode the bulk sulfur can likely be removed in the gasifier by using calcium-based sorbents to the level needed for emission restrictions. In this respect, the task of hot-gas cleaning may be easier than that of coal gasification by itself. On a smaller scale, biomass-based power can be generated with a combination of a gasifier and an engine. The process can be based on fluidized-bed or updraft gasification at atmospheric pressure followed by a hot-gas cleaning unit and a set of diesel engines for power generation.

1.2 Catalytic hot-gas cleaning

In the most simple case of the simplified IGCC concept, biomass is gasified at a temperature range of 1 073 - 1 273 K and in the pressure range of 2 - 2.5 MPa followed by gas filtration at 673 - 773 K. Gas cooling prior to filtration is required to reduce the concentration of vapor-phase alkali metals before burning the gas in a gas turbine. Almost complete removal of particulates and alkalis is required to protect the gas turbine blades from erosion and corrosion. An optional gas-cleaning step may be needed if the formation of heavy polyaromatic tars cannot be prevented directly in the gasifier. Under some operational conditions (Kurkela 1996) tars may block gas coolers and ceramic filters due to condensing or polymerization into sootlike deposits. In gasification diesel power plant applications, very efficient tar removal is needed because, after gas cooling, the condensed tar aerosols would rapidly block the engine inlet channels and valves. Formation of ammonia and other nitrogen compounds may also be problematic in gasification of nitrogen-containing fuels, since these are potential sources of fuel-bound NO_x emissions when the gas is burned. These problems can be avoided by employing a catalytic gas purification unit for decomposing tars and ammonia. In addition, the gas quality can be improved by using efficient catalysts due to increased concentration of hydrogen and carbon monoxide. Improvement in gas ignition properties and utilization of the gas for synthesis gas production could thus be expected. The operational temperature of this unit should be similar to that of the gasifier outlet temperature, i.e. about 1 173 K (fluidized-bed applications) such that catalyst deactivation especially by H_2S or carbon formation can be avoided. Due to the endothermic reactions, the heat required can be produced by the partial combustion of gas. The catalytic gas-cleaning unit should also tolerate the high particulate content of gasification gas.

Various metal catalysts for tar and ammonia removal in coal and biomass gas have been studied (Hill 1945, Krishnan et al. 1988, Hepola 1993, Simell 1997). Calcium-containing materials and nickel catalysts have been proven to be most effective in tar decomposition. Dolomite and limestones have proved to be effective tar decomposers only in calcined forms (Simell 1997); hence, limestones are best suited for atmospheric processes since under pressurized conditions the partial pressure of CO_2 in a gasifier is too high for calcination (Kurkela et al. 1991). Transition-metal catalysts, especially nickel catalysts, have also been found to have high catalytic activities for ammonia decomposition (Hepola 1993). The product gas from a gasifier, however, is a complex mixture of different gas compounds and impurities that can deactivate catalyst performance (Hepola 1993). Sulfur, halogens, alkalis, and various trace-metal compounds may deactivate the catalyst used during operation. Fouling with carbon, sintering, and poor mechanical strength of catalyst materials or blocking of the catalyst reactor due to particulates can also result in difficulty at least in long-term operation at high temperature and pressure. Probably the most serious poisoning encountered in catalytic systems is that induced by sulfur on metal catalysts. In the following a summary of the behavior of sulfur compounds under catalytic hot-gas cleaning conditions is presented.

1.3 Scope of the work

Under catalytic hot-gas cleaning conditions, understanding of the behavior of sulfur compounds when using the above-mentioned catalytic materials is still insufficient. Few studies have shown the effect of sulfur on catalyst performance under these conditions (Krishnan et al. 1988, Mojtahedi & Abbasian 1995, Mojtahedi et al. 1995, Koningen & Sjöström 1998) compared with the number of studies of hot-gas desulfurization mentioned above. Over time, however, a great deal of fundamental information has accumulated regarding sulfur poisoning and adsorption on metals and metal oxides (reducible and nonreducible oxides) under different conditions of industrial interest (Oudar 1980, Bartholomew et al. 1982, Rostrup-Nielsen 1984a, Bartholomew 1987, Wise 1991). In the chemical industry, steam-reforming of naphtha and methane is carried out with nickel catalysts at temperatures comparable to the catalytic hot-gas cleaning conditions of gasification gas. The sulfur content of the feed gas after desulfurization, however, is much lower under steam-reforming conditions compared with the cleanup of gasification gas, even in the case of biomass gasification. Detailed understanding of poisoning mechanisms (Bartholomew et al. 1982), even in many commercial processes, is lacking due to the complexity of the poisoning problem and the lack of careful fundamental studies. Fundamental understanding of gas-solid and solid-solid interactions in complex systems of mixed oxides in coal gas desulfurization processes is similarly unavailable (Flytzani-Stephanopoulos et al. 1988). The need for studies at the fundamental level is apparent for providing the insights necessary for development of a practical solution to poisoning problems such as regeneration schemes and more sulfur-tolerant catalysts. Consequently, the development of catalytic hot-gas cleaning would benefit from a fundamental understanding of sulfur behavior under these conditions. In addition, the development of desulfurization processes would benefit from more fundamental understanding of the sulfur-adsorption phenomena occurring under catalytic hot-gas cleaning conditions.

The interaction of H_2S and other sulfur compounds with metals and supported metal catalysts may involve a number of consecutive steps (Bartholomew 1982a, Wise et al. 1985), including reversible molecular adsorption of the sulfur compounds, its dissociation, reorientation or reconstruction of the metal surface, formation of surface sulfides, multilayer or subsurface sulfur formation, and at even higher H_2S/H_2 ratios, formation of (bulk) metal sulfide. In addition, surface diffusion studies (Rhead 1975) have indicated that the surface phase may even melt due to increased surface diffusion induced by adsorbed sulfur.

The aim of this work was to study the effect of sulfur on different catalytic materials which could be used to decompose tar and ammonia under industrial conditions. The main focus in this work was, however, on supported nickel catalyst performance with sulfur due to its catalytic efficiency and widespread practical interest as a catalytic material. Long-term catalyst performance tests and sulfur poisoning tests were carried out, in which the effect of operational parameters on sulfur poisoning of nickel catalysts was studied. Research into the effect of gasification gas components on sulfur poisoning of nickel catalysts and the reversibility of catalytic activity was also performed. Fundamental understanding of sulfur adsorption was obtained by analyzing spent catalysts from sulfur poisoning experiments and by performing sulfur chemisorption studies with different nickel catalysts under well-defined conditions in a hydrogen/hydrogen sulfide atmosphere.

2. Sulfur transformations in gasification

Sulfur is known to be one of the major impurities in coal. The total sulfur in coal varies in the range of 0.2 - 11 wt%, although the range for the world's economically recoverable coal reserves is narrower, about 0.5 - 5 wt% (Attar 1978, Morrison 1981). Most of the sulfur is in the form of FeS_2. The amount of organic sulfur is usually one half to one third of the total sulfur present, depending on the quality of the coal. The amount of sulfate sulfur rarely exceeds 0.1 wt% and is usually negligible (Attar 1978). All the organic sulfur is believed (Attar 1978) to be bivalent (most important sulfur groups: thiophenes, aryl sulfides, cyclic sulfides, aliphatic sulfides, aryl and aliphatic thiols) and is distributed throughout the organic matrix. The sulfate sulfur appears mainly in the form of calcium and iron sulfates. The amount of sulfur in peat ranges from 0.05 to 1 wt%; however, it is usually quite low, only about 0.15 wt% (KTM 1983). In wood, sulfur is included in the main nutrient and its content is low, in the range of 0.015 - 0.03 wt% (Keitaanniemi 1979).

According to the review of Attar (1978), most of the sulfur volatilized from coal in reducing (H_2) atmospheres (Figure 1) is released below about 1 073 K, because FeS_2 is reduced almost completely to FeS and H_2S below 1 073 K. The sulfur that is volatilized above 1073 K is released at a rate proportional to that of volatilization of the organic matter. Most of this sulfur is in the form of H_2S and CS_2; only a small fraction of sulfur is released in the form of organosulfur compounds (other than CS_2). At high temperatures H_2S and CS_2 are the only stable species that can remain unchanged during the secondary reactions in the gas.

The main sulfur compound evolved during gasification of different feedstocks is H_2S, with small portions of COS and very small amounts of CS_2 and mercaptans (MERC/SP 1978, Kurkela et al. 1991); therefore, H_2S and COS are the only gases of concern. It has been observed (MERC/SP 1978, Purdy et al. 1984, Kurkela et al. 1991) that at gasifier outlet temperatures H_2S and COS can be estimated to be in equilibrium with each other according to the reactions:

$$COS + H_2 = H_2S + CO \qquad (1)$$

$$COS + H_2O = H_2S + CO_2 \qquad (2)$$

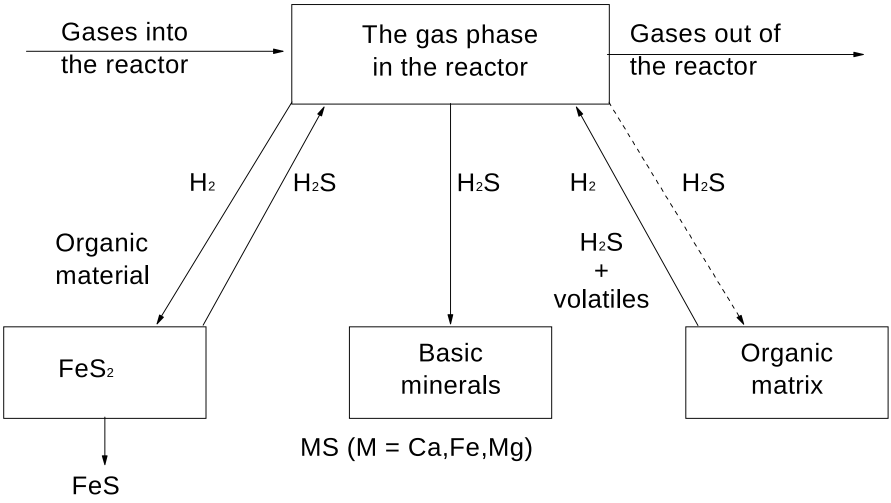

Figure 1. Schematics of the dominant reaction modes of sulfur in coal in reducing environment (Attar 1978).

