CO hydrogenation over Co/SiO$_2$: catalytic tests and surface analysis of adsorbed hydrocarbons

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We have studied the CO hydrogenation over a Co/SiO$_2$ catalyst under mild reaction conditions (up to 4.4 bar total pressure, $H_2/CO = 2$, $T = 483$ K) and performed a post-reaction analysis of the chemical surface composition by means of secondary ion mass spectrometry (SIMS) and temperature-programmed reaction (TPR) in hydrogen gas. A hydrocarbon chain growth probability $\alpha = 0.78$ was found in the catalytic studies. The SIMS analysis revealed the existence of individually adsorbed C_xH_y species up to C_8H_y, in accordance with end-on bonding to the catalyst surface. These species were removed from the catalyst surface in the subsequent H$_2$-TPR experiment. Significant methane desorption occurred at temperatures ($\geqslant$500 K) well above those of the longer-chain hydrocarbons indicating either an increasing hydrogenolysis activity of Co metal during H$_2$-TPR or the presence of a more tightly bound "carbidic" adsorbate under FT conditions.

Keywords: Co/SiO$_2$ catalysts, Fischer–Tropsch synthesis, Schulz–Flory distribution, H$_2$-temperature-programmed reaction, secondary ion mass spectrometry

1. Introduction

The CO hydrogenation reaction over Co-based catalysts to produce hydrocarbons received considerable interest early on in the development of the low- and high-pressure Fischer–Tropsch process (F–T) [1,2]. The product distribution typically follows the one-parameter Schulz–Flory distribution [3,4], with amounts of straight-chain-saturated hydrocarbons usually exceeding those of unsaturated and oxygenated ones. While only little research on Co F–T catalysts was performed during the time period from the 1950's to the later 1970's, an increasing number of recent patents by, among others, Gulf, Shell and Exxon companies, demonstrate a considerable rise of the commercial interest in F–T catalysis.

A number of detailed reviews on the mechanistic features of the Fischer–Tropsch synthesis have appeared in the literature (see, for example, [5,6]). As already stated by Biloen and Sachtler [6], the chain growth in hydrocarbon synthesis has to be regarded as an act of *cis*-insertion of a CH$_x$ group ($x = 2$). The vast amount of surface analytical work, see [7–10], has focused on model catalysts other than Co. In fact, we are not aware of any study trying to identify adsorbed hydrocarbon entities on Co/SiO$_2$ catalysts. Clearly, Auger and X-ray photoelectron spectroscopy (AES, XPS) seem to be less well suited for such kind of analysis since they possess little chemical specificity. Secondary ion mass spectrometry (SIMS) may, in principle, identify individual species in complex adlayers. Despite the surface damage caused by the sputter process, trustworthy information can be obtained after careful calibration of the method (see, for example, [11–13]). We have, therefore, performed a SIMS study on Co/SiO$_2$ catalysts and shall demonstrate here the capability of this method to reveal the nature of adsorbed C_xH_y species after CO hydrogenation. In addition, we present temperature-programmed reduction for both precursor activation and catalyst clearing with the latter carried out posterior to the synthesis reaction.

2. Experimental

2.1. Catalyst preparation

For the studies reported here, a 15 wt% Co/SiO$_2$ catalyst was prepared using the incipient wetness technique. Before its use as support material, the SiO$_2$ (Degussa Aerosil 200, 220 m^2 g^{-1}) was compacted to generate a porous structure, then ground and sieved. The fraction with grain sizes between 125 and 250 μm was used for impregnation with the precursor salt. Prior to any precursor salt deposition, the SiO$_2$ was calcined at 673 K in flowing 10% O$_2$/Ar for 4 h.

A concentrated solution of Co(NO$_3$)$_2$ (Fluka, for analysis) was then added at room temperature to the support such that its volume equaled the pore volume of the silica.

The catalyst was subsequently dried in air at 423 K for 2 h. The cobalt loading was determined by plasma emission spectroscopy. The catalyst precursor activation was studied by temperature-programmed reduction in a classical atmospheric flow microreactor using hydrogen (100 mbar) in Ar as carrier gas.

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The active surface area of the catalyst was determined by hydrogen chemisorption in a conventional volumetric adsorption system, as described in detail elsewhere [14].

