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THE FISCHER-TROPSCH REACTION ON A COBALT (0001) SINGLE CRYSTAL

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The Fischer-Tropsch reaction is studied on a cobalt (0001) single crystal. Under the reaction conditions (1 bar synthesis gas; $H_2:CO = 2:1$; $T = 250\,^\circ C$) methane is the major product, with lesser amounts of heavier hydrocarbons. It is shown that the readsorption and subsequent hydrogenation of initially formed ethene is an important pathway to ethane. The activation energies for methane, ethane and propane formation are equal, which suggests that the rate-determining steps are similar.

The mechanism of CO hydrogenation over Group VIII metals has been investigated by many authors. Surface science techniques are well suited for obtaining detailed information on a molecular level [1]. With these techniques one can examine well-defined catalysts, in particular single crystals, both in UHV and at elevated pressures in a reactor. Although the Fischer-Tropsch reaction has been studied on single crystals of nickel and iron [2,3], the reaction on cobalt has not yet been investigated.

In this letter we give our first account of a series of experiments on the Fischer-Tropsch reactivity of cobalt surfaces. We report specifically on results obtained from a cobalt (0001) surface. In essence the experimental set-up consists of a UHV chamber, which is described in ref. [4], connected to a reactor. A transfer system ports the sample from the UHV chamber to the reactor and back. The UHV chamber, which has a base pressure of 10^{-10} mbar, is equipped with LEED, Auger, EELS and a differentially pumped ion gun for sputtering. The residual gas can be analysed with a mass spectrometer. The reactor is a small UHV chamber with a volume of about 80 ml. The pressure in the reactor can be varied between 10^{-9} mbar, during sample transfer, and 1 bar, under reaction conditions. The synthesis gas is prepared from H_2 (99.999%), which is obtained from a palladium diffuser unit, and CO (99.997%). The CO is passed through a heated trap to remove impurity carbonyls, in particular $Ni(CO)_4$. The Co(0001) crystal is polished mechanically and mounted with platinum wires onto a molybdenum support. The crystal is heated by passing a current through the platinum wires. The temperature is measured with a Pt/Pt-10% Rh thermocouple, which is spot-welded onto the back of the crystal.

The Co(0001) surface is cleaned with 2 keV Ne^+ sputtering. During sputtering the crystal is kept at a temperature of 350 ° C. This process results, according to Auger, in a clean surface with a good LEED pattern. After cleaning, the crystal is transferred into the reactor, which is subsequently filled with one bar of synthesis gas ($H_2 : CO = 2 : 1$), and heated to the desired temperature. The reactor experiments are performed in a flow mode. Synthesis gas is continuously fed into the reactor, while the pressure is maintained with a back-pressure regulator. The reaction products in the outgoing stream are analysed with a gas chromatograph. After a few hours of reaction, the crystal is cooled down in synthesis gas and subsequently transferred to the UHV chamber, where it is inspected by EELS and Auger spectroscopy.

In order to perform accurate measurements on the reactivity of the Co(0001) front face, it is necessary to eliminate any contributions from other sides of the crystal. Therefore a thin layer of gold (0.1 mm), which is not active in the Fischer-Tropsch reaction, was evaporated on these parts of the crystal. In a separate experiment with another Co(0001) crystal we carefully checked that no gold atoms diffused over the (0001) front face of the crystal. After a heat treatment of 100 hours at 350 ° C, which is long compared to the time scale of the experiments, no gold contamination was detected with XPS. It is known that cobalt undergoes a hcp-fcc phase transition above approximately 400 ° C. To ensure the integrity of the single crystal face, the crystals used for the experiments were never heated above 350 ° C.

It is also necessary to check the reactivity of other parts of the reactor, in particular the hot platinum wires, towards the reactants and products of the Fischer-Tropsch reaction. Experiments were performed with a polycrystalline silver crystal, which is not active in the Fischer-Tropsch reaction. Under typical reaction conditions ($P = 1$ bar; $H_2 : CO = 2 : 1$; $T = 250\,°C$) the platinum wires produced only methane, in quantities less than 10% of the production over Co(0001). By adding 100 ppm of propene to the synthesis gas feed in the above experiment, and subsequently performing a similar experiment with a cobalt (0001) crystal, we showed that the hydrogenation of propene was at least a factor of 20 faster over cobalt than over the platinum wires. The CO very efficiently poisons the hydrogenation of propene over platinum. It is to be expected that this is also true for other olefins. From these experiments we conclude that the internals of the reactor neither make a significant contribution to the measured activity nor influence the product distribution.