The interaction of sulfur with the mineral matter of the fuel (coal) during pyrolysis and gasification can be complicated, as reviewed by Attar (1978). The reactions of the basic minerals with H_2S are one of the major reasons for the retention of sulfur in char. The important reactions between H_2S and the basic minerals in reducing environment are of the forms (Attar 1978):

$$MO + H_2S = MS + H_2O \tag{3}$$

$$MCO_3 + H_2S = MS + H_2O + CO_2 \tag{4}$$

M denotes a bivalent metal ion such as Ca^{2+}, Mg^{2+} or Fe^{2+}. These reactions belong to the class of gas-solid reactions in which the solid is consumed and solid and gaseous products are formed. Addition of basic minerals containing materials such as limestones and dolomites into the gasifier are used extensively for sulfur-capture purposes. This type of sulfur removal by calcium-based sorbents was studied by Goyal et al. (1990) and by Kurkela et al. (1991, 1995) in pressurized fluidized-bed gasification. The equilibrium correlations of equations (3) and (4) could quite well be used to evaluate the experimental data obtained.

3. Main reactions and thermodynamics

Under catalytic hot-gas cleaning conditions (Figure 2) the gasification gas mixture after the gasifier contains the main gas compounds N_2, H_2, CO, CO_2, CH_4, C_xH_y, H_2O, and, depending on the fuel used (wood, peat, coal, different types of waste material, mixed or separate), various types of impurities. In addition to nitrogen compounds (NH_3, HCN) and polyaromatic hydrocarbons (tar) the gasification gas contains sulfur compounds (H_2S, COS), particulates (fine dust), trace-metal compounds (Na, K, Fe, As, Zn, Pb, Hg, etc.) and halogens (Cl, etc.). These impurities may affect catalyst performance during operation.

Due to the many gas compounds present a number of possible reactions can occur under hot-gas cleaning conditions (III, IV, Simell 1997). Hydrocarbons can be steam-reformed or dry-reformed by CO_2. Dealkylation and hydrocracking reactions can occur. Thermal cracking reactions and carbon formation reactions may also occur. Ammonia can decompose to gaseous hydrogen and nitrogen. Simultaneously, many equilibrium reactions of the main gas components occur. Measurements (Simell et al. 1993, I) have shown that the near-equilibrium composition of gasification gas can be achieved after nickel at

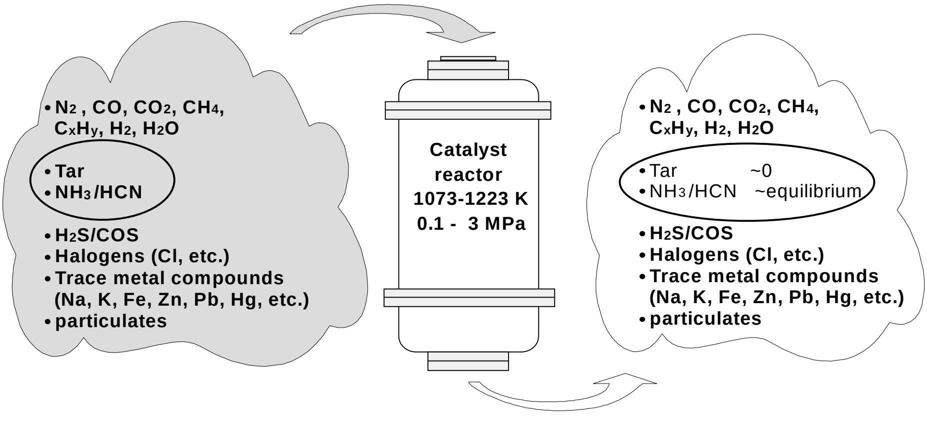

Figure 2. Operational conditions in catalytic hot-gas cleaning.

about 1 173 K under the reaction conditions applied. Under the same conditions with simulated gasification gas (IV) H_2S and COS concentrations were also measured to be in near equilibrium with each other after the catalyst bed. The high temperature and low pressure favor the low equilibrium concentration of ammonia and methane in gasification gas; however, tar decomposition is not restricted by thermodynamics.

According to thermodynamic studies (Hepola 1993, IV), sulfur adsorption and carbon formation on the catalyst may be significant reasons for deactivation of nickel catalysts for tar and ammonia decomposition in gasification gas, depending on the process conditions applied. The high temperature and low pressure favor the nickel sulfide-free and carbon-free operation. The low H_2S concentration in the gas also decreases the possibility of nickel sulfide formation. The formation of elemental sulfur or the allotropes of elemental sulfur S_2 - S_8 appeared to be negligible under the conditions studied (V). Under pressurized conditions, however, the assumption of unity fugacity may not be reasonable especially for sulfur gases. In steam-reforming of methane the amount of carbon can usually be predicted sufficiently from thermodynamic data for reactions of steam-reforming, water-gas shift, methane decomposition and Boudouard (Bartholomew 1982). In steam reforming of higher hydrocarbons, however, carbon formation may occur by the irreversible reaction

$$C_n H_m \rightarrow nC + m/2H_2 \tag{5}$$

even if equilibrium based on the reactions mentioned predicts no such formation. Thus, in practice, experimental data may be necessary to predict carbon formation when hydrocarbons higher than methane are involved and especially when considering gasification gas mixtures. Thermodynamically bulk nickel sulfide formation is predicted to occur in pressurized fluidized-bed gasification gas mixtures when the H_2S concentration in the gas is above about 800 ppmv. In atmospheric fixed-bed updraft gasifier gas the content of hydrogen (Simell 1997) is higher than in fluidized-bed gasifier and therefore the respective H_2S concentration limit for bulk nickel sulfide formation is somewhat higher. Below this concentration, however, the poisoning effect of sulfur in nickel must be interpreted in terms of sulfur adsorption on the surface of the metal, i.e. surface sulfide formation (Bartholomew et al. 1982).

4. Tests performed

Long-term performance tests of nickel catalysts with real product gas were carried out in a steel fixed-bed tube reactor (I) and in a ceramic nickel-based monolith reactor (II). By-pass gas stream was taken from the PDU pressurized fluidized-bed gasifier of VTT and led to the catalyst reactors through heated gas lines. The fixed-bed reactor operated (50 - 190 h, 100 - 800 ppmv H_2S, SV = 1 200 - 1 600 1/h) mainly near atmospheric pressure at about 1 173 - 1 223 K under dust-free conditions. The monolith reactor operated with dusty gas (500 h, 30 - 250 ppmv H_2S, dust 0.6 - 6 g/m^3n , SV = 1 000 - 5 000 1/h) at 0.5 MPa pressure and 1 153 - 1 233 K.

To determine the most important reactions under catalytic hot-gas cleaning conditions during tar and ammonia decomposition, a series of tests were carried out in which the activities of dolomite and nickel catalysts as well as reference materials (SiC and α–Al_2O_3) were measured in different synthetic gas atmospheres (without H_2S) (III). Toluene was used as a tar model compound. Tests were performed in a pressurized (0.5 and 2.0 MPa, different SV values) fixed-bed quartz reactor at 1 173 K. Each test value was the mean of two to eight repeated measurements.

Sulfur poisoning tests (IV,V) with different nickel catalysts and the SiC and Al_2O_3 (α) reference materials were carried out in atmospheric (SV = 750 - 3 500 1/h) and pressurized (0.5 and 2.0 MPa, SV = 3 500 - 30 000 1/h) fixed-bed quartz reactors at 1 073 - 1 223 K, using synthetic gasification gas mixtures with several different H_2S (50 - 2 000 ppmv) levels. Toluene was used as a tar model compound. The effect of different main gas components on catalyst performance and the reversibility of catalytic activity with sulfur was also studied. Each test value was the mean of two to six repeated measurements.

Sulfur desorption from the poisoned nickel catalysts was studied using a temperature-programmed hydrogenation (TPH) technique (V). The reaction gas in the atmospheric TPH tests was an argon/hydrogen mixture (flow rate 77 cm^3_n/min, SV = 7 000 l/h). The catalyst bed was heated from room temperature up to 1 243 K at a rate of 20 K/min. Each test was repeated.

A closed-loop gas-recirculation system was used to measure isosteric heats of sulfur chemisorption on supported nickel catalysts in H_2S/H_2 atmosphere (VI). The sulfur chemisorption was studied under hot-gas cleaning conditions of gasification gas, i.e., at temperatures of 1 073 - 1 223 K and at P_{H_2S}/P_{H_2} levels of 150 - 3750 x 10^{-6} which were comparable to the respective levels used in fixed-bed sulfur poisoning tests with synthetic gasification gas. Least-square analysis of the obtained data was presented (VI).

