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Reactions of Sulphur Compounds on Silica-Supported Nickel

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The reaction behavior of 13 sulphur compounds on silica-supported nickel was analyzed by thermodesorption and ir transmission measurements. All sulphur compounds are chemisorbed dissociatively on silica-supported nickel by rupture of S–H, C–S, and S–S bonds. Surface recombination reactions take place in parallel yielding hydrocarbons. The sulfur remaining on the catalyst surface blocks the sites active for the dissociation of carbon monoxide.

1. INTRODUCTION

The activity of nickel catalysts is strongly affected by sulphur (*1, 2*), but as yet there is no detailed knowledge of the mechanism of the poisoning effect of sulphur (*3*). Infrared investigations of chemisorption (*4–10*) and investigations with the aid of thermodesorption (*5, 6, 11, 12*) have yielded valuable hints on the phenomenological reaction behavior of sulphur compounds on nickel films (*8, 9, 12*) and on silica-supported nickel (*4–6, 10*). These investigations have shown that sulphur compounds are chemisorbed dissociatively on nickel surfaces. Chemisorption of carbon monoxide on silica-supported nickel is modified by preadsorption of sulphur compounds (*5, 13*).

Rhodin and Adams (*14*) have reviewed the knowledge on the geometrical structure of adsorbed sulphur on the (100), (110), and (111) planes of nickel gained from numerous LEED investigations by various authors prior to 1975. Accordingly adsorbed sulphur forms $p(2 \times 2)$ ($\theta = \frac{1}{4}$) or $c(2 \times 2)$ ($\theta = \frac{1}{2}$) structures on the (100), (110), and (111) planes depending on the coverage. The sulphur atoms occupy sites of high coordination on the nonreconstructed adsorbent at a spacing of 0.93 (110), 1.3 (100), or 1.4 Å (111) above the underlying nickel layer.

Values pointing to covalently bonded sulphur surface atoms result from the spacing of 1.3 Å and the measured change of work function ($\Delta\Phi = +0.24$ eV) on the (100) plane after formation of the $p(2 \times 2)$ structure ($\theta = \frac{1}{4}$) for the effective radii, the dipole moment (0.16 D), and the charge transfer (0.03 *e*). The occurrence of complex surface structures after adsorption of sulphur on the (111) plane at higher temperatures indicates a higher activity of the (111) plane and the formation of nonstoichiometric compounds of nickel arsenide type.

Fischer (*15*) has summarized the knowledge on the bonding of sulphur obtained by photoemission measurements on solid sulphur and on the $c(2 \times 2)$ and $p(2 \times 2)$ structures formed by sulphur on the (100) plane of nickel, including the results obtained by other authors prior to 1976. According to this, the sulphur atoms arranged on fourfold coordinated sites on the (100) plane are bonded to two nickel surface atoms in the $c(2 \times 2)$ structure ($\theta = \frac{1}{2}$) and to four nickel surface atoms in the $p(2 \times 2)$ structure ($\theta = \frac{1}{4}$).

We have carried out thermodesorption and ir investigations of the reaction behavior between silica-supported nickel and mercaptans, sulphides, disulphides, thiophene, thiophane, and carbon disulphide in order to obtain the chemical composition of the reaction products and structures of chemisorbed surface compounds. The influence of chemisorption of sulphur

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compounds on the state of the surface was analyzed by chemisorption of carbon monoxide.

2. EXPERIMENTAL

The reaction behavior of sulphur compounds on silica-supported nickel was analyzed by thermodesorption and ir transmission measurements. The gaseous desorption products were characterized by means of a mass spectrometer (Varian CH 8) or by a gas chromatograph. The ir investigations were made with a UR 20 spectrometer (VEB Carl Zeiss Jena). Silica-supported nickel (adsorbent) was obtained by impregnating silica (Aerosil 300, Degussa) with nickel nitrate, thermal decomposition and reduction at 1100 K for 1 hr in a stream of purified hydrogen. All specimens contained 20 wt% nickel. As adsorptives were used mercaptans R–S–H (R = H, CH_3, C_3H_7, C_6H_5, C_7H_7), sulphides R–S–R (R = CH_3, C_3H_7, C_3H_5), disulphides R–S–S–R (R = C_4H_9), carbon disulfide, thiophene, and thiophane. All adsorptives were gas chromatographically pure. Carbon monoxide was distilled repeatedly at low temperatures. The adsorptives were added stepwise to the adsorbents. The adsorbed quantities were determined volumetrically by membrane pressure gauges.