The chemisorption uptake (at 373 K) was measured using the double-isotherms method (difference between reversible and irreversible hydrogen species), as described by Bartholomew et al. [15,16].

2.2. Catalytic measurements

The syngas reaction was studied in a tubular flow reactor of quartz surrounded by a stainless steel jacket. The apparatus allows experiments to be performed at pressures up to 100 bar. In the present study, a pressure of 5 bar was used in order to meet the operating conditions of a second reactor attached to the ultra-high vacuum (UHV) surface analytical system (see below). Flow rates of 1–200 $\mathrm{ml\,min^{-1}}$ were fixed using mass-flow controllers (Brooks-5850 S). Reaction products were measured on-line by gas chromatography using a capillary column (Cpsil5Cb from Chrompack, separating saturated and unsaturated hydrocarbons from C_1 to C_{15} and alcohols from C_1 to C_9) and a filled column (Haysep D, separating CO, CO_2, H_2O, N_2, lower hydrocarbons and alcohols).

The catalyst was activated in flowing hydrogen (20 $\mathrm{ml\,min^{-1}}$) at atmospheric pressure. Starting at room temperature the catalyst was slowly heated to 623 K at a rate of 1 $\mathrm{K\,min^{-1}}$. This final temperature was maintained for 90 min. After activation, the catalyst was cooled to room temperature before passing a flow of N_2–CO–H_2 (15 $\mathrm{ml\,min^{-1}}$ N_2–20 $\mathrm{ml\,min^{-1}}$ CO–40 $\mathrm{ml\,min^{-1}}$ H_2) through the catalytic bed. The pressure in the reactor was subsequently increased to 5 bar before adjusting the temperature carefully such that a conversion between 1 and 10% was obtained.

2.3. Model catalytic studies and surface analysis

The XPS/SIMS surface analytical system has been described in detail elsewhere [17]. It is connected to a flow reactor which can be operated at pressures up to 15 bar.

The Co/SiO$_2$ catalyst was reduced *in situ* at 623 K in this reactor by using a flow of pure hydrogen at 1 bar (90 min).

Catalytic measurements were performed at a total pressure of 4.4 bar using a H_2/CO ratio of 2. In order to reach the reaction temperature of 483 K the sample was heated at a rate of 2 $\mathrm{K\,min^{-1}}$. The kinetic studies were finished by pumping off the syngas and decreasing the temperature simultaneously. The subsequent SIMS analysis was performed at room temperature.

The detailed experimental setup of the surface analysis system can be found elsewhere [18]. SIMS spectra were acquired using an Ar^+ beam with an ion energy of 5 kV. The ion source was operated at 1 mA emission with an Ar partial pressure of 2×10^{-8} mbar. These parameters resulted in an Ar ion current density of approximately 10 nA/cm^2. To further reduce the current density the ion beam was scanned over a surface area of 1×1 mm^2. The charge compensation of the otherwise non-conducting samples Co/SiO$_2$ was achieved by means of an electron flood gun ($E_{\mathrm{kin}} = 5$–10 eV).

3. Results and discussion

3.1. Temperature-programmed reduction

The TPR spectrum of the catalyst precursor is presented in figure 1. Clearly, the H_2 consumption is correlated with