5. Sampling and analytical methods

Tar sampling was performed by absorbing tar in dichloromethane, which was then analyzed using capillary gas chromatography. The conversion of aromatics was calculated based on the total analyzed hydrocarbon (GC-eluable compounds) content of a tar sample [(toluene in - total aromatic hydrocarbons out)/ (toluene in) x 100 wt%]. Toluene decomposed mainly to gases (H_2, CO, CO_2, CH_4), benzene and carbon (Simell et al. 1995). On-line gas chromatography (GC) was also used for tar (toluene, benzene) and methane analysis in sulfur poisoning tests. Gas composition (CO, CO_2, H_2, CH_4) was analyzed using on-line gas analyzers. Ammonia was determined by absorption in H_2SO_4 solution and titration of the solvent. HCN was determined by absorption in NaOH solution and potentiometric titration (III, IV). Ammonia conversion (mol%) was calculated as toluene conversion based on the ammonia content of a sample. Methane conversion was calculated by using the data measured with an on-line gas analyzer or GC (IV).

The H_2S and COS contents of the gas were measured using different methods: In catalytic performance tests (I,II) and sulfur poisoning tests (IV,V), sulfur was analyzed by collecting the gas into 10 dm^3 Teflon bags. The gas in the bag was analyzed by using GC with a FPD. An on-line mass spectrometer and an industrial photometer were also used for sulfur analysis in sulfur poisoning tests. In the TPH tests (V) the gases leaving the catalyst bed were continuously analyzed by sucking a small fraction of the reactor effluent into a mass spectrometer. The changes in intensity of the sulfur compound (mass numbers: 32, 33, 34, fragment ions: S^+, H_2S^+) peaks were monitored during the desorption tests. In sulfur chemisorption tests the H_2S concentration of the gas was measured using GC with a PID.

The specific surface area (BET) of the catalyst materials was measured using the nitrogen adsorption method (IV - VI). The pore size distributions of the catalysts were measured by mercury intrusion porosimetry (V). The metal surface area of the fresh catalyst was determined using static volumetric hydrogen chemisorption (V,VI). Prior to measurements the samples were reduced in situ in pure hydrogen (flow rate 28 cm^3_n/min, SV = 3 500 l/h, reduction time one hour) by raising the temperature to the level used in the sulfur poisoning or sulfur chemisorption tests. The samples were cooled in helium flow, and the adsorption was performed at 298 - 303 K. For comparison, an atmospheric TPH apparatus was also used for hydrogen chemisorption measurements (V).

Chemical analyses were performed to determine the main elements in the catalysts used (IV, VI), especially the sulfur and carbon contents of catalyst samples (V, VI), X-ray diffraction analyses and SEM/EDX analyses were carried out for some selected poisoned catalysts (V,VI). ESCA and SIMS analyses (V) of a few samples were also performed to determine the binding state of the adsorbed sulfur on the catalyst. A special arrangement of ESCA (V) was used to evaluate if elemental sulfur was present on the poisoned catalyst samples.

6. Catalyst materials

Special nickel catalysts obtained from the catalyst manufacturers for research purposes and commercial nickel catalyst materials were mainly used in the tests. Nickel catalysts with alpha alumina support (impregnated) were used as such or sieved for use in the tests. Ceramic-supported homogeneous catalysts were crushed and sieved prior to the tests. One catalyst for sulfur chemisorption tests (VI) was prepared by impregnating the support $LaAl_{11}O_{18}$ with an aqueous solution of $Ni(NO_3)_2$ using the incipient wetness technique. Al_2O_3 (α), SiC, and $LaAl_{11}O_{18}$ were used as reference materials in the tests (III, IV, V, VI). In addition, one dolomite was used in the tests (III). Table 1 shows the chemical analyses of the catalyst bed materials used and the results from the BET and metal surface area measurements. Ceramic nickel monolith catalysts (Ni/Al_2O_3, square channels) obtained from a catalyst manufacturer were used in the long-term catalyst performance tests (II).

Table 1. Chemical composition of tested catalyst bed materials.

Catalyst/ support	Content, wt%										BET m^2/g	Metal surface area * m^2/g
	Ni	Al	C	Na	Ca	Si	Fe	Zr	Mg	La		
Ni/Al_2O_3 (α)(1)	13.3	57		0.14		<0.11	0.04				5.9	1.6
Ni/Al_2O_3 (α)(2)	11.2	53		0.1		<0.1	0.05				5.1	0.56
Ni/Al_2O_3 (α)(3)	1.48	54.7		0.16							6.6	0.54
$Ni/Al_2O_3/ZrO_2$	23.1	22.9						18.6			52.6	5.7
$Ni/Al_2O_3/CaO$	22.7	29	<0.1	0.11	7.5	0.18	0.07				20.6	
$Ni/LaAl_{11}O_{18}$	7.4	34.6								14.3	40.1	3.7
Al_2O_3 (α)	<0.2	>25			<0.2	<0.7	<0.2				5.2	
SiC		<1	2.4			>50	<0.1					
$LaAl_{11}O_{18}$ **											36.5	
Dolomite	<0.4	0.6			19	2.5	1.5		11		8.1	

* Based on total H_2 uptake at 303 K and the assumption of H/Ni = 1 and 6.5×10^{-2} nm^2/Ni atom. ** Synthesis conditions, etc. in Lowe et al. 1995.

7. Long-term catalyst performance and sulfur poisoning tests

7.1 Comparison of test facilities

To determine if the experiments were performed within the mass-transfer limiting regime, experimental first-order rate constants for hydrocarbons and ammonia decomposition for Ni/Al_2O_3 (α)(1) catalyst pellets were calculated according to the following equation derived from an integral plug-flow reactor model (III):

$$k = F_o / (C_i \cdot w_{cat}) \ln\left[1 / (1 - X_i)\right] \tag{6}$$

Experimental data from the sulfur-free atmospheric fixed-bed synthetic gasification gas tests (Simell et al., unpublished data) were used in the calculations. Benzene (tar) and ammonia conversions ranged from 5 to 50% in these tests. Experimental rate constants were calculated to be 1.5×10^4 and 1.4×10^4 $m^3/kg_{cat}h$ for benzene and ammonia respectively at 1 173 K. The experimental rate constants based on external surface area (m/s) were compared with calculated mass-transfer coefficients k_c (m/s), based on the correlations presented by Froment and Bischoff (1990). Since the experimental rate constants were comparable to or larger than the theoretical mass-transfer coefficients, it is evident that the fixed-bed experiments were carried out in mass-transfer-influenced regime with respect to hydrocarbons and ammonia decomposition. Since diffusivity and hence the mass-transfer coefficient are inversely dependent on pressure, the completely mass-transfer-limited conditions predominated, especially under pressurized test conditions. On the other hand, the effect of pressure probably decreases somewhat the rate constant values of tar and ammonia due to increased partial pressure of hydrogen (Rostrup-Nielsen 1984a, Krishnan et al. 1988). Comparable experimental rate constants for the monolith were not available; however, the calculated theoretical values of mass-transfer coefficients k_c (m/s) according to Uberoi and Pereira (1996) were significantly higher for the monolith than for pellets under all conditions. In addition, the superior activity of the monolithic catalyst relative to pellets can also be expected, because the pore diffusion resistances for the monolith are known to be much smaller than in pellet catalysts

(Villermaux & Schweich 1994, Cybulski & Moulijn 1994) due to the shorter diffusion path in the thin nickel/alumina coating within each channel. In the case of the monolith, however, the poorer heat transfer to the catalyst surface than in the fixed bed can reduce the monolith surface temperature more than in the fixed bed under otherwise comparable conditions (Cybulski & Moulijn 1994, II).

7.2 Sulfur poisoning

In sulfur poisoning tests, the H_2S poisoning phenomenon apparently proceeded rather quickly, depending on the H_2S level in the gas and the catalyst particle size (from a few minutes to some dozens of minutes). After the detected poisoning, an equilibrium sulfur level (steady state) was probably formed on the catalyst particles. At high sulfur levels, however, especially when bulk nickel sulfide was formed, it required a somewhat longer time until the poisoning effect was stabilized. This phenomenon could be partly due to reconstruction of the catalyst surface resulting from the sulfur adsorption discussed in VI or bulk sulfide formation.

The experimental results from pressurized fixed-bed tests indicated that diffusion restrictions of hydrogen sulfide into the particles did not influence the establishment of the chemisorption equilibrium state within the applied run lengths. This could be illustrated by means of a modified version of the equation for diffusion-controlled elution from a catalyst pellet derived by Gorring & DeRosset (1964) and used by Rostrup-Nielsen (1974) (V):

$$\begin{aligned} s_t / s_\infty &= 1 - (6/\pi^2)\sum_{n=1}^{\infty}(1/n^2)\left[\exp((-n^2 D_{eff}\pi^2 t)\,(\varepsilon\,(B+1)R_{eq}^2)^{-1})\right] \\ &= 1 - (6/\pi^2)\sum_{n=1}^{\infty}(1/n^2)\,e^{-n^2\beta t} \end{aligned} \tag{7}$$

The calculated times (V, equation 7) were similar to the previously-mentioned experimental observations of sulfur poisoning time for the catalysts used in the experiments. The calculated time periods (equation 7) vary in proportion to R_{eq}; hence, diffusion restrictions may be significant for the distribution of sulfur in full-scale reactors. The results also indicate that the increase in sulfur concentration in the feed for a short period of time may be detrimental, since it may result in a significant increase in coverage at the external particle layer. The most practical catalyst reactor for the application of particulate-containing gas, however, is probably a monolith type of reactor. In this type of reactor the pore diffusion resistances are known to be much smaller.