3. RESULTS

3.1. CHEMISORPTION OF SULPHUR COMPOUNDS

3.1.1. Thermodesorption Experiments

The results of thermodesorption experiments will be presented by using the chemisorption of *n*-propyl mercaptan as an example. A mass spectrum of the gas phase after the admission of $2.08 \cdot 10^{-6}$ mol *n*-propyl mercaptan to 111.4 mg Ni/SiO_2 at room temperature is shown in Fig. 1a. A comparison with the mass spectrum of pure *n*-propyl mercaptan (Fig. 1b) shows that propyl mercaptan cannot be found in the gas phase. The gas phase mainly consists of propane (compare Fig. 1a with Fig. 1c). In addition to propane, the gas phase contains small amounts of methane ($m/e = 16$) and ethane ($m/e = 30$). After evacuation of the gas phase the propyl mercaptan adsorbates were heated from room temperature to 1100 K (heating rate 40 K/min). The gaseous desorption products formed during heating were continuously analyzed with the aid of the mass spectrometer. The latter records the mass spectra of desorption products (partial pressures) and the total ion current (which is directly proportional to the total pressure of the desorption products) as a function of temperature (thermodesorptogram) (Fig. 2). Two pressure peaks at 400 and 1020 K can be seen in the thermodesorptogram. Mainly propane, propene, and hydrogen desorb between room temperature and 550 K. In addition, small amounts of methane, ethane, and benzene are observed. Carbon monoxide desorbs between 800 and 1100 K. Organic compounds containing sulphur could not be detected. Only a peak of very low intensity at $m/e = 34$ which sometimes occurs is indicative of a very low partial pressure of hydrogen sulphide or sulphur during thermodesorption. (Sulphur is difficult to identify by means of the peak at $m/e = 32$ because oxygen which is contained in the residual gas reveals a relatively intensive line at this value.)

The mass spectroscopic identification of the thermodesorption products was confirmed by gas chromatography. The thermodesorption products were condensed in a microtrap and injected into the gas chromatograph by rapid heating to 500 K. A 3 m column packed with Porapak Q yielded a complete separation of the desorption products under temperature-programmed operation (4 K/min) starting at room temperature.

The chemisorption of the other sulphur compounds was studied in the same manner. A summary of the results is given in Table 1. The main reaction products are in italics in each case. The desorption of pure

