The effects of promoters in carbon monoxide hydrogenation on cobalt foil model catalysts

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Abstract

Carbon monoxide hydrogenation has been studied on polycrystalline cobalt foils, using a combination of UHV studies and atmospheric pressure reactions at 525 and 575 K and the effects of different promoters (K and Mg) have been investigated. The selectivity towards methane was decreased due to both promoters. The main effect with potassium was, however, the suppression of carbon deposition at higher reaction temperatures. © 1998 Elsevier Science B.V.

1. Introduction

Cobalt has been used to catalyze the hydrogenation of carbon monoxide to produce liquid hydrocarbons (Fischer–Tropsch synthesis) since 1920's [1,2]. In spite of the many studies performed by catalyst scientists on transition metals in general and especially on cobalt, the complete picture of CO hydrogenation still remains unresolved on the atomic scale [3].

In this paper we want to focus on one part of the CO hydrogenation reaction, namely, on the promotion of the cobalt catalyst with metallic K and Mg. On clean cobalt, carbon monoxide hydrogenation has been studied on foils [4–7], single crystals [8,9] and with submonolayer coverages of cobalt on W(110) and W(100) [10]. The promotion of CO hydrogenation with K has been studied on cobalt foils by Wesner et al. [11]. The effect of K and Mg on the CO adsorption on cobalt has been studied earlier: K does not promote CO dissociation but increases the saturation coverage of CO by 50% [12,13]. Mg induces CO dissociation with simultaneous oxidation of the Mg species and an increase in the saturation coverage has also been observed [14–16]. The effects on the carbon residuals on the surface has been studied on both clean cobalt, where carbon starts to convert to graphite around 700 K [17] and on K covered Co(0001), where potassium has been seen to reduce the graphite formation from adsorbed acetylene [18].

The main conclusion from the data obtained in this work combined with the previous surface science studies indicate that the effect of the potassium promoter in CO hydrogenation is mainly to inhibit the graphite formation at reac-

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tion temperatures. The results are also compared to the post-reaction surface studies on K-covered Fe [19,20] and Ni [21] model catalysts after CO hydrogenation reactions.

2. Experimental

The research was carried out in a combined ultrahigh vacuum (UHV) atmospheric pressure chamber pumped with a diffusion pump and equipped with a double-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), a 3 keV sputter ion gun and a quadrupole mass spectrometer. For catalytic reaction rate studies the sample was enclosed in a special isolation cell that constitutes part of a microbatch reactor operating at atmospheric pressures. Products generated during the reaction experiment were separated with a gas chromatograph. The system has earlier been described by us [5] and originally by Cabrera et al. [22].

The reactants were introduced via a gas handling manifold where the pressure was measured with a differential pressure gauge. The purities of the gases used in the experiments were 99.5% (CO) and 99.99% (H_2) and the gases were cleaned prior to use by passing them trough liquid nitrogen cooled molecular sieve traps as described earlier [5].

The cobalt samples were foils of 125 μm thickness with surface areas < 1 cm^2. The samples were spotwelded on 0.9 mm Au wires connected to a rotatable manipulator using Cu supports. The rotatable sample holder allows both sides of the cobalt foil to be cleaned, modified and measured. The backside of the sample was defined as the one having the gold wires. During the reaction rate studies, when typical heating currents of 40 A were used, the Cu feedtroughs were cooled by air flow. The sample temperature was measured via a chromel–alumel thermocouple spotwelded on the backside of the sample and maintained using a proportional temperature controller within ± 3 K. At the start of the reaction experiment the

sample temperature was raised during a 90 s time span.

Both sides of the cobalt foils were cleaned by Ar$^+$ sputtering followed by H_2 exposure at 101 kPa for several hours to react with the carbon segregating to the surface. This produced a cobalt surface with small amounts of Cl that was easily removed by sputtering. After the reaction rate measurements the surface was cleaned by sputtering followed by annealing at 770 K.

The potassium deposition was performed using a SAES getter source located 5 cm apart from the sample. A manual shutter was used to control the deposition time. The magnesium evaporation source consists of a 0.5 mm W-wire around which the high purity Mg grains were squeezed and a manual shutter in front of the source. The source was surrounded by a Ta shield to prevent Mg deposition all over the chamber. The pressure in the UHV chamber during both K and Mg evaporation was below 1 μPa.

3. Results and discussion

The catalytic hydrogenation of carbon monoxide was investigated on cobalt foils promoted with potassium and magnesium at 101 kPa and with the H_2/CO ratio of 3.