7.3 Sulfur distribution and carbon deposition

When the sulfur and carbon contents of some spent catalysts (1 173 K, 2.0 MPa) from the sulfur poisoning tests were analyzed as a function of bed length after the tests, the content of these components at the inlet part of the bed proved to be higher than in the middle and at the bottom of the bed. Due to the presence of endothermic reactions, i.e., steam-reforming of hydrocarbons and ammonia decomposition, the temperature decreased considerably (max. about 100 K at 2.0 MPa) during the tests at the top of the catalyst bed, and after deactivation increased. Based on thermodynamics, sulfur is more probably adsorbed on the catalyst at low temperatures. In addition, rapid adsorption of sulfur in nickel catalyst beds begins at the front of the bed to saturation; the saturated portion of the bed expands through the bed. Carbon deposition would similarly be initially higher at the entrance to the bed, where most of the reaction is occurring. These phenomena explain the higher sulfur and carbon contents at the inlet of the bed compared with those of the other parts of the bed. On the other hand, when the content of sulfur in the gas was sufficiently high (1 000 - 2 000 ppmv) for bulk nickel sulfide (Ni_3S_2) formation (ascertained by X-ray diffraction analysis), the distribution of sulfur in the catalyst bed was fairly even and also within catalyst particles (V). According to ESCA and SIMS analyses the sulfur on the catalyst was, on the basis of binding energies (161 - 162 eV), in the form of sulfides. No elemental sulfur was detected by special ESCA measurements when the analyzed sample was cooled to liquid nitrogen temperature before analysis, to avoid easily volatile sulfur to escape from the sample.

The interaction of adsorbed sulfur and carbon formation could have influenced the carbon content, as during the tests it was also clearly discovered that a small concentration of H_2S (below 100 ppm) in the gas enhanced carbon formation on the catalyst surface compared with higher H_2S concentrations in the gas. This observation is consistent with studies presented in the literature. Masuda et al. (1991) found that during steam-reforming of naphtha over nickel the carbon deposition was significantly increased when very small amounts of hydrogen sulfide were added to the feed. According to Owens et al. (1994) the observed enhancement in carbon filament growth following pre-treatment of nickel at low levels of H_2S (4 - 50 ppm) was related to reconstruction of the metal surface. Sulfur at low concentrations, as in the present case, is adsorbed on the surface. Accordingly, it could affect carbon species formed at the catalyst surface.

8. Catalyst performance with sulfur

8.1 Tests with real gasification gas

Long-term fixed-bed tests in a real product gas stream under atmospheric pressure and under dust-free conditions with nickel catalysts indicated no decline in tar or ammonia decomposing activity in the conditions applied. A clear decline in methane conversion, however, was detected during the operation, most probably due to sulfur adsorption on the nickel surface. Analyses clearly indicated the presence of sulfur adsorption on the catalyst. A slight carbon deposition on the catalyst was also observed, but its effect was negligible (I).

Space velocities lower than 2 500 1/h were required for high tar and ammonia conversion in pressurized long-term monolith reactor tests with particulate-containing gasification gas. The increase in space velocity decreased tar and ammonia conversions linearly. In addition, temperature decrease (between 1 153 and 1 233 K) decreased the ammonia conversion. The overall changes in operational conditions more affected ammonia conversion than tar conversion in the condition range applied. After the long-term tests, the monolith appeared quite intact, and no blocking due to particulates or excess carbon deposition in the channels was observed (II). Small amounts of sulfur, carbon, and some other impurities were analyzed on the surface of the monolith used.

8.2 Tests with synthetic gas mixtures

8.2.1 Effect of temperature, pressure, and space velocity

Temperature greatly influences the poisoning effect of H_2S in toluene, methane and ammonia decomposition in synthetic gasification gas with nickel catalysts at 1 073 - 1 223 K under 2.0 MPa pressure. At 1 073 K the decline in ammonia, methane and toluene conversion was considerable even at low sulfur levels, irrespective of the nickel catalysts used (IV,V). Similar trends with ammonia and methane were also observed in atmospheric tests at 1 073 K; however, toluene conversion was not affected by sulfur as much as methane and ammonia conversions. This was especially true when the temperature was raised to

1 173 and 1 223 K at 2.0 MPa. At 1 223 K no decline in toluene conversion occurred, even at high (up to 500 ppmv H_2S) sulfur levels. Ammonia and methane conversion levels also increased as the temperature was increased. The differing behavior of toluene, ammonia and methane decomposition with H_2S detected in the gas can probably be attributed to various decomposition mechanisms of the components (III, IV) and to the competition of reactants (V) for active reaction sites on the catalyst surfaces. The effect of temperature on conversion can be illustrated by the fact that the possibility of sulfur adsorption (based on thermodynamics) on the catalyst surfaces is decreased as the temperature is increased (V). Overall, it appears that the nickel-catalytic process should operate at above 1 173 K to prevent sulfur poisoning.

Comparison of the results (ammonia and methane) of the experiments performed at 1 173 K under 0.5 and 2.0 MPa with different nickel catalysts was reported in (IV). In these tests the H_2S concentration and the contact time of gasification gas with the catalyst were kept constant at different pressures. The effect of sulfur poisoning was more significant at high pressure than at low pressure for all of the components studied. For toluene, the effect was not as pronounced, due to high conversion values, as for ammonia and methane. The indicated pressure effect can be explained by the amount and/or mode of sulfur (layered sulfur formation) adsorbed on the surface of the catalyst at higher pressure, and/or surface diffusion phenomena of sulfur species on the catalyst (nickel) surfaces (V,VI). When pressure is increased the surface diffusion or the mobility of sulfur on the catalyst surface may increase (IV).

For all components (toluene, ammonia and methane) the conversion was not significantly affected by space velocities of 7 500 - 30 000 1/h at 2.0 MPa in sulfur-free gasification gas atmospheres. With sulfur the conversions decreased as the space velocity increased (the gas residence time in the catalyst bed decreased). The decline in ammonia conversions at 1 173 K and under 2.0 MPa as a function of H_2S concentration (50 - 500 ppmv) was different compared to toluene and methane conversions. The small amount of H_2S in the gas decreased the activity of the catalyst, while further increase in sulfur concentration of the gas appeared not to have a more detrimental effect. Under the same conditions the decline in conversion for toluene and methane as a function of hydrogen sulfide concentration was relatively linear. In general, the phenomenon can be related as shown earlier (in the case of temperature) to decomposition mechanisms of the compounds. Ammonia decomposition takes place on active nickel sites. Furthermore, the dissociative adsorption of ammonia on catalyst surfaces is proposed to be the rate-controlling step (IV). In the case of hydrocarbons the support also has a significant effect on the catalytic reactions. The hydrocarbons could decompose more rapidly (Chapter 7.1) than ammonia under test conditions, and therefore the sulfur-poisoning effect with respect to ammonia conversion is indicated more clearly. It is obvious that if the space velocity is decreased, i.e. the time for transport phenomena and reactions in the catalyst surfaces increases, the sulfur-poisoning effect could be compensated for under the conditions applied (IV).

8.2.2 Effect of gas atmosphere

It was observed that when toluene and/or methane was removed from the synthetic gasification gas, the conversion of ammonia increased in H_2S-containing atmospheres. The results indicated that all the gas components studied (hydrocarbons and ammonia) most probably utilize at least some of the same active nickel sites on the catalyst surface. When increasing the content of water, carbon dioxide, or hydrogen in synthetic gasification gas, it was noted that the expected inhibition effect of H_2 was quite clear in ammonia conversion. A slight decrease in ammonia conversion with increasing water content was also observed, probably due to the effect of water vapor reported by Friedlander et al. (1977), suggesting that water vapor in reducing gas interferes with formation of the reduced state of the metal surface required for high activity. The increase in CO_2 had no substantial effect on ammonia conversion. Toluene and methane decompositions were also affected, especially by the increase in water vapor. As expected, due to enhancement of reforming reactions, the conversions of toluene and methane were higher in sulfur-containing atmospheres when the water content of the gas was increased. When ammonia was removed from the gasification gas mixture, the conversions of toluene and methane were not substantially changed (V).

It can be concluded (V, Figure 3) that bulk nickel sulfide ($P_{H_2S}/P_{H_2} \approx 4\,000 \times 10^{-6}$) is, in addition to metallic nickel, active in decomposing ammonia under high-temperature gasification gas cleaning conditions. Moreover, the activity of the catalyst was starting to increase with respect to ammonia decomposition even before bulk nickel sulfide formation, indicating that the change in activity caused by adsorbed sulfur species was not sharp. The observation is consistent with the results of Beavon et al. (1974) and Ayala (1993), according to which metal sulfides (iron, nickel, cobalt, molybdenum, vanadium, thorium) are active in decomposing ammonia compounds in high-temperature gas mixtures. In addition, according to Zeuthen et al. (1991) and Jobic et al. (1995) the dissociative adsorption of ammonia can also occur on sulfide catalysts, and the reaction with ammonia results in replacement of some catalytic sulfur. Figure 3 shows the heat of adsorption of sulfur on nickel presented in VI. The conversion of ammonia correlates well with the values obtained for enthalpy change in adsorption (ΔH). The conversion of ammonia is increased prior to bulk sulfide formation due to the decreased binding energy of sulfur on nickel. The dissociative adsorption of ammonia is probably 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 to levels near those for bulk sulfide formation, the sulfur adsorption energy approaches the formation energy of bulk nickel sulfide, which is also capable of decomposing ammonia, as was stated above.