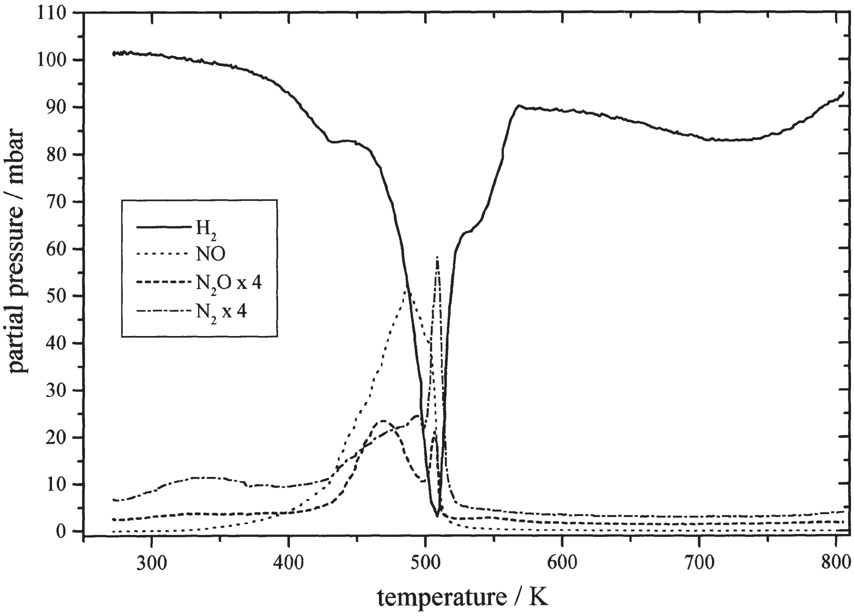

Figure 1. TPR spectrum of the Co(NO$_3$)$_2$/SiO$_2$ catalyst precursor. The hydrogen uptake and the desorption of the precursor decomposition products are depicted.

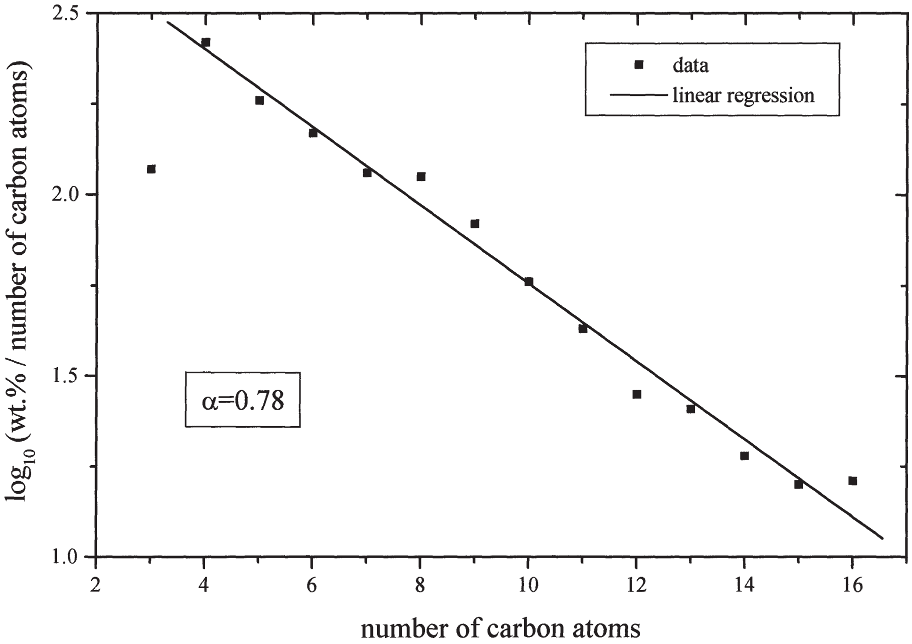

Figure 2. Schultz–Flory plot for the Co/SiO$_2$ catalysts in the range between C$_4$ and C$_{16}$. A linear regression of the data ($R^2 = 0.99$) gives an α value of 0.78.

the appearance of nitrogen containing compounds (N_2, NO, N_2O) resulting from reduction. Also H_2O was formed which, however, was not considered in figure 1 (the evolution of its partial pressure is not correlated with the catalyst temperature during heating).

According to figure 1, NO is the major product of the reduction process. A significant increase of the NO partial pressure is only seen above 400 K. The behavior of N_2 and N_2O is similar but more involved due to the appearance of additional desorption peaks above 500 K. The nature of the desorption products suggests the precursor decomposition is associated with the formation of oxides. An accurate calculation of the amount of oxygen remaining in the sample at ~570 K, i.e., after occurrence of the major H_2 consumption, was not possible because the evolution of water could not be considered in the mass balance.

A broad H_2 consumption feature appears at higher temperatures (570–800 K) and is associated with the reduction of cobalt oxides formed during the decomposition of the nitrate precursor [19]. The total hydrogen consumption indicates that 93% of the cobalt oxide has been converted to cobalt metal by the end of the reduction process. This calculation takes into account the modification of the flow rate due to product desorption.

Following this activation procedure, hydrogen chemisorption revealed a dispersion of 32% (this value is based on a stoichiometry H/Co$_{\text{surface}} = 1$).

