relaxation time of the solvent, which increases strongly with HMPT concentrations [14]. Unfortunately the dielectric relaxation time in H_2O-DMSO has not yet been reported. The experimental data on the Walden product [6] seems to indicate that a simple Stokes friction force is operating in that system.

The relaxation processes are indexed with the kind of molecules replaced by the sulphate ion (W for water and H for HMPT). As in the earlier systems investigated the exchange of a water molecule leads to a common relaxation process irrespective of the composition of the solvate species $Be(H_2O)_{4-i}(HMPT)_i$. This is different for an exchange of HMPT by the sulphate ion. The second index on the relaxation times (and amplitudes) refers to the i of the solvate species. Relaxation 2 is attributed to the partial reaction (2). The opposite sign of the amplitude is expected from the different reaction volumes for the steps of reaction scheme (1) as explained in the earlier paper [6]. Also the observed relative large amplitudes which are calculated with a reasonable set of the volumes of reaction in scheme (1), is a strong argument in favour of attributing relaxation 2 to reaction (2). The attribution of the process indexed with W to the complete set of the sulphate-water interchanges (i = 0 to 3 in $Be(HMPT)_i(H_2O)_{4-i}^{2+}$) is suggested by the amplitudes (Fig. 1), which are large at high water content converging to the value in pure water and by the fact that the amplitude A_W remains measurable even at the highest HMPT mole fraction used in this investigation. The further indexing of the relaxation processes has also been deduced from the observed amplitude-mole fraction dependence.

Whereas the substitution rate decreases strongly with the number of solvating HMPT molecules i for i = 1 to 3, the species $Be(HMPT)_4^{2+}$ is substituted much faster by the sulphate ion than the solvate $Be(HMPT)_3(H_2O)^{2+}$ and even faster than $Be(HMPT)_2(H_2O)_2^{2+}$. A similar behaviour was observed in the $BeSO_4 - H_2O$-DMSO system, where, however, the substitution of the species $Be(DMSO)_4^{2+}$ by sulphate was only observed in pure DMSO. To explain this nonmonotonous dependence of the substitution rate on i, a steric effect has been proposed [6]. The cavity formed by four bulky organic molecules solvating the beryllium ion is too large thus reducing the strong electrostatic interaction between the ion and the first solvation layer. Therefore, the rate of the substitution process will be increased.

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(Eingegangen am 25. November 1980) E 4804

Decomposition of Carbon Monoxide and Its Reaction with Hydrogen on Iron Films under Static Conditions at Pressures between 2 and 25 mbar and at Temperatures between 373 and 573 K

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Adsorption / Hydrierung / Katalyse / Kohlenmonoxid

When carbon monoxide is adsorbed on iron films at temperatures $T \geq 373$ K carbon dioxide and carbon are formed. The Boudouard equilibrium is, however, not established at the chosen reaction conditions. In the presence of hydrogen the carbon monoxide adsorption leads to the formation of methane, carbon dioxide, and water. There is no correlation between the formation of water and of methane. The methane formation increases with both the increase in the total pressure and the increase in the partial pressure ratio $p_{H_2} : p_{CO}$. The ratio of the partial pressures of CO, H_2, CO_2, and H_2O point to the establishment of the water gas equilibrium at medium temperatures.

1. Introduction

There are many papers dealing with the interaction of hydrogen and carbon monoxide in the Fischer-Tropsch reactions [1,2]. They may be classified into two groups, one of which is concerned with investigations under conditions as similar as possible to those in the technical process, while the other is concerned with investigations under ultrahigh vacuum conditions. The former [3–7] have shown how the reaction

Ber. Bunsenges. Phys. Chem. *85*, 283–288 (1981) – © Verlag Chemie, D-6940 Weinheim, 1981.
0005-9021/81/0404-0283 $ 02.50/0

conditions and the composition of the catalysts influence the product distribution, the latter [8 – 14] have shown how the chemisorption influences the properties of both hydrogen and carbon monoxide when adsorbed on very clean surfaces, either alone or in co-adsorption with the other educt. Thus it has become possible to understand why the activation energy of the hydrogenation reaction is lowered by the presence of the catalyst. It was, however, not possible to detect either well defined intermediates or the products of the hydrogenation reaction under ultrahigh vacuum conditions.