The Fischer-Tropsch reaction has been studied at 220, 250 and 280 ° C. Figure 1 shows the measured product distribution as a function of reaction time for a temperature of 250 ° C and a feed gas flow of 1 ml/min. The measurements show an interesting difference between methane and ethane on the one hand and

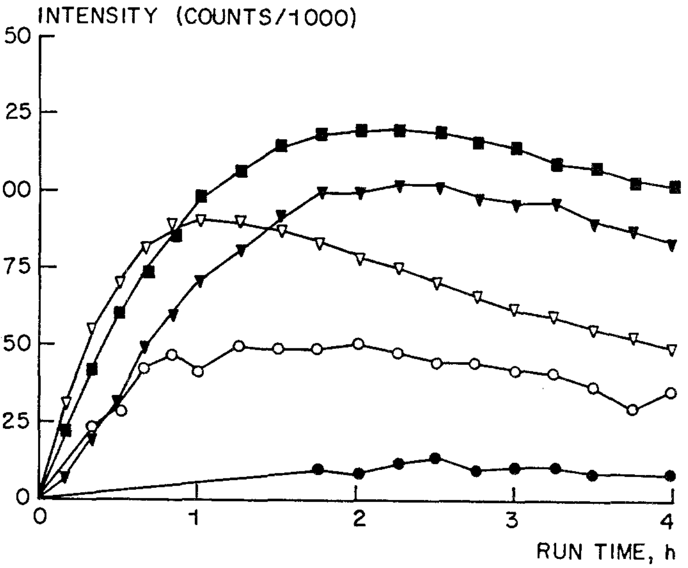

Fig. 1. The measured product distribution as a function of reaction time ($T = 250\,^\circ C$; flow 1 ml/min). The products are denoted by ■ for methane, ▽ for ethene, ▼ for ethane, ○ for propene and ● for propane. The data points for methane are divided by a factor of 10. One volume ppm CH_4 corresponds to 25,000 counts.

ethene on the other. The methane and ethane curves have similar shapes. The concentration of these products rises as a function of time and becomes roughly constant after 2.5 hours. This behaviour is expected for a continuously stirred tank reactor with a "delay time" (= volume/flow) of 80 minutes and an approximately constant production rate.

The similar behaviour of methane and ethane is illustrated by the Arrhenius plot in fig. 2. The propane measurements are also depicted in this figure. The data points plotted refer to measurements made after 2.5 hours run time. The turnover numbers are obtained by dividing the production rate by the total number of cobalt surface atoms. Note that the methane, ethane and propane lines are almost parallel. The activation energy is approximately 70 kJ/mol. The simplest explanation for this result is that the rate-determining steps for methane, ethane and propane formation are of similar nature. A possible rate-determining step is the hydrogenation of CH_3, C_2H_5 and C_3H_7 surface species.

The ethene measurements do not fit into the simple picture sketched above. The ethene concentration rises relatively quickly compared to the delay time of the reactor, reaches a maximum and decreases afterwards. A likely explanation for the differences between ethene on the one hand and the saturated products on the other, is the occurrence of secondary reactions. As the interaction with the cobalt surface is expected to be much larger for alkenes than for alkanes, ethene is more likely to readsorb on the surface than the saturated molecules. Note that

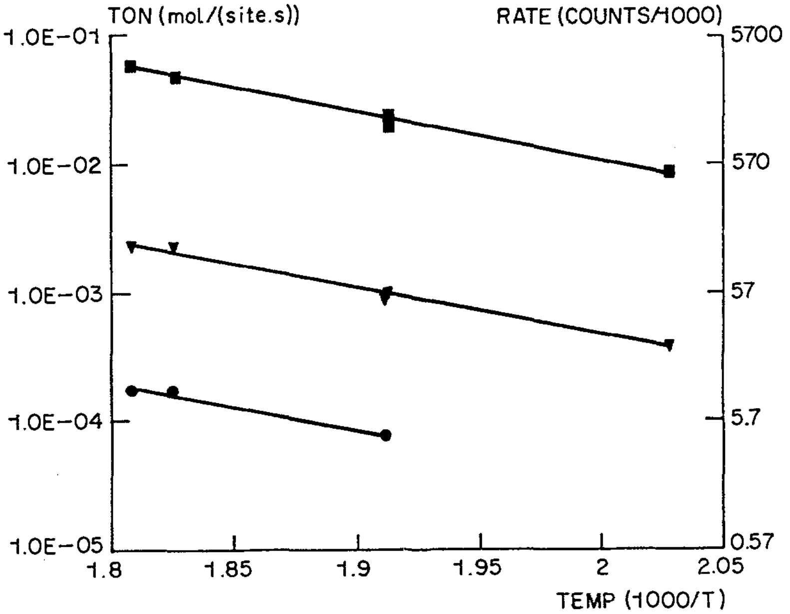

Fig. 2. Arrhenius plots of methane, ethane and propane after 2.5 hours run time ($T = 250\,^{\circ}\mathrm{C}$, 1 ml/min). The turnover numbers are obtained by dividing the production rate by the total number of cobalt surface atoms. See also the caption of fig. 1.