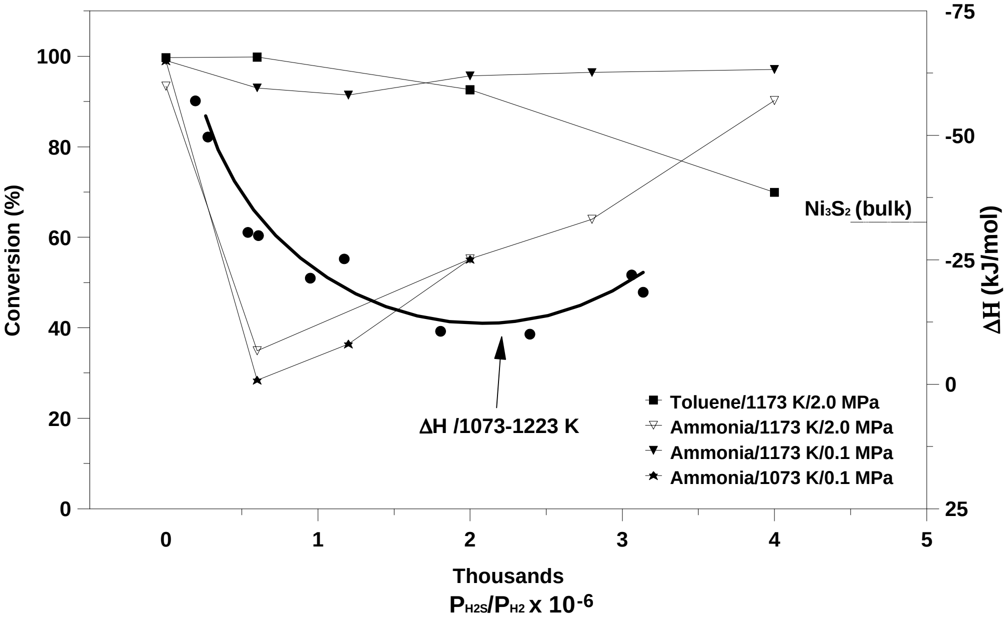

Figure 3. Effect of sulfur on the conversion of ammonia and toluene with catalyst Ni/Al_2O_3 (α) (1) in synthetic gasification gas. H_2 estimated to be 25 % in synthetic gasification gas. ΔH values obtained in P_{H_2S}/P_{H_2} atmosphere (VI).

A phenomenon of interest in the case of methane was that the conversion at 2.0 MPa was insensitive to bulk nickel sulfide formation on the catalyst (V). Rostrup-Nielsen (1984b) and Rostrup-Nielsen & Alstrup (1987) suggested that the ensembles of free nickel atoms available at high coverages of sulfur are sufficient for the conversion of adsorbed methane with steam or carbon dioxide. On the basis of the results given in (V) these active sites appeared to be sufficient for methane decomposition even after the bulk nickel sulfide formation. Furthermore, under the same conditions when the H_2S content of the gas was low (< 500 ppmv) the conversion of toluene was fairly insensitive to the presence of sulfur. The reasons for this could be the suggestions presented by Ng & Martin (1978) that hydrogen from adsorbed H_2S probably interacts with the unsaturated (C_2H_2, C_6H_6) hydrocarbons to give a hydrogenated adspecies. The decrease in toluene conversion when the sulfur content of the gas was high (> 500 ppmv) can be explained by the large molecular size of toluene/benzene compared with that of methane. Tar decomposition could, therefore, need a larger number of active nickel sites than methane. During increased sulfur adsorption and finally bulk nickel sulfide formation not enough active nickel sites were available for this reaction (V).

8.2.3 Effect of catalyst composition

Ammonia conversion was affected by the catalyst type (IV). The catalyst $Ni/Al_2O_3/CaO$ was more active in the sulfur-containing atmosphere than catalyst Ni/Al_2O_3 (α) (1). This was probably due to the higher specific surface area of catalyst $Ni/Al_2O_3/CaO$ and its higher capability of adsorbing sulfur resulting from higher basicity of support (VI). The support can adsorb sulfur preferentially and therefore decrease (delay) the sulfur adsorption on nickel and loss of activity. The higher nickel content and varying dispersion of catalyst $Ni/Al_2O_3/CaO$ compared with catalyst Ni/Al_2O_3 (α) (1) (IV) could also have some effect on the results. Catalyst Ni/Al_2O_3 (α) (3) (nickel content about 1.5 wt%), however, was as active as catalyst Ni/Al_2O_3 (α) (1) (nickel content about 11 wt%) in ammonia decomposition with and without sulfur in the gas. This indicates that only a small amount of nickel in the catalyst is needed for ammonia decomposition under the conditions applied, although only about three times the values for total H_2 adsorption were measured for catalyst Ni/Al_2O_3 (α) (1) compared with catalyst Ni/Al_2O_3 (α) (3). On the other hand, toluene and methane conversions with catalyst Ni/Al_2O_3 (α) (3) were clearly lower (IV) especially in sulfur-containing atmospheres than the respective conversions with catalysts Ni/Al_2O_3 (α) (1) and $Ni/Al_2O_3/CaO$. However, on the basis of these results, definite conclusions cannot be made regarding the influence of metal content and dispersion on catalytic performance.

The results obtained using reference bed materials SiC and Al_2O_3 (α) under the same test conditions as the nickel catalysts (with and without H_2S in the gas) (IV) indicated that Al_2O_3 appeared to be a slightly more active material than SiC and that sulfur had some negative effect on the conversions. Conversion values for toluene and ammonia ranged from 0 to 40%; however, methane was not decomposed with the reference materials. According to study III the most abundant reaction of toluene occurring in the gasification gas mixture without sulfur, either in an empty tube or with SiC and alumina, was hydrocracking. Ammonia reacted readily with CO_2 even in an empty reactor tube or with the reference materials SiC and Al_2O_3. The reaction rates with Al_2O_3 were higher than with SiC, which meant that the Al_2O_3 surface was active and enhanced reactions with ammonia. The presence of steam and toluene, however, clearly decreased the ammonia reaction rate with SiC and Al_2O_3. The decomposition rate of ammonia was as low in the gasification gas as in the N_2+ H_2+H_2O gas mixture.

8.2.4 Sulfur desorption from poisoned catalysts with H_2

At 1 173 K the catalytic activity recovered rapidly when H_2S was removed from the gas in fixed-bed experiments, especially with respect to methane and toluene; however at 1 073 K the rate of regeneration was lower compared with that at 1 173 K. The catalyst could also be regenerated by increasing temperature; however, the conversion of ammonia did not attain as high a level as that before sulfur addition. This phenomenon could be explained by the fact that the adsorbed sulfur was probably not totally removed from the catalyst by increasing temperature or even by removing the H_2S from the gas. Literature references concerning steam-reforming of hydrocarbons on nickel catalysts (Morita & Inoue 1965, Rostrup-Nielsen 1984a) also indicate that the reversibility of sulfur poisoning can be indicated by high-temperature laboratory-scale experiments. On the industrial scale, however, the methods applied normally result in slow regeneration, because the rate of diffusion-controlled elution decreases exponentially with time (Rostrup-Nielsen 1974) (V).

It can be seen from Figure 4 that the sulfur desorption with H_2 (TPH experiments) from the catalyst beds that had been poisoned (sulfur poisoning tests) at 1 073 - 1 173 K under 0.1 and 2.0 MPa at 500 ppm begins when the temperature of the bed is above 673 K, the main part being desorbed rapidly between 773 and 973 K. On the other hand, when the H_2S concentration of the bed had been sufficiently high (H_2S = 2000 ppm) for bulk nickel sulfide formation, the desorption of sulfur in the atmospheric tests occurred at the same temperature, at which the catalyst had been treated in the fixed-bed poisoning tests. In the 2.0-MPa tests, however, the desorption of sulfur began at about 923 K. This temperature is lower than the bulk nickel sulfide formation temperature (about 1 173 K) but higher than the desorption temperature of the adsorbed (multilayer) sulfur species mentioned above. Some adsorbed sulfur, therefore, in addition to bulk nickel sulfide, may have been present on the catalyst. Figure 4 also shows that the desorption of highly stable sulfide (bulk sulfide) occurs more slowly than that of moderately stable (multilayer) sulfide (V).

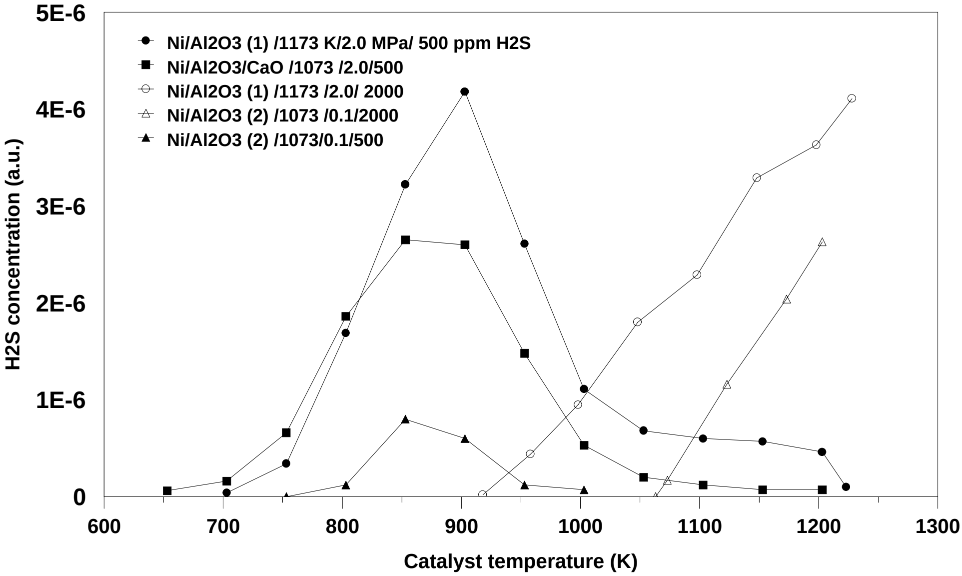

Figure 4. Temperature-programmed hydrogenation of sulfur from poisoned nickel catalysts. Heating rate 20 K/min, gas atmosphere Ar/H_2 (V).