The initial rate of methane formation for clean cobalt surfaces at 525 K when the H_2/CO ratio was 3 and the total pressure 101 kPa was 0.52 methane molecules produced per surface cobalt atom per second. The geometrical surface area of the two-sided sample with 10^{15} atoms/cm^2 was used to estimate the initial turnover rates from the accumulated methane versus time data.

3.1. Carbon monoxide hydrogenation on potassium covered surfaces

The deposition of K on transition metals at room temperature is characterized by the formation of a single monolayer due to the low heat

of sublimation of potassium [11,12]. The coverage of potassium was determined using the ratio of the potassium KLL (252 eV) and cobalt KLL (775 eV) Auger transitions. The increase in the K signal was linear with coverage up to the completion of the first monolayer as seen both with AES and XPS [12]. Using this information, the coverage was calibrated by measuring the intensities of the saturation coverage. Our previous data [12] as well as that of Wesner et al. [11] indicates that the Auger peak ratio of the K(KLL) and Co(KLL) lines multiplied by 0.75 gives the potassium coverage defined as overlayer coverage.

Because the reaction temperature was higher than the onset of the desorption of K on cobalt [12], the stability of the potassium exposed surfaces was checked by annealing the sample in vacuum and in the reaction gas mixture. According to the Auger peak ratio, only minor losses of potassium were detected below 600 K in vacuum. The AES data taken immediately

after the reaction experiments indicated less than 5% loss of potassium at 525 K but around 15% loss at 575 K. The coverage values used in this work were based on the post-reaction measurements because the desorption of K was assumed to be fast at elevated temperatures.

In Fig. 1 is shown the product distributions on cobalt surfaces with low and high potassium coverages at 525 and 575 K after 2 h reaction time using H_2/CO ratio of 3 and 101 kPa total pressure. The main effect of K was the decrease in the fraction of methane formed though it still remained as the main product. In the case of 525 K, the effect was more clear. Also, it seemed that only a small amount of K was required to achieve this effect and depositing more K on the surface reversed the direction of the change. The minor effect was the change in the fractions of C_4 and C_5 hydrocarbons that was seen to increase due to the small amounts of K. The result with a K deposited surface at 575 K was analogous with the 525 K data,
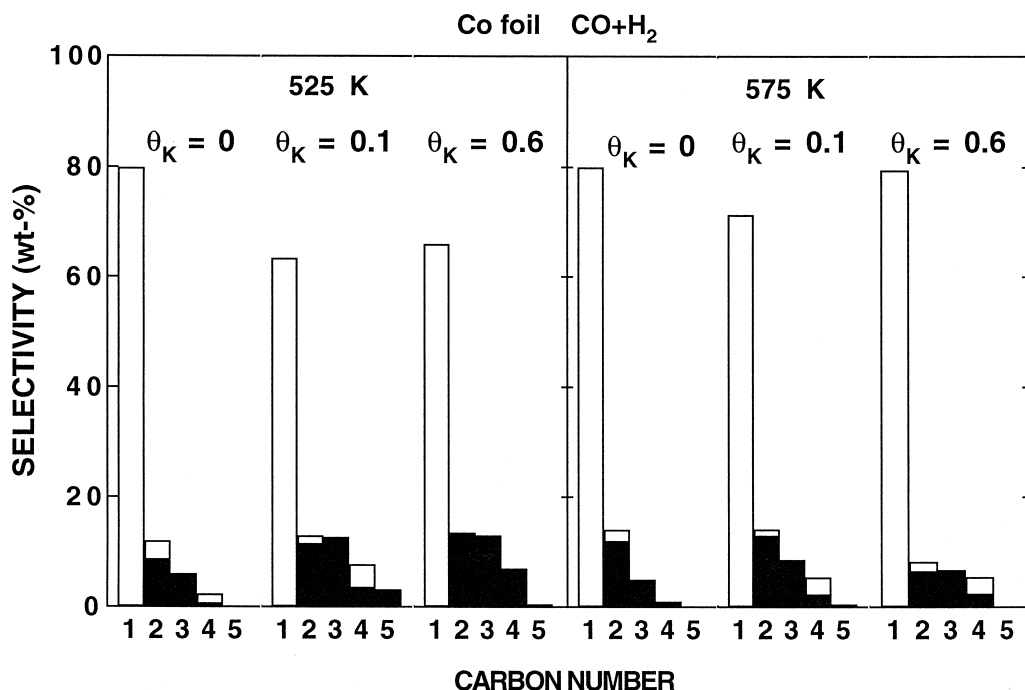

Fig. 1. Product distributions at two different temperatures and for low and high potassium coverages on cobalt. The total pressure was 101 kPa and the H_2/CO ratio 3. The saturated hydrocarbons are represented by white columns whereas unsaturated are denoted by black.