There was a broad gap between the two groups of investigations. Only recently efforts have been undertaken in order to bridge this gap by producing very clean and well defined catalyst surfaces under ultrahigh vacuum conditions and by studying the reaction on these surfaces under higher pressures and at higher temperatures than usually applied in modern techniques of surface investigations [15 – 21]. In most cases flow systems have been used, and the gas phase and (after evacuation) the catalyst surface have been analyzed by means of partial pressure determinations or electron spectroscopies, respectively.

In earlier papers [8, 10 – 12, 14] using Fe films and ultrahigh vacuum conditions it has been shown that hydrogen is dissociatively adsorbed, even at temperatures as low as 77 K. There exist different adsorption states for the hydrogen atoms as could be deduced from thermal desorption spectra. The heat of adsorption of hydrogen is smaller than that of carbon monoxide. This gas is molecularly adsorbed at temperatures below room temperature whereas a slow decomposition is observed at room temperature and above. XPS measurements showed that two different kinds of carbon deposits are formed due to the decomposition of CO. These results are in full agreement with those obtained by other authors using single crystals of iron or another kind of polycrystalline material [9, 13, 18, 20].

The aim of this work is to use as catalysts polycrystalline iron films evaporated and annealed under ultrahigh vacuum conditions and to study the decomposition and the hydrogenation of carbon monoxide at higher pressures (2 to 25 mbar) and higher temperatures (up to 573 K) under static conditions. In this regard the work differs fundamentally from most papers concerned with the hydrogenation of carbon monoxide at elevated temperatures.

2. Experimental

The apparatus used is schematically shown in Fig. 1. It is a combined metal-glass system comprising the high pumping speed of ion pumped metal systems and the inert behaviour of glass concerning the catalysis of Fischer-Tropsch reactions. The two parts of the apparatus can be separated from one another by means of an ultrahigh vacuum metal valve (MV3) and a set of two ground-in ball and socket valves (GV, Duran 50). After baking out the metal part at 440 K and the glass part at 580 K a vacuum of $2 \cdot 10^{-8}$ Pa is obtained. Iron films are evaporated at a rate of about 1 nm min^{-1} at 77 K onto the inner wall of the spherical reaction cell RC. The films are annealed at 373 K for one hour. During this procedure the gas pressure is always below $5 \cdot 10^{-8}$ Pa.

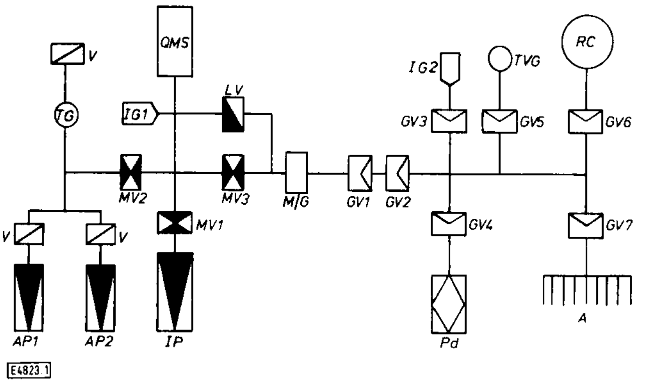

Fig. 1
Schematic diagram of the ultrahigh vacuum apparatus. A = ampoules, AP = adsorption pump, GV = ground-in ball and socket valve, IG = ionization gauge, IP = ion pump, LV = leak valve, M/G = metal/glass junction, MV = metal valve, Pd = palladium thimble, QMS = quadrupole mass spectrometer, RC = reaction cell, TG = thermotron gauge, TVG = thermovac gauge, V = viton valve

Hydrogen is introduced into the system by diffusion through a palladium thimble (Pd), carbon monoxide is admitted from ampoules (A) by magnetically smashing a break seal. The pressure of the gases can be determined by means of a thermal conductivity gauge (TVG) or from the known amount of gas in the ampoules. The gases are allowed to interact with the iron film and (on the film) with one another at different temperatures without any contact with the metal part of the apparatus.

In order to analyze the gas phase above the catalyst the adjustable leak valve is opened to a destinct degree while the metal valve MV1 is open and the metal valves MV2 and MV3 are closed. Then the gas passes the quadrupole mass spectrometer before it is pumped off by the ion pump. The ion current in the quadrupole mass spectometer is calibrated against the partial pressure in the glass part of the system for each gas observed in the reaction.