3.2. CO hydrogenation

After activating the catalyst, CO hydrogenation was performed at 458 K and 5 bar. Under these conditions, a conversion of 4.5% (TOF: 1.2×10^{-3} s^{-1}) was obtained leading to the formation of saturated (up to C$_{18}$) and unsaturated hydrocarbons (up to C$_{11}$), with a maximum of the distributions at octane and 1-butene, respectively. We have also observed the presence of small amounts of alcohol ranging from C$_1$ to C$_7$.

Figure 2 demonstrates the catalytic performance of the catalyst in terms of a Schulz–Flory diagram. Using linear regression, a value of $\alpha = 0.78$ was obtained for the chain growth probability. These results are in good agreement with those found in the literature ([5,6,20] and references therein).

Kinetic tests of the CO hydrogenation reaction were also performed in the flow reactor attached to the XPS/SIMS analytical system. The formation of C$_1$–C$_5$ hydrocarbons was followed mass spectrometrically in this reactor. A quantitative analysis was not performed because (i) of instrumental limitations (mass range 0–100 amu) and (ii) complicated fragmentation patterns.

3.3. SIMS analysis after CO hydrogenation

XPS studies of the catalyst surface after Fischer–Tropsch synthesis revealed the existence of a C 1s peak which was so broad that its chemical nature was unclear. In order to render this analysis possible, we performed a SIMS study after both reduction and CO hydrogenation maintaining strictly static operating conditions for the ion gun. In a previous static SIMS investigation of promoted Pd/SiO$_2$ catalysts [21], we demonstrated that the catalytic activity of the catalyst remained unaltered even after several cycles of ion bombardment. Following the same procedure as in [21] the count rate of the most intense peak at $m/e = 28$ was normalized to a fixed value (here 10000 cps) for all spectra.

Figure 3 shows the mass range up to $m/e = 120$. Peaks at $m/e = 28$–30 (Si), 44 (SiO), 45 (SiOH), 59 (Co) and,

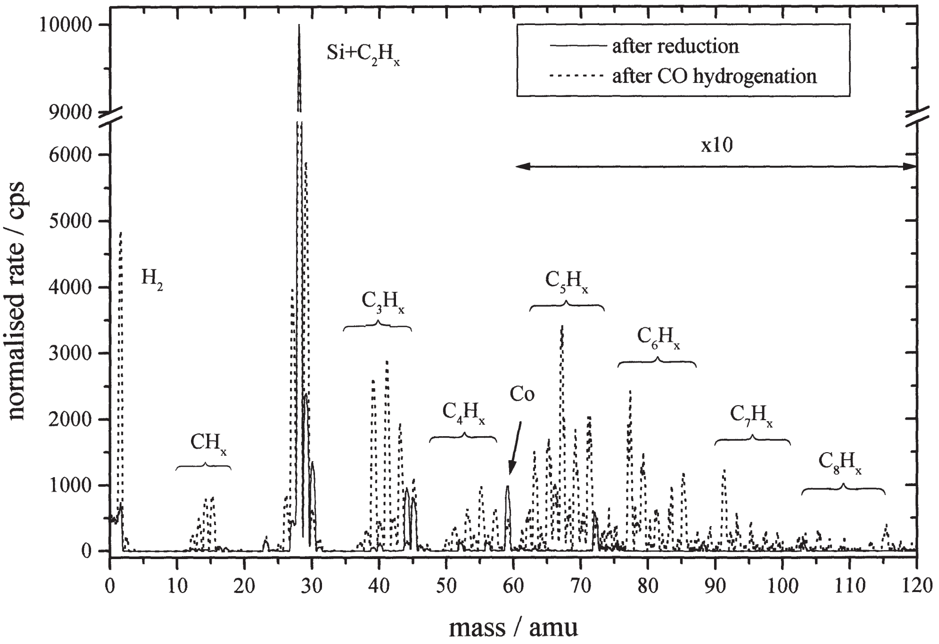

Figure 3. SIMS data recorded after the reduction at 623 K (solid line) and after the CO hydrogenation at 4.4 bar and 483 K (dashed line).