In atmospheric sulfur poisoning tests at 1 173 K, when as much as 500 ppm H_2S had been present in the gas phase, the sulfur was not desorbed from the catalyst Ni/Al_2O_3 (α) (2) in TPH experiments. The same phenomenon was noted in the tests performed at 1 173 K under 0.5 MPa pressure with catalyst Ni/Al_2O_3 (α) (1) and $Ni/Al_2O_3/CaO$. When the sulfur content of these catalysts was analyzed after the TPH experiment, it was observed that a small amount of sulfur (Table 1 of Paper V) existed on the catalyst. Chemisorption uptakes of H_2 at 298 - 303 K for alumina-supported nickel catalysts were measured. The corresponding nickel surface areas were calculated and the sulfur content of the catalyst when in saturation (S/Ni = 0.5) was subsequently determined. The mean values were similar to the amount of sulfur that was not desorbed from the catalyst during the TPH treatment. Hence, it may be concluded that roughly the saturation layer of sulfur remained on the catalyst even after regeneration in a hydrogen atmosphere (V).

Evidence for the formation of multilayer or subsurface sulfides under conditions in which bulk sulfides are not expected has been reported (Ng & Martin 1978, Alstrup et al. 1981, Buckley et al. 1987, Lamy-Pitara et al. 1990, Marécot et al. 1992, Poels et al. 1995); however, the nature of these sulfides is not clear. Buckley et al. (1987) concluded that the multilayer sulfur deposit does not have the properties of bulk elemental sulfur, and this indicates that substantial interaction occurs between the multilayer sulfur and the underlying metal sulfide and substrate metal (V).

In the present studies, the high sulfur content of the catalysts observed at 1 073 - 1 173 K especially under pressurized conditions can most probably be attributed to the formation of a multilayer or subsulfides on the adsorbed sulfur. These sulfur species were desorbed at > 673 K, which was much lower than the observed (Paragraph 2 in the present Chapter) decomposition temperature of bulk nickel sulfide. These observations are consistent with the sulfur chemisorption studies with the same nickel catalyst in an H_2/H_2S atmosphere described in (VI). However, based on that study, it appears that catalyst properties may have a significant influence on the amount and nature of the adsorbed sulfur (see Chapter 9.2). When the temperature was raised to and above 1 173 K in the sulfur poisoning tests the formation of the multilayer sulfur was likely decreased, and consequently the content of sulfur on the catalyst approached the monolayer coverage. This again resulted in increased catalyst performance. Under pressurized conditions the formation of multilayer sulfur is enhanced, probably due to higher surface diffusion phenomena of sulfur on the catalyst surfaces. Pressure is known to increase the mobility of the adsorbed species on the surface of catalysts (Satterfield 1981, Vedrine 1981). In addition, according to Satterfield (1981), the surface diffusion flux per unit cross-sectional area of a porous catalyst should always decrease with increasing temperature. This is consistent with the observed decrease of multilayer sulfur formation at high temperature mentioned above.

9. Sulfur adsorption

9.1 Sulfur chemisorption tests

Sulfur chemisorption on supported nickel catalysts was studied (VI) under hot-gas cleaning conditions of gasification gas. A strange behavior involving increased pressure drop in the catalyst bed at high flow rates with some catalysts was experienced. In addition, unexpected sulfur desorption from the catalyst during gas recirculation was observed.

The increased pressure drop noted above (VI) could most probably be explained by melting of the surface phase. Since it is known that bulk nickel sulfide forms a liquid sulfide at temperatures above 908 K (Rosenqvist 1954), it can be expected that the Ni-S system is capable of forming a similar type of two-dimensional liquid, as was suggested with the Ag-S system (Rhead 1975).

The increased amount of sulfur adsorption probably increased the self-diffusion rate of nickel on the catalyst surfaces to such a degree that the sticky liquid-like solution formed blocking the catalyst pores and bed voids resulting in an increased pressure drop (VI). Since this type of behavior did not occur with all of the catalysts studied the phenomenon was likely dependent on the catalyst properties, i.e. dispersion, pore structure and nature of support. Surface diffusion is most likely significant under conditions of high surface area and therefore finely pored pellets, as shown by Satterfield (1981).

Desorption of the adsorbed sulfur into the gas phase from the catalysts during gas recirculation may have been mainly due to sintering of the catalyst surface as a consequence of sulfur adsorption. In fact, adsorbed H_2S is known to increase the mobility of surface species and thus enhance metal sintering.

9.2 Adsorption stoichiometries

Sulfur adsorption on nickel catalysts has been studied under different conditions, applying varying types of methods. All studies, however, have been conducted at partial pressures of H_2S and temperatures significantly lower than conditions comparable to the hot-gas cleaning of gasification gas, in which the

P_{H_2S}/P_{H_2} ratios can be as high as 3 x 10^{-4} - 3 x 10^{-3} at 1 073 - 1 223 K. In research relevant to the hot-gas cleaning conditions (VI), the stoichiometry of H_2S adsorption on nickel could be best understood (because of negligible sulfur adsorption on the catalysts support) using the data for Ni/Al_2O_3 (α) (1). It was observed that the values of S/Ni = 0.63 - 0.72, obtained for the highest H_2S concentrations (below the limit of bulk nickel sulfide formation) used in the tests, were similar to the stoichiometry of Ni_3S_2 (S/Ni = 0.67). This adsorption stoichiometry is the same as the stoichiometry of bulk Ni_3S_2. The stoichiometry, however, may not be the same at the lower levels of P_{H_2S}/P_{H_2} also used in that study.

It has been well established that with single metal crystals the sulfur adsorbed on Ni(100) (Alstrup et al. 1981, Bartholomew et al. 1982) forms a p(2x2) structure, at small H_2S doses, in which one sulfur atom is bonded to four nickel atoms, at 0.25 monolayer coverage. As the coverage with high H_2S doses is increased to 0.5 monolayers the arrangement changes to a c(2x2) structure in which each sulfur is now bonded to only two nickel atoms. In both cases the sulfur atoms reside in the high-coordination sites, i.e. the atomic hollows of the surface. It has been determined (Rostrup-Nielsen 1984a) that the sulfur content of the saturation layer (S/Ni = 0.5), which does not vary significantly from face to face, approaches 445 μg S/m^2 Ni. There is only a fair agreement, however, as to the stoichiometry of H_2S adsorbed on polycrystalline and supported nickel (Bartholomew et al. 1982). The saturation stoichiometry is apparently dependent on P_{H_2S} and varies with temperature. Based on different adsorption studies on polycrystalline or supported Ni, the S/Ni values reported have ranged 0.25 - 1.3 (Bartholomew et al. 1982). The near-unity values of S/Ni observed by Oliphant et al. (1978) for supported and unsupported Ni obtained by desorption after saturation at 25 - 30 x 10^{-6} P_{H_2S}/P_{H_2} could be explained best by surface reconstruction leading to new surface phases. The results of Erekson and Bartholomew (1983) showed that the S/Ni ratio increases with increasing P_{H_2S}/P_{H_2} between 0.2 and 30 x 10^{-6}. Moreover, it was suggested in that study that Ni-S surfaces vary from well-defined structures (S/Ni = 0.5) at low H_2S concentrations to reconstructed surfaces of Ni_3S_2 and NiS stoichiometries under intermediate conditions and to multilayer sulfides for high H_2S concentrations.

Adsorption of H_2S on irreducible oxide supports such as Al_2O_3, SiO_2, ZrO_2, etc., at temperatures of 650 - 725 K is typically small in comparison to that of metals when the H_2S concentration has been very low. At lower temperatures (500 - 625 K), however, the amount of H_2S adsorbed on Al_2O_3 has been found to be fairly significant compared with that on the metal (Bartholomew et al. 1982). Since sulfur adsorption on the above-mentioned materials is known to be small compared with that on many metals and metal oxides, no fundamental sulfur adsorption data are available for those materials under the conditions of hot-gas cleaning of gasification gas. Several studies (DeRosset et al. 1962, Deo et al. 1971, Khulbe & Mann 1978) on H_2S adsorption on alumina, however, have been reported especially in connection with Claus reaction studies, in which the conditions are very different from those in hot-gas cleaning. Sulfur adsorption on dolomite (Hepola 1996) and on different support materials above 1 173 K was reported in VI. The results of these studies indicated most plausibly that in addition to the higher surface area of dolomite, Al_2O_3/ZrO_2 and $LaAl_{11}O_{18}$ compared with α-Al_2O_3, the higher basicity of these materials (Waqif et al. 1992) resulted in a significantly higher adsorption of H_2S on these materials than on α-Al_2O_3 support.