indicating a small decrease in the fraction of methane and a small increase in the fraction of C^{3+} hydrocarbons. The potassium induced effect on selectivity was not as clear as it was on Ni(100), where the product distribution without potassium at 500 K with a H_2:CO ratio of 4:1 at 120 Torr exhibited 93% (wt%), 5.9 and 1.5% of methane, C_2 and C_3 products, respectively, but 53, 25.6 and 22% of methane, C_2 and C_3 products with $\theta_K = 0.1$ [21]. The large change was explained by the enhancement of CO dissociation on Ni due to K. Our data thus indicates that the promotion of CO dissociation is not the main effect of K on the Co surfaces as it is on Ni surfaces.

The Anderson–Schultz–Flory distributions for 525 and 575 K after 2 h of reaction indicated a chain growth parameter change from 0.26 to 0.38 at 525 K and from 0.18 to 0.22 at 575 K when the surface coverage increased from $\theta_K = 0$ and $\theta_K = 0.1$ ML, in accordance with the product distribution shown in Fig. 1. On the Fe foil surface, the initial chain growth parameter changed from about 0.3 to 0.4 when the surface coverage increased from $\theta_K = 0$ and $\theta_K = 1$ ML [19].

The initial turnover rate of the surface decreased by one order of magnitude when the potassium coverage was increased from zero to 0.6 ML as shown in Fig. 2. A decrease in the turnover rate due to potassium has also been observed on Ni(100) [21], Fe [19,20] and Co foil [11] surfaces. In the case of K on Ni(100) the decrease was linear and was extrapolated to zero at the saturation K coverage [21]. The observed decrease in our studies was not explained by mere site blocking, because K has been found to increase the amount of CO adsorbed on Co(0001) [13], Ni(111) [23] and Pt(111) [24] and because the decrease in Fig. 2 was not linear with coverage. Obviously, the reactivity of the C species on the surface was lower in the presence of K than on the clean surface.

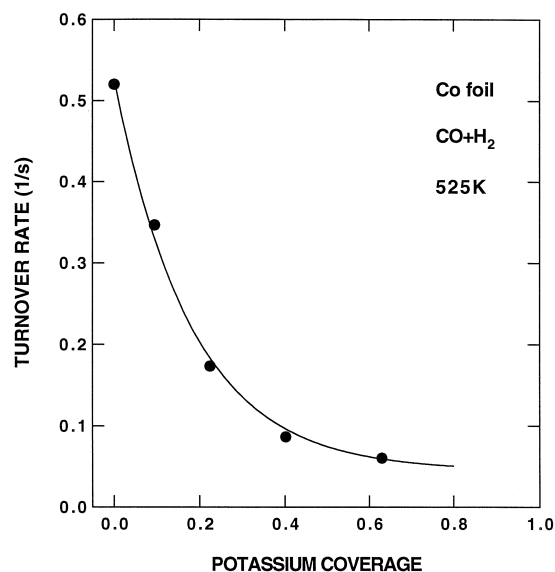The surface of the catalyst was characterized using AES immediately after evacuation of the

Fig. 2. Turnover rate per surface site in CO hydrogenation at 101 kPa as a function of potassium coverage at 525 K with H_2/CO ratio of 3. The solid line is drawn to guide the eye.

reaction cell. The post reaction spectroscopy revealed that carbon deposition observed on the clean surface was suppressed more as the reaction temperature was increased as shown in Fig. 3. At 575 K, C/Co ratios exceeding one were observed for the clean surface but 0.1 ML of K was able to keep the C/Co ratio below 0.5. Because the turnover rate decreased only by 18% due to potassium, the decrease in the carbon deposition cannot be due to the smaller turnover rate alone. Similar suppression of graphite formation due to K has also been seen on oxidized Fe surfaces [25]. On Ni(100), however, the carbon deposition during CO hydrogenation was increased due to potassium. This was explained by an increase in the CO dissociation due to K on a surface where the CO dissociation is not favored in its clean state [21]. Taking together the turnover data and the inhibition of carbon formation, small potassium coverages should be ideal for maximizing the performance of the catalyst.