the consecutive reaction reduces the effective delay time of the reactor for ethene. This offers a qualitative explanation for the relatively fast attainment of the maximum ethene concentration. However, it does not explain the subsequent decrease. This decline can only be attributed to a decrease in the production rate of ethene. The importance of readsorption of olefins on Fe(111) was already demonstrated in a study by Dwyer and Somorjai [3]. The occurrence of readsorption of ethene in our experiment is illustrated in fig. 3. This figure shows the measured ethene and ethane concentrations as a function of reaction time for gas flows of 1 and 4 ml/min. These results serve to illustrate the effect of varying the residence time of molecules in the reactor. For a flow of 1 ml/min the ethane concentration rises above the ethene concentration after approximately 1.5 hours. In the 4 ml/min experiment, however, the ethane concentration is always below the ethene concentration. Apparently, part of the ethane is formed via hydrogenation of readsorbed ethene. The longer residence time in the 1 ml/min experiment compared to the 4 ml/min case results in a larger conversion to ethane. In a separate experiment a small amount of ethene (7.5 ppm) was added to the synthesis gas feed. This amount of ethene is slightly greater than the amount produced in the reaction (1–2 ppm). As expected, a large part of the added ethene is hydrogenated to ethane. The experiments gave no evidence of enhanced propene or propane production.

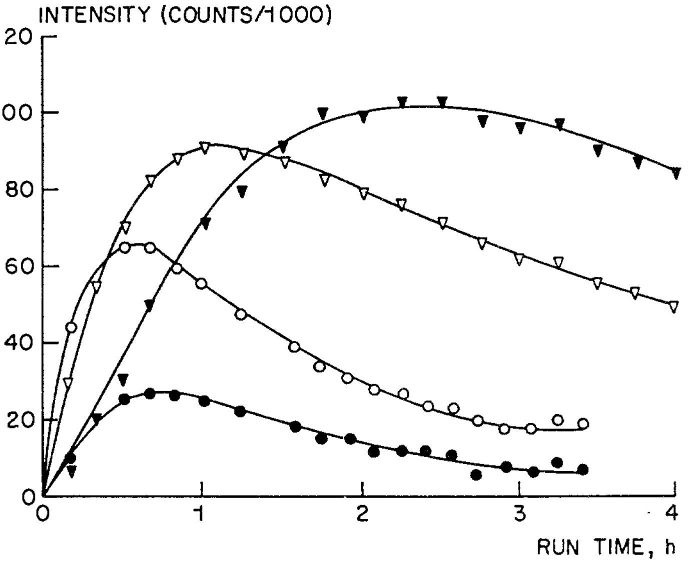

Fig. 3. The measured ethene and ethane concentrations as a function of reaction time for gas flows of 1 ml/min and 4 ml/min. Ethene is denoted by ▽ for 1 ml/min and by ○ for 4 ml/min. Ethane is denoted by ▼ for 1 ml/min and by ● for 4 ml/min. The lines are drawn to guide the eye.

The EELS spectrum, taken after the reaction, shows large peaks at 490 and 1990 cm^{-1}, which can be attributed to adsorbed CO. Smaller peaks at 2980, 1420 and 845 cm^{-1} are attributed to vibrations of CH_x ($x = 1, 2, 3$) groups. A large part of the CO is probably adsorbed during cooling in synthesis gas. Flashing the surface above roughly 150 °C in vacuum results in desorption of most of the CO. The Auger spectrum recorded after the reaction shows the presence of cobalt and carbon (peak to peak ratio C/Co775 = 0.21). Furthermore the spectrum contains a small sulfur peak (S/Co775 = 0.1). The heights of the cobalt peaks after the reaction are equal to those of the clean surface. Because of the limited resolution of our retarding field Auger system, the nature of the carbon species (carbidic, graphitic) could not be determined. To obtain a rough estimate of the sulfur coverage after the reaction, we note that the highest S/Co775 ratio observed in one of our experiments is 2.3. This value is very close to the S/Ni848 ratio (2.4) reported for half a monolayer of sulfur on Ni(100), which is the saturation coverage [5]. If we assume that a S/Co775 ratio of 2.3 corresponds to half a monolayer, the sulfur coverage after the present experiment is of the order of 0.02 monolayer. In this regime the influence of sulfur, which is known to be an efficient poison for the Fischer-Tropsch reaction, is still small [6].

In summary, the Fischer-Tropsch reaction has been studied on a Co(0001) single crystal. The activation energies for methane, ethane and propane formation are equal, which suggests a similar rate-determining step. Part of the ethane is formed via readsorption of ethene.

We note that the Auger and EELS spectra of Co(0001) are not representative of other cobalt surfaces. For example, on Co(1120), a carbonaceous layer deposits during the reaction. As a result, the intensity of the Auger peaks of cobalt decrease during the reaction until cobalt is no longer observed. However, during this growth process the reaction rate remains approximately constant. These studies will be discussed in a future paper.

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