9.3 Stability of adsorbed sulfur

The chemisorption isosteres of three nickel catalysts were determined by measuring the gaseous sulfur compound as a function of temperature for several sulfur coverages (VI). The enthalpy and entropy for dissociative H_2S adsorption

$$\mathrm{Ni} + \mathrm{H_2S(g)} = \mathrm{(Ni\text{-}S)(a)} + \mathrm{H_2} \qquad (8)$$

were calculated from the least-squares analysis of the logarithm of sulfur chemical potential versus reciprocal temperature (McCarty & Wise 1980).

$$RT \ln (P_{H_2S}/P_{H_2}) = \Delta H - T\Delta S \qquad (9)$$

The heat of adsorption data calculated from the isosteres (VI) show that the adsorption energy decreases as the sulfur content in the gas phase (or coverage) increases. This is consistent with the data obtained from the literature (McCarty & Wise 1980, Alstrup et al. 1981, Bartholomew et al. 1982). Only with catalyst $Ni/LaAl_{11}O_{18}$ such a decrease of ΔH cannot be observed. No measurements with this catalyst could be made, because of the high amount of desorbed sulfur from the catalyst during the tests (VI). At low sulfur coverages the adsorbed sulfur is strongly bound to the surface of nickel (Figure 5). Bulk Ni_3S_2 has a heat of formation per mol sulfur of –32.6 kJ at 1 148 K. The chemisorbed sulfur was hence, at maximum, from 24 (catalyst Ni/Al_2O_3 (α) (1)) to 54 kJ/mol (catalyst $Ni/Al_2O_3/ZrO_2$) energetically more stabile than the sulfur in bulk Ni_3S_2 (Figure 5). A significant phenomenon, seen especially with catalyst Ni/Al_2O_3 (α) (1), was that the adsorption energy decreased to a lower level than the enthalpy of formation of bulk Ni_3S_2 at 1 073 - 1 223 K. ΔH, however, increased again with a high gas H_2S content, near to the enthalpy value of bulk Ni_3S_2 formation. The adsorption entropies (ΔS) changed (Figure 6) somewhat coincidently with ΔH at levels near the entropy of bulk Ni_3S_2 formation (14.6 J/mol K).

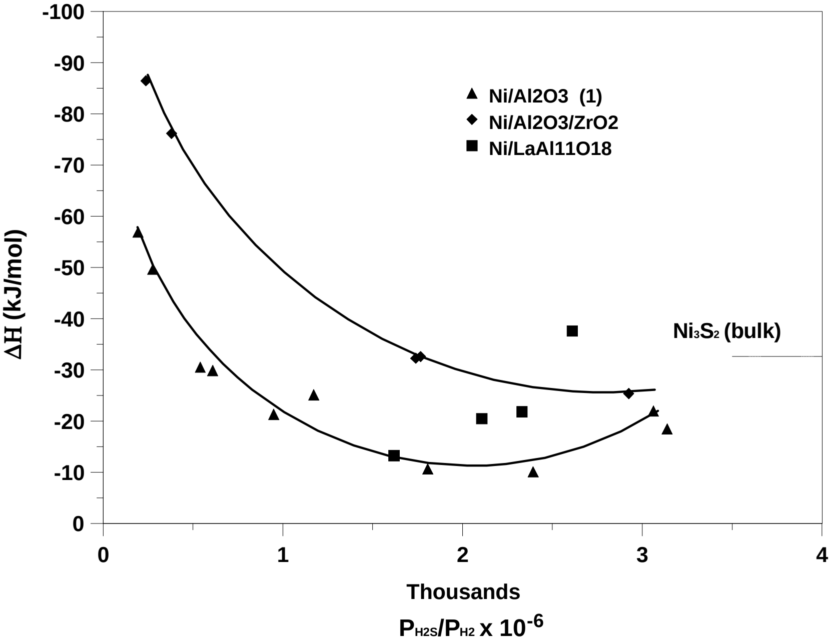

Figure 5. Heat of adsorption of sulfur on nickel catalysts. Temperature 1 073 - 1 223 K (Table 2 of Paper VI).

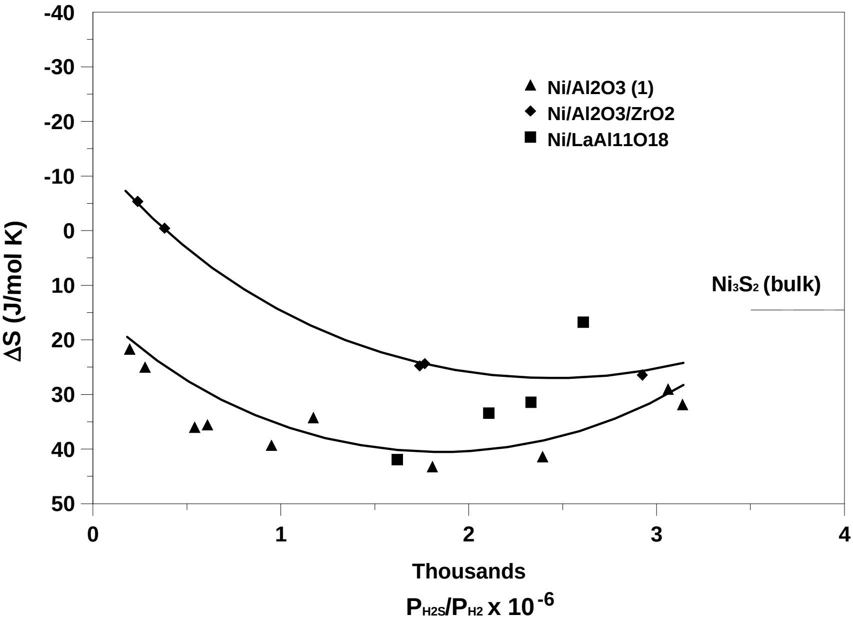

Figure 6. Adsorption entropies of sulfur on nickel catalysts. Temperature 1 073 - 1 223 K (Table 2 of Paper VI).

The decrease in ΔH with increased sulfur coverage can probably be explained by the presence of repulsive interaction between adjacent chemisorbed sulfur atoms. The adsorption energy decrease to values lower than the enthalpy of bulk Ni_3S_2 formation, however, can likely be explained by the multilayer or subsurface sulfur formation on nickel before the bulk sulfide (Ni_3S_2, S/Ni = 0.67, $P_{H_2S}/P_{H_2} \approx 4\ 500 - 7\ 000 \times 10^{-6}$ at 1 073 - 1 223 K) development at higher ratios of P_{H_2S}/P_{H_2}. Although evidence of the formation of multilayer or subsurface sulfides has been reported, the nature of these sulfides is not well-known under different conditions, as was stated previously. It is, however, quite reasonable to expect that when accumulation of multilayers occurs, likely after completion of monolayer, the binding energy of layered sulfur on nickel can then be even smaller than the enthalpy of formation of bulk nickel sulfide. This assumption is supported by the studies of Buckley et al. (1987), who observed with gold in aqueous acid media that the multilayers of sulfur had a smaller electron binding energy than bulk elemental sulfur. Those sulfur species adsorbed on nickel were desorbed at much lower temperatures (Section 8.2.4) than the sulfur from bulk nickel sulfide (V). In these tests (V), however, it was observed, as was discussed previously (Section 8.2.4), that part of the adsorbed sulfur (approximately a monolayer) remained on the catalyst even after regeneration in a hydrogen atmosphere, indicating that the sulfur monolayer is tightly bound on nickel.

By comparing the values of adsorption energies of sulfur with catalyst Ni/Al_2O_3 (α) (1) and $Ni/Al_2O_3/ZrO_2$, it can be seen that the values are much higher with catalyst $Ni/Al_2O_3/ZrO_2$ than with catalyst Ni/Al_2O_3 (α) (1) (Figure 5). The phenomenon can be likely explained by different properties of the catalyst materials. In comparing the supported nickel catalysts with unsupported nickel catalysts, Oliphant et al. (1978) observed that the monolayer 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, probably resulting from catalyst support and extent of reduction effects. Further results (VI) support this finding, i.e., the smaller average crystallite size for $Ni/Al_2O_3/ZrO_2$.

9.4 Experimental data and a Temkin-type adsorption model

Alstrup et al. (1981) showed that their high-temperature (773 - 1 023 K) data for H_2S adsorption on supported nickel, the data of McCarty and Wise (1981) for Ni/Al_2O_3, and the data of Oliphant et al. (1978) for Ni/Al_2O_3 were all well fitted by a Temkin-type expression of the form:

$$P_{H_2S}/P_{H_2} = \exp\left[\Delta H\,(1-\alpha\theta)/(RT) - \Delta S/R\right] \qquad (10)$$

where $\Delta H = -280$ kJ/mol, $\Delta S = -19$ J/molK, and $\alpha = 0.69$. As in the classical Temkin theory, this model predicts a linear decrease in ΔH with increasing coverage, but differs from the classical theory in that the entropy is independent of coverage. The constant entropy suggests the possibility of subsurface sulfur adsorption consistent with observations by Weeks and Plummer (1977) of a subsurface species formed in addition to the c(2x2) layer on Ni(100) surface. According to Alstrup et al. (1981) the p(2x2) structure and not the c(2x2) structure is stable at high temperature and that, if the P_{H_2S}/P_{H_2} ratio is larger than is necessary for the formation of the p(2x2) overlayer, the excess sulfur goes into subsurface sites below the first nickel atom layer. Under these conditions a p(2x2) sulfur overlayer forms the interface between the gas phase and the crystal, probably with properties nearly independent of the sulfur uptake in the subsurface layers.