3. Results

Only those components are regarded as products of the catalytic reaction on the iron film, the partial pressures of which surmount a value of 10^{-3} mbar. This limiting value is given by

i) the limit of detection of the method applied, determined by the limit of detection of the quadrupole mass spectrometer and the uncertainty in the pressure reducing device.

ii) the demand that the measured signal should be considerably greater than that of the blank experiment.

iii) the fact that the amount of gas present in the gas phase under this partial pressure would produce a tenth of a monolayer when adsorbed on the film. Smaller coverages should be without any significance in catalysis.

3.1. Reaction of Carbon Monoxide on the Iron Film

Fig. 2 shows a semilogarithmic plot of the partial pressures against the reaction time, when the temperature is discontinuously increased from 373 K to 573 K. The CO pressure was 1.85 mbar at the beginning of the experiment. In the low temperature range it slightly rose with increasing temperature since the volume was kept constant. In the high temperature range it decreased due to the reaction on the catalyst surface and reached a value of 1.1 mbar at the end of the experiment.

The only gas detectable besides carbon monoxide was carbon dioxide. During a reaction time of one hour at 373 K its partial pressure was less than 10^{-3} mbar. At 423 K it surmounted this limit and increased with both time and rising temperature. The rate of increase rose with temperature. While the temperature was kept at 573 K for 4 hours the partial pressure of CO_2 increased from 0.11 mbar to 0.25 mbar. A linear plot shows that the rate of increase only slightly decreases during this time. The same is true for the rate of decrease of the CO partial pressure.

After having finished the experiment the iron film was solved in hydrochloric acid. There remained in the cell small black leaves which could be identified as carbon.

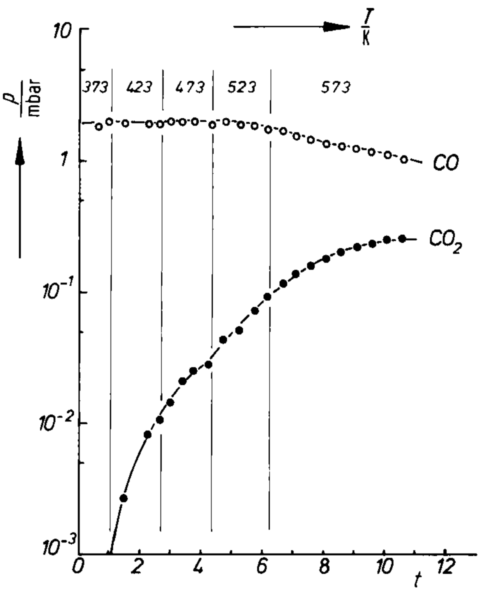

Fig. 2
Partial pressures of CO and CO_2 as functions of time for increasing temperatures with the interaction of CO with the iron film

3.2. The Reaction of Carbon Monoxide with Hydrogen on the Iron Film

The catalytic hydrogenation of carbon monoxide was studied as a function of temperature, total pressure and ratio $p_{H_2}:p_{CO}$. Since earlier experiments [12] had shown that carbon monoxide is able to replace hydrogen from the surface while hydrogen cannot be adsorbed on a surface covered with carbon monoxide at first hydrogen was adsorbed followed by the admission of carbon monoxide if not stated otherwise.

Carbon dioxide, water and methane were found to be the reaction products independent on the conditions under which the reaction was carried out. Small amounts of ethane and ethylene could not surely be identified as products of the catalytic reaction on the iron. They may have been formed on the hot cathode of the quadrupole mass spectrometer as could be seen from blank experiments. After each experiment carbon was found after solving the iron film in hydrochloric acid.

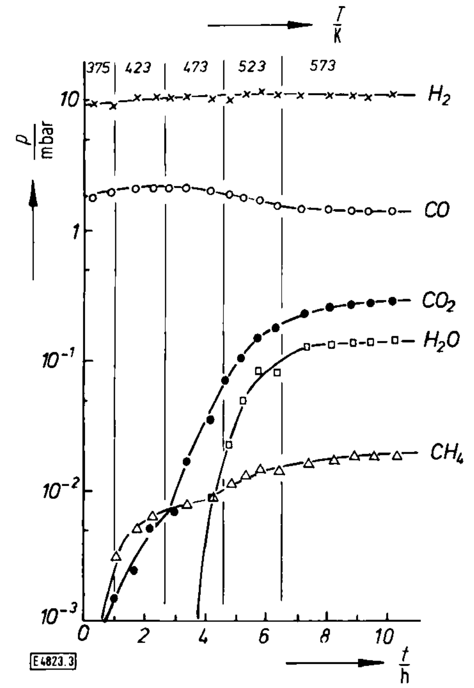

Fig. 3
Partial pressures of H_2, CO, CO_2, H_2O, and CH_4 as functions of time for increasing temperatures with the interaction of H_2 and CO with/on the iron film. H_2 admitted prior to CO