of lower intensity, at 72 (Si_2O) and 88 (Si_2O_2) represent sputter fragments of the support and of Co metal itself. A variety of additional species occur as a result of the CO hydrogenation reaction. In particular, there are groups with masses ranging from C_1 to C_8 and absolute count rates up to 1000 s^{-1}. More specifically, we conclude that individual hydrocarbon species up to at least C_8H_y are adsorbed on the catalyst surface after CO hydrogenation. While there is no doubt as to the qualitative nature of our analysis of the hydrogenated C_1–C_8 species, a quantitative assessment of the ion intensities in terms of abundance is not possible due to the occurrence of sputter-induced fragmentation. This phenomenon has been studied in detail by Van Ooij et al. [22] and Briggs [23,24] for adsorbed aliphatic hydrocarbons. Accordingly, the high intensity of odd mass numbers seems to be a characteristic feature of the ion-induced fragmentation of hydrocarbons. We note here that for the C_3 hydrocarbons the relative intensities of the odd mass numbers, $m/e = 39$, 41 and 43, recorded in all SIMS spectra, are identical with the relative intensities obtained in the gas-phase analysis of the reaction products. On the other hand, the mass distribution remained unchanged when using lower ion energies and/or primary ion current densities. Thus, despite some fragmentation inherent to the mechanism of ion formation in the SIMS process, a significant ion-induced damage of the surface did not occur in our studies.

Van Ooij et al. [22] and Briggs [23] also addressed the question of whether SIMS can be used as a fingerprint method to identify specific features of hydrocarbons like pendant methyl groups or unsaturation. In the case of polypropylene, poly-i-butylene and poly-1-butene, they found a significant increase of the cluster intensities with $m/e = 41$, 55, 69, 83 and 97 which they ascribed to the stabilizing effect of the pendant methyl groups of these polymers. Such cluster ions are definitely not observed in our post-reaction SIMS analysis of the catalyst, so that the formation of hydrocarbons with pendant methyl groups can be ruled out here. According to Van Ooij at al. [22] the adsorption of hydrocarbons with unsaturated CC bonds like poly-*cis*-butadiene and poly-*cis*-isoprene, resulted in a drastic increase of the fragments at $m/e = 77$, 91 and 105. They explained this behavior as follows: the presence of a CC double bond facilitates the release of a CH_3^+ group which is followed by a rearrangement of the remaining fragment such that characteristic aromatic fragments are formed. In all data we recorded after CO hydrogenation, this effect was clearly observable for the peak at $m/e = 91$. We conclude that unsaturated species are most probably present on the catalyst surface, in accordance with well-known performance of Co-based catalysts ([1], [2] and references therein, [5,6]). However, a more quantitative deconvolution into saturated and unsaturated amounts of hydrocarbons was not possible.

In this paragraph, we conclude by making a few more general remarks on our SIMS analysis. To begin with, the ion intensities of metal-related clusters such as $Co_xCO_y^+$ or CoH_z^+ are below the detection limit. Such cluster species were frequently observed in the SIMS analysis of CO- or hydrogen-covered metal surfaces [11–13] and offer, in studies with real catalysts, a straightforward means to differentiate between metal-related species and support effects [21]. Interestingly, absence of these species in the present work parallels the result that $CoC_xH_y^+$ species were not observed either. Thus no conclusions can be drawn as to the local chemical environment of the hydrocarbon entities.

Previous surface analytical work by means of AES and XPS on Ni and Fe model catalysts [7–10] focused on the