The Temkin model was tested with data of (VI). The data obtained with catalyst Ni/Al_2O_3 (α) (1) were tested only for reasons given in Chapter 9.2. The model fit the experimental data qualitatively quite well for values of $\theta < 1$ at P_{H_2S}/P_{H_2}: 200 - 500 x 10^{-6} (Figure 7). At higher P_{H_2S}/P_{H_2} ratios the coverage increased, probably due to multilayers of sulfur adsorption above unity, when the model could not be used to predict the experimental data. According to Rostrup-Nielsen (1984a) the above model fits reasonably well with other published data but is not valid for values of near zero and unity. Additional data for detailed description of the sulfur adsorption by a model at high θ values are required.

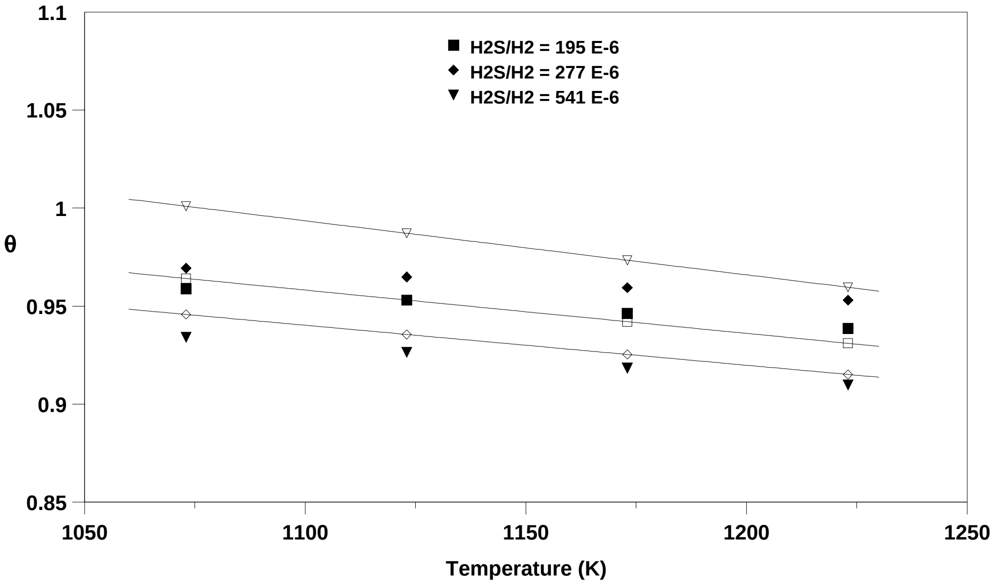

Figure 7. Sulfur chemisorption on nickel. Solid lines/open symbols calculated according to equation 10; solid symbols, experimental points (VI) with Ni/Al_2O_3 *(α) (1).*

10. Conclusions

Both the long-term catalyst performance and sulfur poisoning tests showed that when temperature was increased or total pressure decreased, the effect of sulfur poisoning was decreased. The phenomenon was more pronounced in ammonia decomposition than in hydrocarbon (tar, methane) decomposition. To prevent sulfur poisoning of nickel catalyst performance in the tar and ammonia decomposition at high pressures (2 - 3 MPa), the catalytic process should operate at as high a temperature as possible (above 1 173 K). Moreover, it was found that steam/carbon dioxide reforming of hydrocarbons and ammonia decomposition partly utilize the same active nickel sites and consequently affect the catalyst performance in a sulfur atmosphere. It was established that bulk nickel sulfide was also active in decomposing ammonia under high-temperature gasification gas cleaning conditions. On the other hand, under the pressurized conditions the tar (toluene)-decomposing activity, but not the methane decomposing activity, of the sulfidated catalyst decreased significantly. The catalyst ammonia decomposition activity, however, had already increased in H_2S concentration below those required for bulk nickel sulfide formation, indicating that the activity change caused by the adsorbed sulfur species was not related to a phase change only.

The TPH experiments revealed that sulfur remained in the catalyst in different chemical states, depending on the process conditions applied. At T> 1 173 K the sulfur adsorbed on the catalyst may have formed a monolayer on the catalyst surface; however, this adsorbed sulfur cannot be removed by the hydrogen atmosphere even at a temperature as high as 1 243 K. On the other hand, at T< 1 173 K, especially in pressurized tests, the excess sulfur (probably multilayer sulfur) adsorbed on the catalyst was desorbed from the catalyst in a hydrogen-containing atmosphere. The main part of this sulfur was desorbed quickly at 673 - 973 K; however, a monolayer of sulfur still remained on the catalyst after desorption with H_2. The enhanced effect of high total pressure on sulfur-poisoning of nickel catalysts, therefore, could be accounted for by the increased amount of sulfur adsorbed on the catalyst.

Sulfur chemisorption on supported nickel catalysts was studied under hot-gas cleaning conditions of gasification gas, i.e. at higher temperatures (1 073 - 1 223 K) and at higher P_{H_2S}/P_{H_2} levels (150 - 3 750 x 10^{-6}) than in previous comparable studies. The steady-state heat of sulfur adsorption on nickel decreases with increasing values of sulfur coverage (or P_{H_2S}/P_{H_2} ratio) consistently with the literature data; however, the heat of adsorption decreases below the limit of the formation enthalpy of bulk nickel sulfide. This phenomenon likely reflected the multilayer or subsurface nature of the sulfur adsorption. Due to the decreased sulfur adsorption energy with increased H_2S concentration, dissociative ammonia adsorption on nickel could probably be facilitated. At P_{H_2S}/P_{H_2} ratios near the bulk sulfide formation limit, S/Ni stoichiometry was consistent with Ni_3S_2; however, the properties of the catalysts used, i.e. support, nickel content, metal dispersion, apparently, significantly affected the results obtained. During sulfur adsorption, reconstruction or sintering of the catalysts surface may have occurred and probably, due to high surface diffusion, melt formation on the catalyst surface. In addition, a high surface area and high basicity of support materials favored H_2S adsorption on these materials. At steady-state conditions, the strong sulfur adsorption on a catalyst could be facilitated due to small crystallites of nickel.

New information for sulfur adsorption on supported nickel catalysts under the conditions relevant to catalytic hot-gas cleaning of gasification gas was obtained. This information, together with catalyst activity data, can be used to evaluate catalyst and process requirements for improved resistance to sulfur poisoning in catalytic hot-gas cleaning. In addition, the development of desulfurization processes can benefit from the results; however, a more quantitative investigation of sulfur adsorption on supported nickel catalysts (support/ active metal) together with catalyst activity tests would be worthwhile.

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Title

Sulfur transformations in catalytic hot-gas cleaning of gasification gas

Abstract

The aim of the present work was to obtain new knowledge on the poisoning effects of sulfur on nickel catalysts used for tar and ammonia decomposition in gasification gas. Catalyst performance tests and sulfur poisoning tests were carried out in atmospheric and pressurized fixed-bed tube reactors and in a pressurized honeycomb reactor. The desorption behavior of chemisorbed sulfur from the bed materials was monitored using temperature-programmed hydrogenation. A closed-loop gas-recirculation system was used to measure the isosteric heat of sulfur chemisorption on supported nickel catalysts under hot-gas cleaning conditions.

Under the same conditions, sulfur affected the hydrocarbon (tar, methane)-decomposing activity less than the ammonia decomposing activity. When the temperature was increased or the total pressure decreased, the effect of sulfur poisoning likewise decreased. To prevent sulfur poisoning of nickel catalysts in tar and ammonia decomposition, the catalytic process should operate at temperatures above 1173 K. It turned out that bulk nickel sulfide was active in decomposing ammonia under high-temperature gasification gas-cleaning conditions. The methane decomposing activity of the catalyst, however, was not affected by bulk nickel sulfide formation under pressurized conditions, but that of toluene clearly decreased. The activity of the catalyst in ammonia decomposing already increased before the H_2S concentration in the gas phase reached the bulk nickel sulfide formation limit. This activity change caused by adsorbed sulfur species, therefore, was not related to the phase change only but was explained by the decrease in enthalpy resulting from sulfur chemisorption on nickel. The dissociative adsorption of ammonia is probably facilitated on the nickel surfaces when the binding energy of sulfur on nickel decreases.

Sulfur was adsorbed on nickel catalysts in different chemical states, depending on the process conditions applied. In high-temperature gasification gas ($T > 1\,173$ K) the sulfur adsorbed on the catalyst formed an irreversible monolayer on the catalyst surfaces, while at lower temperatures ($T < 1\,173$ K) the adsorbed sulfur, probably composed of multilayer sulfur, was desorbed from the catalyst in a sulfur-free hydrogen-containing atmosphere. A monolayer of sulfur, however, still remained on the catalyst after desorption. The enhanced effect of high total pressure on sulfur-poisoning of nickel catalysts could be accounted for by the increased amount of sulfur adsorbed on the catalyst.

During sulfur adsorption in an H_2S/H_2 atmosphere, reconstruction (sintering) of the catalysts occurred and probably under some conditions, melt formation on the catalyst surfaces. High surface area and high basicity of support materials favored H_2S adsorption on these materials. Under steady-state conditions, the strong sulfur adsorption on a catalyst could be facilitated due to smaller crystallites of nickel.

Keywords
gasification, hot gas cleanup, catalysts, nickel, catalyst poisoning, sulfur compounds, chemisorption, adsorption, desorption, hydrogenation

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