The curves shown in Fig. 3 are representative for the results obtained. At low temperatures methane and carbon dioxide are the only products. The carbon dioxide production is only slightly influenced by the reaction conditions whereas the amount of methane strongly depends on the ratio $p_{H_2}:p_{CO}$. Water can only be found at higher temperatures. The rate of reaction increases with temperature for all products. After a reaction time of about four hours at 573 K the partial pressures of all the substances seem to approach a limiting value in most of the experiments. A long time experiment, however, in which the partial pressures were measured for a period of 28 hours (21 hours at 573 K) showed a slight further increase of the partial pressures of CO_2, H_2O, and CH_4. The strongest increase was observed with the H_2O partial pressure. At 573 K the partial pressure of methane is always the lowest.

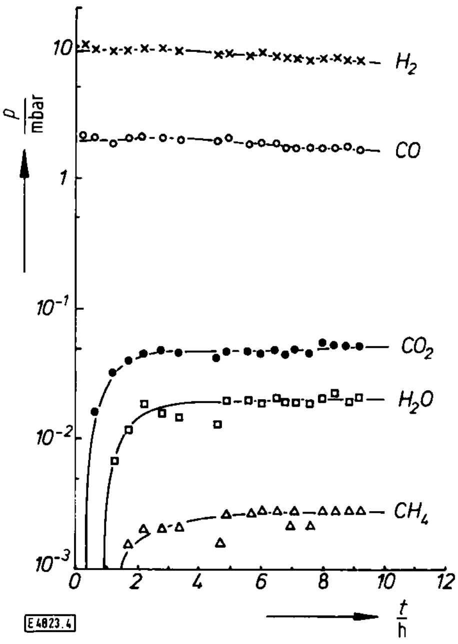

Fig. 4
Partial pressures of H_2, CO, CO_2, H_2O, and CH_4 as functions of time with the interaction of H_2 and CO with/on the iron film at 573 K

Fig. 4 shows the change in the partial pressures when the temperature of the catalyst is 573 K for the whole time of the experiment.

In order to study the influence of both the total pressure and the ratio $p_{H_2}:p_{CO}$ on the formation of methane experiments have been performed in the same kind as that shown in Fig. 3 but with varying total pressures and partial pressure ratios. The results are given in Tables 1 and 2. The pressures in columns 1 and 2 refer to the initial

Table 1
The influence of the total pressure on the formation of methane

p_{total}/mbar (298 K)	p_{CO}/mbar (298 K)	$p_{H_2}:p_{CO}$	p_{CH_4}/10^{-2} mbar T_c = 573 K	(298 K)	CO conversion to CH_4 in %
3.55	0.55	5.4:1	0.3	0.3	0.5
8.90	1.80	4.0:1	0.9	0.8	0.4
11.15	1.85	5.1:1	1.9	1.6	0.9
24.85	6.25	3.0:1	6.8	5.7	0.9
6.65	3.35	1:1	0.9	0.8	0.2
11.40	5.45	1:1	1.4	1.2	0.2

Table 2
The influence of the partial pressure ratio on the formation of methane

p_{total} / mbar (298 K)	p_{CO} / mbar (298 K)	$p_{H_2}:p_{CO}$	p_{CH_4} / 10^{-2} mbar T_c = 573 K	p_{CH_4} / 10^{-2} mbar (298 K)	CO conversion to CH_4 in %
11.15	1.85	5.1 : 1	1.9	1.6	0.9
11.40	5.45	1 : 1	1.4	1.2	0.2
11.15	7.45	1 : 2	0.8	0.7	0.1

total pressure and the initial partial pressure of CO at 298 K, respectively. The pressures in column 4 refer to the pressure of methane measured when the reaction cell was at a temperature of T_c = 573 K and to the pressure the methane would have when the whole volume of the apparatus would have a temperature of 298 K. The percentage of carbon monoxide converted into methane has been calculated from the latter pressures and from those shown in column 2.