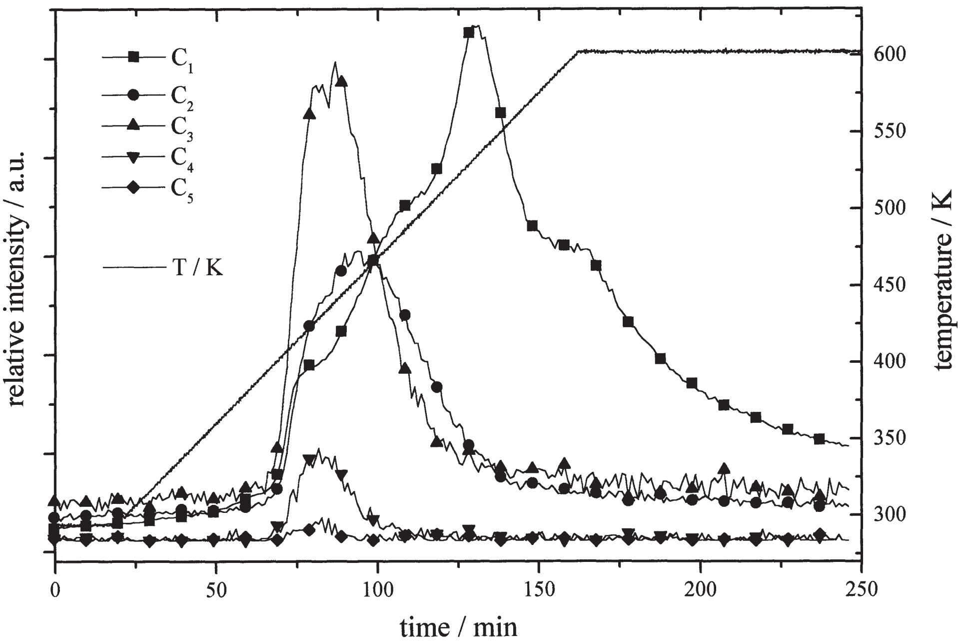

Figure 4. Temperature-programmed reaction spectrum taken directly after the CO hydrogenation. The following masses were chosen as representative for the different hydrocarbons: $m/e = 15$ (C_1), 30 (C_2), 41 (C_3), 57 (C_4), 71 (C_5).

chemical composition of the catalytically active phase. Accordingly, much of what was initially present in a metallic form appeared to be transformed into carbidic and oxidic phases during the initial stages of the Fischer–Tropsch process (see, for example, [1,25,26]). In the present study, neither $Co_xC_y^+$ nor $Co_xO_y^+$ were detected in significant amounts. In order to account for this "negative" result which, however, is in agreement with the general kinetic concept already proposed by Anderson ([2,27] and references therein), we mention here that (i) Co catalysts exhibit a much less complicated phase composition than, for example, Fe catalysts [2], (ii) the gas atmosphere is overall reducing for the low conversion used during our catalytic studies, and (iii) the low reaction temperatures used in this study (458–483 K) are not in favor of carbide and oxide formation. On the other hand, it can also be speculated that large amounts of hydrocarbons inhibit the ionic desorption of Co-bonded cluster species.

3.4. TPR study after CO hydrogenation

After analyzing the catalyst by SIMS, a TPR study was performed in the reactor part of the apparatus. In this study, the sample was heated at 2 $K\,s^{-1}$ up to 603 K in an atmosphere of hydrogen at 1 bar under flow conditions. The desorption spectrum of C_1–C_5 hydrocarbons is shown in figure 4. Since the time delay between the desorption of the hydrocarbons and their detection by the mass spectrometer is unknown, all data are plotted versus time and the temperature is indicated separately in figure 4. The analysis of the different hydrocarbons is based on the detection of mass fragments $m/e = 15$ (C_1), 27 (C_2), 41 (C_3), 57 (C_4) and 71 (C_5). Again, no quantitative assessment of ion intensities can be made.

It is evident from figure 4 that hydrocarbons up to at least C_5 can desorb intact from the catalyst surface. On the one hand, major amounts of CH_4 undergo desorption at temperatures well above 500 K, i.e., when C_{2+} hydrocarbons have already largely disappeared from the catalyst surface. This result can be explained by an increasing hydrogenolysis activity of Co metal sites liberated during the H_2-TPR experiment (leading to a cocktail of multiple bound hydrocarbon fragments). The absence of $Co_xC_y^+$ and $Co_xO_y^+$ species in SIMS, however, does not rule out that a "carbidic" phase (containing variable amounts of hydrogen) is formed under FT conditions. On the other hand, higher hydrocarbons can undergo some fragmentation and, thus, contribute to the low-temperature part of the $m/e = 15$ mass signal. This interpretation is in accordance with the observation that the C_2–C_5 species desorb in the same range of low temperatures. More specifically, they appear in a single desorption state with the peak maximum slightly decreasing with an increasing number of carbon atoms.

It is well known that the hydrocarbon radicals formed during Fischer–Tropsch synthesis are bound end-on to the catalyst surface. Hydrogen acts as a scavenger and, after reaction, these C_xH_y species desorb into the gas phase as intact hydrocarbons. Our observations are not compatible with the hypothetical model of a multiple-bonded side-on hydrocarbon under FT conditions. This is also confirmed in separate studies of n-heptane adsorption on the same sample reduced prior to adsorption: the SIMS analysis only contained C_1 and C_2 hydrocarbon ions implying a different adsorption geometry of the n-heptane molecule as compared to hydrocarbons produced via CO hydrogenation.