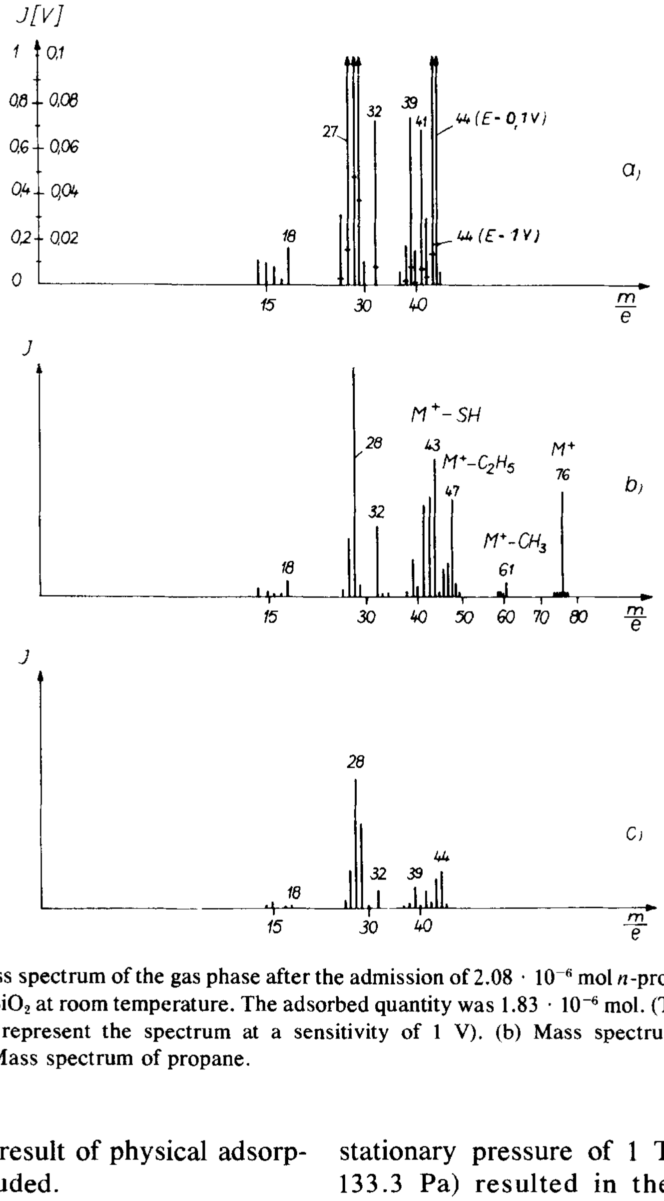

FIG. 1. (a) Mass spectrum of the gas phase after the admission of 2.08 · 10^{-6} mol *n*-propyl mercaptan to 111.4 mg Ni/SiO$_2$ at room temperature. The adsorbed quantity was 1.83 · 10^{-6} mol. (The bars on the individual lines represent the spectrum at a sensitivity of 1 V). (b) Mass spectrum of *n*-propyl mercaptan. (c) Mass spectrum of propane.

adsorptives as a result of physical adsorption was not included.

3.1.2. *Infrared Studies*

Infrared studies were carried out in a special infrared cell on silica-supported nickel pressed into thin disks. Due to absorption of silica only the spectral range >1300 cm^{-1} could be observed.

The chemisorption of hydrogen sulphide could only be detected indirectly. The addition of hydrogen sulphide to a freshly reduced sample at room temperature up to stationary pressure of 1 Torr (1 Torr = 133.3 Pa) resulted in the formation of the S–H stretching vibration at 2600 cm^{-1} of physically adsorbed hydrogen sulphide. After removal of the gas phase, no bands caused by hydrogen sulphide could be detected.

An infrared spectrum after chemisorption of methyl mercaptan on freshly reduced silica-supported nickel is shown in Fig. 3c. For comparison, the infrared spectrum of gaseous methyl mercaptan is shown in Fig. 3a and that of methyl mercaptan adsorbed on silica in Fig. 3b. The bands of

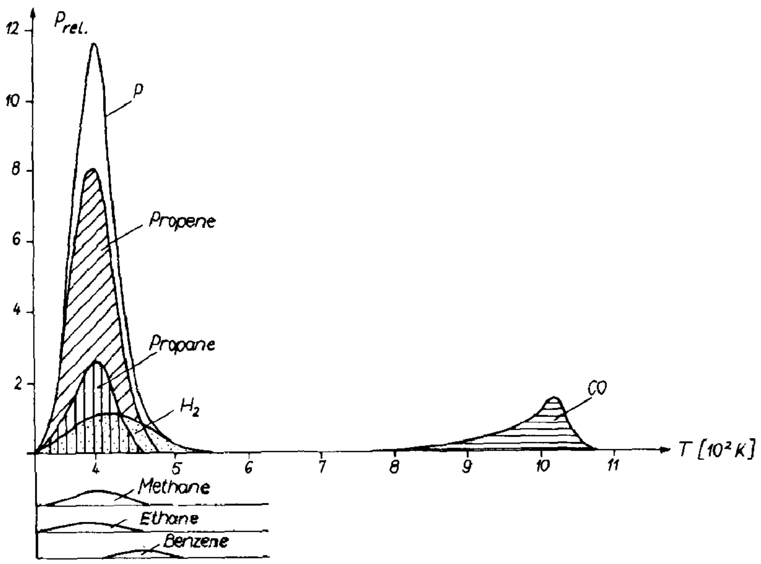

FIG. 2. Thermodesorptogram and partial pressures during desorption after chemisorption of 1.83 10^{-6} mol *n*-propyl mercaptan on 111.4 mg Ni/SiO_2 at room temperature.