Both the total amount of methane formed in the catalytic reaction and the relative conversion of carbon monoxide to methane increase as well with increasing total pressure as with increasing ratio $p_{H_2}:p_{CO}$.

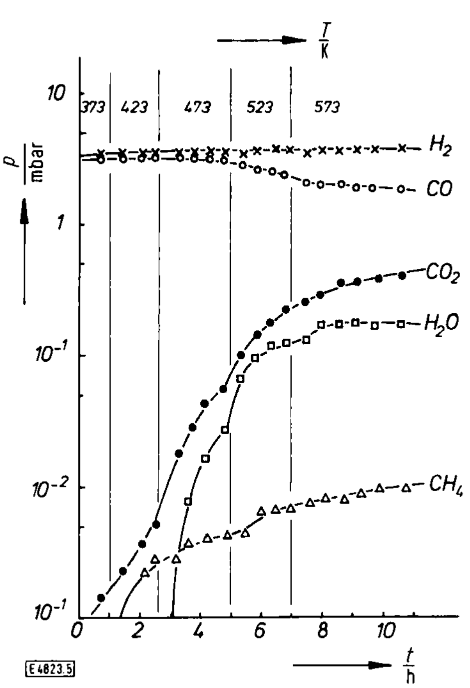

Fig. 5
Partial pressures of H_2, CO, CO_2, H_2O, and CH_4 as functions of time for increasing temperatures with the interaction of H_2 and CO with/on the iron film. CO admitted prior to H_2

There seems to be no significant influence of the sequence in which the gases H_2 and CO are admitted at 298 K on the results obtained at higher temperatures as can be deduced from a comparison of Figs. 3 and 5. Fig. 3 refers to an experiment in which, as usually done, hydrogen was adsorbed prior to carbon monoxide, whereas in the experiment shown in Fig. 5 the opposite sequence was chosen.

If, however, carbon monoxide is allowed to react with the iron at elevated temperatures prior to the admission of hydrogen the production of both water and methane is strongly hindered. The experiment shown in Fig. 6 followed the experiment which is exhibited in Fig. 2.

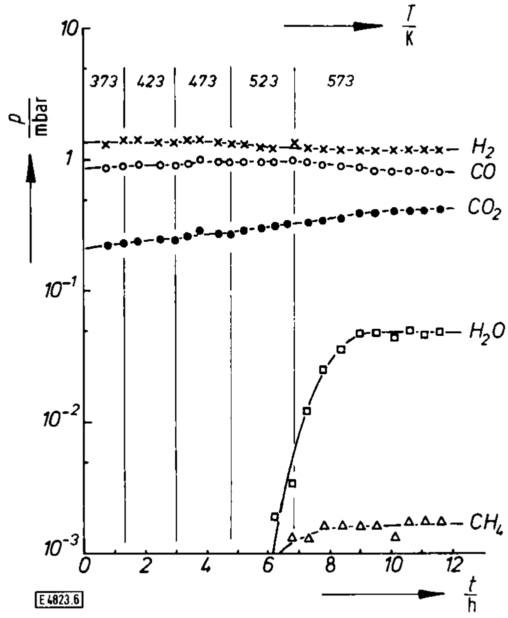

Fig. 6
Partial pressures of H_2, CO, CO_2, H_2O, and CH_4 as functions of time for increasing temperatures with the interaction of H_2 and CO with/on the iron film. The experiment shown in Fig. 2 was performed with the same iron film prior to this experiment

So far, only the influence of the reaction conditions on the formation of methane has been discussed. There are, however, also interesting observations concerning the production of carbon dioxide and water. These results are compiled in Table 3. The pressures in column 1 and 2 were measured at the beginning of the experiment, whereas those in column 5 and 6 were determined at the end of the experiment after a total reaction time of 10.6 hours, when the reaction cell was heated to 573 K for 4 hours. It is interesting to note that the value of the term $(p_{CO} \cdot p_{H_2O}):(p_{H_2} \cdot p_{CO_2})$ is nearly independent on both the total pressure and the initial ratio of $p_{H_2}:p_{CO}$.