In order to estimate the degree of hydrocarbon removal during H_2-TPR, the catalyst surface was analyzed by SIMS

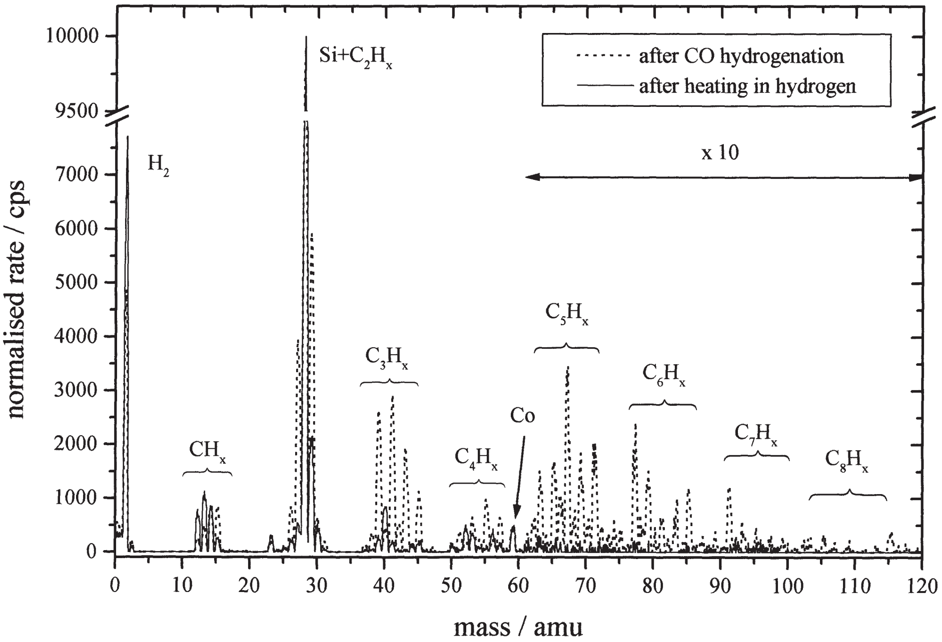

Figure 5. SIMS data taken after CO hydrogenation at 4.4 bar and 483 K (dashed line) and after temperature-programmed reaction in hydrogen (solid line).

again. The resulting spectrum is shown in figure 5. The comparison with the spectrum that was obtained directly after CO hydrogenation makes clear that almost all higher hydrocarbons, C_{2+}, are removed from the catalyst surface during H_2 treatment. Only some small amounts of CH_x persist. These observations are in accordance with the view that the active phase of a Co/SiO$_2$ catalyst can be easily reduced in hydrogen.

4. Summary

(1) We have studied the surface composition of a Fischer–Tropsch Co/SiO$_2$ catalyst. The considerable chain growth probability ($\alpha = 0.78$) observed for hydrocarbon production from synthesis gas ($H_2/CO = 2$, $p = 6$ bar, $T = 484$ K) is also reflected in the spectra of secondary ion emission (SIMS) of the adsorbed layer: species up to C_8 (detection limit) with variable amounts of hydrogen have been detected.

(2) Despite the occurrence of considerable sputter-induced fragmentation, the results prove the existence of individual C_xH_y species bound end-on to the catalyst surface.

(3) Individually adsorbed hydrocarbons undergo thermal desorption in temperature-programmed experiments posterior to catalytic studies in CO/H$_2$ gas. In the presence of hydrogen gas, hydrocarbon species up to C_5 (technical limit) are seen to desorb. The major amounts of methane occur at temperatures (>500 K) well above those of the C_{2+} species. This indicates either increasing hydrogenolysis of Co metal during H_2-TPR or existence of strongly bound “carbidic” species formed under FT conditions. Neither CoC_x^+ nor CoO_x^+ species were seen, however, in the SIMS experiment after CO hydrogenation.

(4) The Co/SiO$_2$ catalyst can be easily cleared from adsorbed hydrocarbons. This is demonstrated in a surface analysis by secondary ion emission subsequent to reduction in hydrogen. The respective mass spectra indicate small amounts of CH_x residuals besides large amounts of Co metal and support material.

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