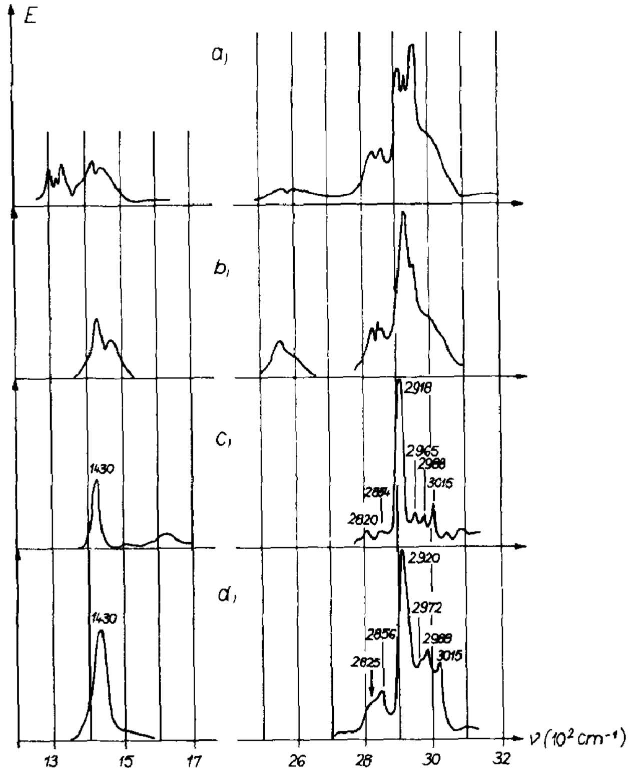

FIG. 3. (a) Infrared absorption spectrum of methyl mercaptan; (b) ir absorption spectrum of methyl mercaptan adsorbed on silica (Aerosil 300); (c) ir absorption spectrum of methyl mercaptan chemisorbed on silica-supported nickel; (d) ir absorption spectrum of dimethylsulphide chemisorbed on silica-supported nickel.

TABLE 1

Composition of the Gas Phase (Column 1) and of the Thermodesorption Products (Column 2) after Admission of Sulphur Compounds to Silica-Supported Nickel at 300 K (Main Products in Italics)

	1	2
Mercaptans (R–S–H)		
R = H	—	H_2
R = CH_3	CH_4	$\mathit{CH_4}$, H_2, CO
R = n-C_3H_7	$\mathit{C_3H_8}$, C_2H_6, CH_4	$\mathit{C_3H_6}$, C_3H_8, H_2, CH_4, C_2H_6, C_6H_6, CO
R = C_6H_5	C_6H_6	$\mathit{C_6H_6}$, C_6H_5–C_6H_5, H_2, CH_4, CO
R = $C_6H_5CH_2$	$C_6H_5CH_3$	$\mathit{C_6H_5CH_3}$, $C_6H_5CH_2$–$C_6H_5CH_2$, C_6H_6, CH_4, CO
Sulphides (R–S–R)		
R = CH_3	CH_4	$\mathit{CH_4}$, H_2, CO
R = n-C_3H_7	$\mathit{C_3H_8}$, C_2H_6, CH_4	$\mathit{C_3H_6}$, C_3H_8, H_2, CH_4, C_2H_6, C_6H_6, CO
R = C_3H_5	$\mathit{C_3H_6}$, C_3H_8, C_2H_6, CH_4	$\mathit{C_3H_6}$, C_3H_8, H_2, CH_4, C_2H_6, C_6H_6, CO
Disulphides (R–S–S–R)		
R = CH_3	CH_3SH, $\mathit{CH_4}$	$\mathit{CH_4}$, $(CH_3)_2S$, CH_3SH, H_2, CO
R = n-C_4H_9	n-C_4H_9SH, $\mathit{C_4H_8}$, C_4H_{10}, C_2H_6, CH_4	$\mathit{C_4H_8}$, n-C_4H_9SH, $(n\text{-}C_4H_9)_2S$, thiophane, H_2, CH_4, C_2H_6, CO
Thiophene	—	$\mathit{C_6H_6}$, C_4H_8, $C_6H_5CH_3$, $C_6H_2C_2H_5$, H_2, CH_4, CO
Thiophane	C_4H_8	$\mathit{C_4H_8}$, C_6H_6, $C_6H_5CH_3$, $C_6H_5C_2H_5$, H_2, CH_4, CO
Carbon disulphide	—	CO