Table 3
The influence of the total pressure and of the partial pressure ratio on the formation of CO_2 and H_2O

p_{total} / mbar (298 K)	p_{CO} / mbar (298 K)	$p_{H_2}:p_{CO}$	d / nm	p_{CO_2} / 10^{-2} mbar T_c = 573 K	p_{H_2O} / 10^{-2} mbar T_c = 573 K	CO conversion to CO_2 in %	$CO_{dissociated}$ in %	$CO_{dissociated}$ in mol	$\frac{p_{CO} \cdot p_{H_2O}}{p_{H_2} \cdot p_{CO_2}}$ at t = 10.6 T_c = 573 K
3.55	0.55	5.4 : 1	14	9	9	14	39	$2.9 \cdot 10^{-5}$	$8.1 \cdot 10^{-2}$
3.00	1.70	. 1 : 1.1	45	41	5	20	19	$4.3 \cdot 10^{-5}$	$1.9 \cdot 10^{-1}$
11.15	1.85	5.1 : 1	29	26	13	12	12	$2.9 \cdot 10^{-5}$	$5.9 \cdot 10^{-2}$
8.90	1.80	4 : 1.	16	22	6	10	4	$1.1 \cdot 10^{-5}$	$5.5 \cdot 10^{-2}$
6.65	3.35	1 : 1	66	40	16.	10	30	$1.3 \cdot 10^{-4}$	$6.6 \cdot 10^{-2}$
11.40	5.45	1 : 1	9	21	1.4	3.2	3	$2.3 \cdot 10^{-5}$	$6.0 \cdot 10^{-2}$
24.85	6.25	3 : 1	9	19	8	2.6	18	$1.4 \cdot 10^{-4}$	$1.4 \cdot 10^{-1}$
11.15	7.45	1 : 2	14	27	7	3.0	6	$5.9 \cdot 10^{-5}$	$7.6 \cdot 10^{-1}$

4. Discussion

4.1. The Decomposition of the Carbon Monoxide

In an earlier investigation [11] the chemisorption of carbon monoxide on iron films has been studied by measuring the change in the resistivity, the change in the surface potential and the heat of adsorption as a function of coverage at 77 K and at 273 K under ultrahigh vacuum conditions. A slow surface decomposition of the adsorbed carbon monoxide was evident at 273 K. UPS and XPS studies [14] showed that two different species of carbon and one species of oxygen is formed by the decomposition of the carbon monoxide between 273 K and 423 K (see also [19, 22]). In none of the experiments any reaction products could be observed in the gas phase.

In this paper the carbon monoxide pressure was considerably increased. As a result carbon dioxide appeared in the gas phase as shown in Fig. 2. The XPS studies had indicated that a reaction

$$\mathrm{CO(gas)} \rightarrow \mathrm{CO(ads.)} \rightarrow \mathrm{C(ads.)} + \mathrm{O(ads.)} \tag{1}$$

takes place. The formation of CO_2 can be due to a reaction

$$\mathrm{CO(ads.)} + \mathrm{O(ads.)} \rightarrow \mathrm{CO_2(gas)} \tag{2}$$

or to a reaction

$$\mathrm{CO(gas)} + \mathrm{O(ads.)} \rightarrow \mathrm{CO_2(gas)}\,. \tag{3}$$

At the present state it is not yet possible to decide from the experimental results whether the formation of the carbon dioxide occurs via Eq. (2) or via Eq. (3). The total process (Eq. (1) plus Eq. (2) or Eq. (3)) is the Boudouard reaction

$$2\,\mathrm{CO(gas)} \rightarrow \mathrm{C(deposited)} + \mathrm{CO_2(gas)}\,. \tag{4}$$

The equilibrium constant for this reaction,

$$K_p = \frac{p_{\mathrm{CO_2}}}{p_{\mathrm{CO}}^2}$$

is calculated from literature data [23] to be $2.12 \cdot 10^3$ mbar^{-1} at 573 K.

After a reaction time of 10.6 h (4 h at 573 K) the CO pressure was 1.1 mbar and the CO_2 pressure was 0.25 mbar, the ratio $p_{\mathrm{CO_2}} : p_{\mathrm{CO}}^2 = 0.21$ mbar^{-1}. This indicates that the system is still far away from equilibrium.