the spectrum shown in Fig. 3b could not be detected after a 30-min evacuation at room temperature. The intensities of the bands of the spectrum shown in Fig. 3c reach constant values after longer evacuation at room temperature, and only the band at 3015 cm^{-1} disappears. The spectrum of $Ni/SiO_2/CH_3SH$ adsorbates (Fig. 3c) contains only C–H stretching and deformation vibrations. The band at 3015 cm^{-1} can be attributed to methane. Assignment of the other bands to surface mercaptide and surface methyl groups can be made by comparison with the infrared spectrum of $Hg(SCH_3)_2$. All bands disappeared after heating the CH_3SH adsorbates to 500 K. The intensity of the band at 3015 cm^{-1} increased simultaneously.

Figure 3d shows a spectrum obtained after adding dimethyl sulphide to freshly reduced silica-supported nickel.

Interaction between thiophene and freshly reduced silica-supported nickel reveals bands at 3100 cm^{-1} (physically adsorbed thiophene) and bands between 2800 and 3000 cm^{-1} (C–H stretching vibrations of aliphatic hydrocarbons). An increase in intensity of the bands between 2800 and 3000 cm^{-1} was observed after adding hydrogen to adsorbed thiophene.

3.2. CHEMISORPTION OF CARBON MONOXIDE AFTER CHEMISORPTION OF SULPHUR COMPOUNDS

3.2.1. Thermodesorption Experiments

Curve 1 in Fig. 4 represents a typical thermodesorptogram obtained after chemisorption of carbon monoxide at room temperature on freshly reduced silica-supported nickel. Two desorption ranges between room temperature and 600 K (α-CO) as well as between 750 and 1100 K (β-CO) can be seen. They are caused by desorption of carbon monoxide. Only a small desorption yield of carbon dioxide can be observed between 450 and 600 K. A decrease in the amount of chemisorbed CO is observed when a sulphur compound has been previously chemisorbed (in the example given in Fig. 4 when $2.37 \cdot 10^{-6}$ mol diallyl sulphide was chemisorbed). Even reduction of silica-supported nickel does not result in chemisorption of the same CO amount as before the interaction of sulphur compound. The thermodesorptogram of CO adsorbates produced on silica-supported nickel poisoned with sulphur compounds revealed distinct variations as compared to unpoisoned samples (curves 2 and 3, Fig. 4). Desorption of α-CO is modified so that the original desorption maximum at 450 K (curve 1) is shifted toward lower temperatures and the shoulder at 520 K gradually disappears. The desorbed amount of β-CO decreases more rapidly than that of chemisorbed CO. At the same time the maximum desorption rate of β-CO shifts toward lower temperatures. After complete coverage of silica-supported nickel with sulphur only desorption of modified α-CO was observed. Merely slight amounts of β-CO (curve 3, Fig. 4) are desorbed after reduction of silica-supported nickel completely covered with sulphur.

3.2.2. Infrared Transmission Studies

Two intense absorption bands between 1700 and 2200 cm^{-1} (Fig. 5a) are observed after chemisorption of CO on unused, freshly reduced silica-supported nickel at room temperature. The extinctions of both bands are proportional to the amount of chemisorbed CO. The band maxima shift slightly toward higher wavenumbers as the CO coverage increases. Another band at 2080 cm^{-1} was observed at CO equilibrium pressures larger than 0.1 Torr. The band