A mass balance supports the assumption that the reaction (1) is a precursor of the Boudouard reaction: During the reaction time $12.3 \cdot 10^{-5}$ mol CO have disappeared, but only $2.8 \cdot 10^{-5}$ mol CO_2 could be found in the gas phase. There is a lack of $6.7 \cdot 10^{-5}$ mol CO. Therefore a total amount of $(2.8 + 6.7) \cdot 10^{-5}$ mol $= 9.5 \cdot 10^{-5}$ mol carbon and of $6.7 \cdot 10^{-5}$ mol oxygen must have remained on the film. These values correspond to $1.1 \cdot 10^{17}$ and $7.8 \cdot 10^{16}$ carbon and oxygen atoms, respectively. The deposited amount is in the order of 50 to 100 monolayers. Taking into account the mass of the iron film ratios of Fe : O = 4.8 : 1 and Fe : C = 3.4 : 1 are calculated.

It is evident that such a large amount of oxygen cannot be present in the adsorbed state, it must have reacted with the iron. The carbon, that has also been found by an analysis (see Chapter 3.1), is present in a graphitic and in a carbidic form [14, 17–20].

4.2. The Reaction of Carbon Monoxide with Hydrogen on the Iron Films

When the results obtained in this paper shall be compared with those reported by other authors it is necessary to take into account the reaction conditions (pressure and temperature) applied in the investigations. Fig. 7 gives a survey of the reaction conditions.

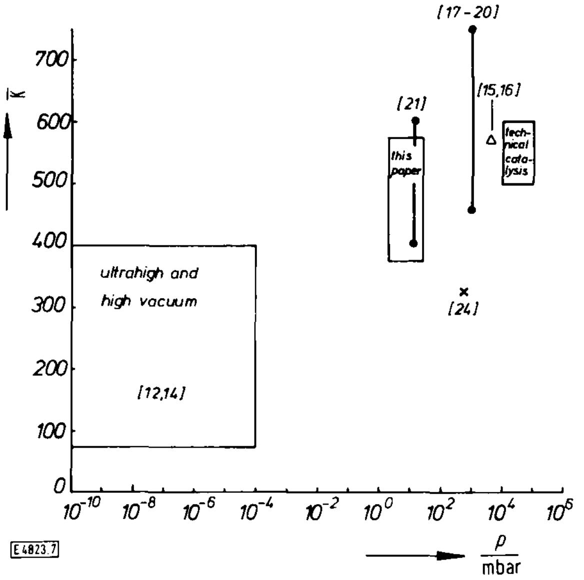

Fig. 7
Conditions applied in more recent papers (see references in square brackets) about the reactions of H_2 and CO on iron

The only hydrocarbon which has been found as a product of the hydrogenation in this paper is methane. At much lower pressures ($p < 10^{-4}$ mbar) there were no products at all [12, 14] which is in agreement with thermodynamic calculations [25] giving a partial pressure of methane in the order of 10^{-11} mbar. Kölbel et al. [24] who used a precipitated iron catalyst observed the formation of C_1, C_2 and C_3 products at 323 K when the total pressure was 520 mbar. Krebs, Bonzel, and Gafner [17] applied a total pressure of 1 bar at temperatures between 460 and 750 K, Dwyer and Somorjai [15, 16] used higher pressures (6 bar) and a temperature of 573 K. These two groups of authors report that C_1 to C_5 products are formed, methane being the main product.

The observation that the amount of methane increases with both total pressure (Table 1) and ratio $p_{\mathrm{H_2}} : p_{\mathrm{CO}}$ (Table 2) is in agreement with the thermodynamic prediction for the reaction

$$\mathrm{CO} + 3\,\mathrm{H_2} \rightarrow \mathrm{CH_4} + \mathrm{H_2O} \tag{5}$$

whatever the detailed steps of the reaction may be.

Methane is only rather weakly adsorbed on the transition metals [26, 27]. Therefore the formation of methane is nearly immediately indicated by its partial pressure. Figs. 3 and 5 show that methane is formed at rather low temperatures, comparable with the formation of CO_2. The same observation has been made by Vielstich and Kitzelmann [21]. The fact that the methane production increases with temperature much less than the formation of CO_2 may be explained by the results discussed in Sect. 4.1. The reaction of CO with the iron surface leads to the deposition of carbon and to the oxidation of the iron. Thus the number of adsorption sites which allow a dissociative adsorption of the hydrogen molecules decreases. This assumption would also explain the observation that the methane production is strongly hindered, when CO reacted with the iron surface at elevated temperatures prior to the admission of hydrogen (Fig. 6). Similar observations have been reported in the literature [15–18].