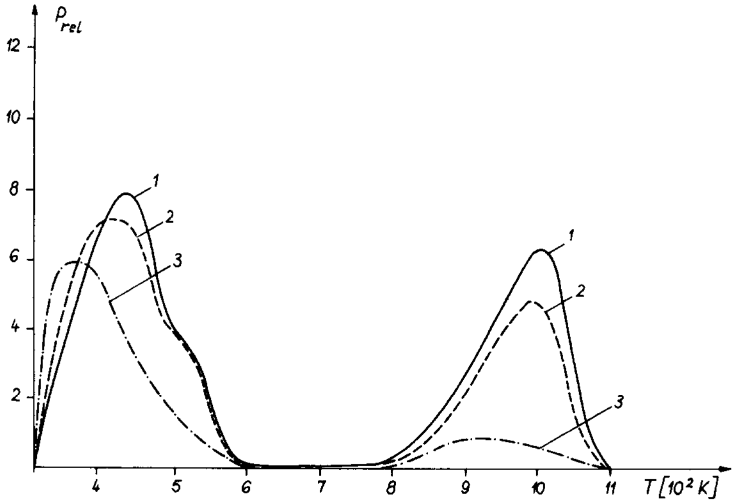

FIG. 4. Thermodesorptogram after (1) chemisorption of $2.38 \cdot 10^{-6}$ mol CO on 111.4 mg Ni/SiO$_2$ at room temperature; (2) chemisorption of $2.32 \cdot 10^{-6}$ mol CO on the same sample after $2.37 \cdot 10^{-6}$ mol diallylsulphide had been previously chemisorbed; (3) chemisorption of $1.49 \cdot 10^{-6}$ mol CO on the sample which was completely poisoned with diallylsulphide after 1-hr reduction.

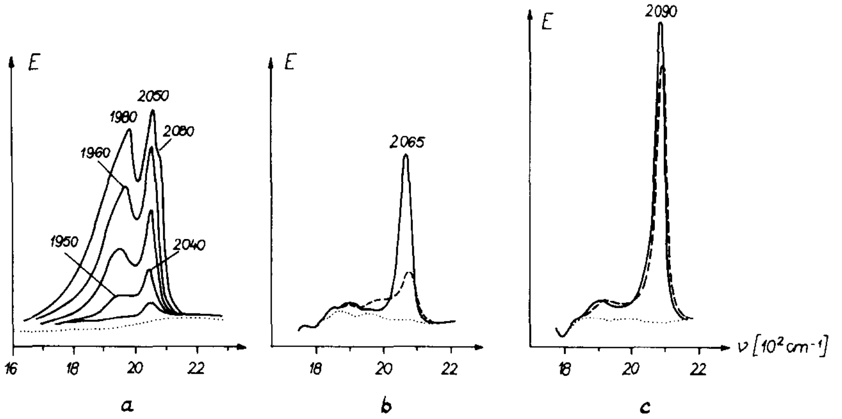

FIG. 5. (a) Infrared absorption spectrum of CO adsorbate on Ni/SiO$_2$. (b) Infrared absorption spectrum of CO adsorbate after the action of methyl mercaptan or dimethylsulphide (solid line) and after evacuation at room temperature (dashed line). (c) Infrared absorption spectrum of CO adsorbate after the action of methyl mercaptan or dimethylsulphide and subsequent reduction (solid line) and after evacuation at room temperature (dashed line). (Dotted lines represent the background of silica-supported nickel.)

intensities decrease at the same rate as the sample temperature increases in the closed cell. The bands can no longer be detected at a sample temperature of 600 K. The bands reappear during cooling to room temperature but with reduced intensity and enhanced background adsorption.

Chemisorption of CO on silica-supported nickel which had been in previous contact with a sulphur compound results in significant variations of the absorption spectrum. In the case of chemisorption of CO on a sample where methyl mercaptan and dimethylsulphide, respectively, were chemisorbed, only an absorption band at 2065 cm^{-1} could be detected (Fig. 5b). The intensity of this band depends on the chemisorbed amount. Repeated treatment with CH_3SH and $(CH_3)_2S$, respectively, made this band disappear. Attempts to regenerate silica-supported nickel by oxidation at 750 K and subsequent reduction failed. Chemisorption of CO on a sample treated in this way did not reveal the typical spectrum of chemisorbed CO (Fig. 5a) but a spectrum with a narrow intense band at 2090 cm^{-1} and a small band at 1900 cm^{-1} (Fig. 5c). Similar variations of the infrared absorption spectrum of chemisorbed CO were detected after preceding chemisorption of H_2S, CS_2, and CH_3SSCH_3 on silica-supported nickel.