Water is only detected in the gas phase at relatively high temperatures ($T \geq 473$ K), and there seems to be no correlation with the formation of methane. This fact must not be taken as a proof against the assumption that methane is formed by a direct hydrogenation of CO according to Eq. (5) without a critical discussion. Nor is it a proof that methane is produced via Eq. (1) and the subsequent reaction

$$C(\text{ads.}) + 4H(\text{ads.}) \rightarrow CH_4(\text{ads.}) \rightarrow CH_4(\text{gas}) \tag{6}$$

which has been postulated by Bonzel et al. [17–20]. This is because water is adsorbed by the glass walls and may react under decomposition with the iron surface [28, 29]. In the experiment shown in Fig. 4, however, water already appears in the gas phase after a reaction time of one hour, when the temperature of the cell is 573 K from the beginning of the measurement. This indicates that the mentioned effects do not influence the detection of water severely. It seems to be necessary for the formation of water that the temperature is equal to or higher than 473 K.

At the end of Sect. 3.2 it was pointed out that the value of the term $K' = (p_{CO} \cdot p_{H_2O}) : (p_{H_2} \cdot p_{CO_2})$ is nearly independent on both the total pressure and the initial ratio of $p_{H_2} : p_{CO}$. The gases H_2, CO, CO_2 and H_2O are the components of the water gas reaction

$$CO_2 + H_2 \rightleftarrows CO + H_2O\,. \tag{7}$$

The equilibrium constant

$$K_p = \frac{p_{CO} \cdot p_{H_2O}}{p_{CO_2} \cdot p_{H_2}} \tag{8}$$

has the value $K_p = 2.5 \cdot 10^{-2}$ at 573 K [23]. The values given in the last column of Table 3 are slightly higher. At first sight this might be explained by systematic errors in the determination of the partial pressures since also Kölbel et al. [30] have found that there is a complete establishment of the equilibrium Eq. (7) at 513 K on iron catalysts. On the other hand the experiments performed in this paper exhibit a slow increase in the values of K' with time. In a long time experiment a maximum value of $K' = 1.9$ was observed after a reaction time of 24 h. This value remained constant for further 4 h. At low temperatures p_{H_2O} is very small so that K' is much smaller than K_p. At $T_c = 573$ K and longer reaction times values $K' > K_p$ are found. Thus at medium temperatures equilibration should have taken place*). An increase of K' to values $> K_p$ is only possible when the equilibrium Eq. (7) can no longer be established due to a contamination of the catalytically active surface. K' can only further increase when p_{H_2O} increases and p_{H_2} decreases which is, indeed, observed. This point to a slow reaction of the oxygen formed by Eq. (1) (probably present as an iron oxide) with hydrogen**).

Kölbel and Engelhardt [30] assumed that the Fischer-Tropsch reaction always follows Eq. (5) and that the carbon dioxide observed with iron catalysts is formed via the water gas reaction Eq. (7). In such a case the CO_2 pressure could never be larger than the methane pressure which is in contradiction to the experimental results of this paper (see Fig. 4).

The authors thank the Deutsche Forschungsgemeinschaft, the Verband der Chemischen Industrie and the Max-Buchner-Forschungsstiftung for financial support.

Added on proof:

*) Further experiments, in which the reaction mixture was kept at 503 K for more than 15 hours, gave values of K' between $5.7 \cdot 10^{-3}$ and $10.0 \cdot 10^{-3}$ which remained independent on time. They are in good agreement with K_p being $7.6 \cdot 10^{-3}$ at 503 K [23].

**) In an additional experiment a clean iron film was treated with oxygen in the presence of 6.7 mbar hydrogen. The amount of oxygen added agreed with the amount of oxygen formed by decomposition of CO in the experiment shown in Fig. 3. The partial pressure of H_2O as a function of both temperature and time was very similar to that shown in Fig. 3. This supports the assumption that water is formed by the reduction of an iron oxide. This process seems to be faster than the water gas reaction (Eq. (7)) on the iron surface contaminated with reaction products at elevated temperatures.

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(Eingegangen am 24. Dezember 1980) E 4823