4. DISCUSSION

The results of thermodesorption and infrared transmission studies lead to the conclusion that sulphur compounds are chemisorbed dissociatively on silica-supported nickel. Dissociative chemisorption results in rupture of the S–H, C–S, and S–S bonds. This is supported by the disappearance of the S–H stretching vibrations after chemisorption of mercaptans (Fig. 3c) and the appearance of hydrocarbons after chemisorption of mercaptans (Fig. 1a, Table 1, Fig. 3c), sulphides (Table 1, Fig. 3d), and disulphides (Table 1) in the gas phase at room temperature. In the case of chemisorption of disulphides, mercaptans can be detected at room temperature in the gas phase as well as pure hydrocarbons (Table 1). The formation of hydrocarbons as a result of the chemisorption of sulphides and disulphides also requires at least partial dissociation of C–H bonds of the chemisorbed alkyl or allyl residues in addition to dissociation of C–S bonds. Surface recombination reactions between chemisorbed alkyl or allyl residues and atomically chemisorbed hydrogen which lead to formation of gaseous alkanes or olefins already at room temperature, proceed in parallel with the dissociation of C–S, S–S, and C–H bonds. The detection of short-chain alkanes in the chemisorption of mercaptans, sulphides, and disulphides also suggests that the chemisorbed alkyl or alyl residues are partly subjected to secondary surface reactions involving splitting of C–C bonds. The resulting chemisorbed products react with chemisorbed hydrogen to give gaseous methane and ethane. It must be concluded from the relative product concentrations observed at room temperature that the extent of the dissociation reactions decreases rapidly in the order C–S, S–H > S–S, C–H > C–C.

During thermodesorption the dissociation reactions of C–H and C–C bonds are favored at higher temperatures of the adsorbate. Desorption of H_2 takes place. Hydrogen-containing carbon species can be detected up to temperatures of 600 K by means of C–H stretching vibrations. Only carbon and sulphur remain above 600 K. Between 800 and 1100 K carbon is subjected to a reaction with surface oxygen which leads to the desorption of CO. Desorption of CO in this range of temperature is typical of all carbon-containing compounds which can be chemisorbed by silica-supported nickel. The mechanism of CO formation was reported in a previous paper (*16*). In parallel with the decomposition of adsorbates during thermodesorption there are surface reactions among the decomposition products previously chemisorbed which result in the desorption of various hydrocarbons between room temperature and 600 K. The main products of these surface recombination reactions are alkanes, olefins, and aromatics (Table 1). Dimerization of the chemisorbed hydrocarbon residues R ($R = C_6H_5$, $C_6H_5CH_2$) or dimerization with subsequent cyclization ($R = C_3H_7$, C_3H_5) can be observed in some cases. Cyclization reactions without preceding dimerization also occur (from $C_4H_9SSC_4H_9$ to C_4H_8S).

Most of the sulphur remains on the silica-supported nickel, whereas the carbon and hydrogen contained in the substituent R of the sulphur compounds is removed from the sample surface during thermodesorption. The thermodesorption method does not permit direct assertions to be made on the structure and bond state of the sulphur. The comparative study of the chemisorption of carbon monoxide on unused, freshly reduced silica-supported nickel or on samples which were previously subjected to the action of a sulphur compound supplied indirect results.

Preadsorbed sulphur impairs the chemisorption of CO in a complex way. This applies both to the chemisorbed quantity and the formation of various chemisorption states. The thermodesorption studies (Fig. 4) revealed that dissociative chemisorption of CO, perceptible by the reduction of the desorbed amount of β-CO and decreasing CO_2 formation, is repressed with increasing sulphur coverage of silica-supported nickel. The changes simultaneously occurring in the desorption range of molecularly chemisorbed α-CO suggest the formation of a weakly adsorbed CO layer under complete sulphur coverage. The results obtained by infrared spectroscopy (Fig. 5b) are in accord with those obtained by thermodesorption studies. The absorption bands at 1980 and 2050 cm^{-1} which are typical of linearly or bridge-bonded CO can no longer be detected in the case of complete sulphur coverage of silica-supported nickel. The new band at 2065 cm^{-1}, whose intensity can be reduced considerably by evacuation, also suggests the presence of loosely bonded CO. It is assumed that this adsorption state is formed by coordination of CO molecules above a chemisorbed sulphur layer.

The observed variations in CO chemisorption permit an explanation of the poisoning effect of sulphur on nickel catalysts in the methanation of CO. The sulphur remaining on the catalyst surface after dissociative chemisorption of sulphur compounds blocks the sites active for the dissociation of CO. Thus a reaction between chemisorbed carbon and hydrogen cannot proceed. The edge and corner atoms available abundantly on the polycrystalline nickel crystallites should act as active sites for dissociation of CO. These sites have a high adsorption affinity as well as a high activity for the dissociation of chemisorbed molecules.

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