The adsorption of acetylene was recently studied on clean and K promoted Co(0001) [18]. The presence of potassium on this surface
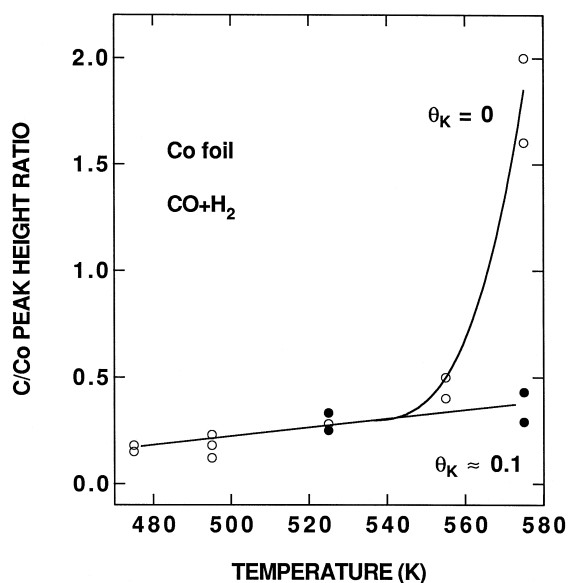
Fig. 3. The amount of carbon deposited during the CO hydrogenation reaction on the surface as a function of reaction temperature. The open circles are measured on the clean surface, while the solid circles are measured with a potassium coverage of about 0.1. The solid lines are drawn to guide the eye.

changed the nature of the carbon species formed due to thermal treatment. On the clean surface, the formation of graphite started above 420 K and was found complete at 570 K. On the K promoted surface, the amount of graphite seen on the surface decreased drastically and other (more active) forms of carbon were postulated to be present. The reactivity of these species were not measured, however. Together with our data this clearly indicates that at least one of the promotion effects of K in the CO hydrogenation on cobalt comes via inhibition of the graphite formation.

3.2. Carbon monoxide hydrogenation on magnesium covered surfaces

The deposition of Mg on transition metals has not been studied to such an extent as the deposition of K. At room temperature several layers of Mg can be grown on cobalt. When the evaporation is performed at around 550 K, a formation of a single monolayer will result and

the increase in the Mg signal is linear with coverage as seen both with XPS and TDS [26]. The coverage calibration can thus be defined similar to the case of potassium. The magnesium coverages used in the reaction experiments were determined using the ratio of magnesium KLL (1186 eV) and cobalt KLL (775 eV) Auger transitions. According to Vaari et al. [26] the magnesium layers are stable on the cobalt surface up to 650 K in vacuum. When the Mg/Co peak height ratios measured before and after the CO hydrogenation experiment were compared, no loss of Mg during the reaction were observed.

Fig. 4 shows the product distributions for a clean and magnesium covered cobalt surface at 525 K after 2 h reaction time using a H_2/CO ratio of 3 and 101 kPa total pressure. The main product was methane in both cases but a small decrease in the methane fraction and an increase in the C_4 and C_5 hydrocarbon fractions was seen. The product distributions were measured also at 575 K with Mg loading but the data showed a smaller promotion effect due to Mg
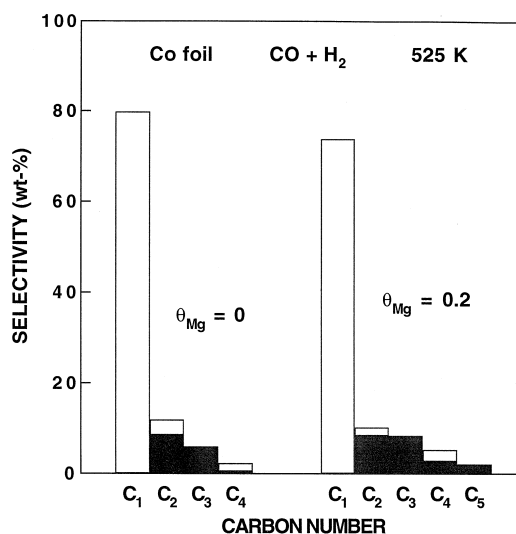

Fig. 4. Product distributions for two different magnesium coverages on cobalt. The total pressure was 101 kPa and the H_2/CO ratio 3. The saturated hydrocarbons are represented by white columns whereas unsaturated are denoted by black.

than at 525 K, as was also the case with potassium. The chain growth parameter in the Anderson–Schultz–Flory distributions, α, increased from 0.26 for the clean surface to 0.34 for the Mg covered surface at 525 K and was very similar to the effects due to potassium.

The surface of the catalyst was characterized using AES immediately after evacuation of the reaction cell. In the case of Mg promoted surface, the deposition of carbon was on the same level as observed earlier on the clean surface and, thus, different to the K modified surface. In summary, this indicates that both additives used in this work, K and Mg, had a similar effect on the product distribution, but the suppression of graphite formation was seen only on the potassium promoted surface.

4. Conclusions

In this work K and Mg metals have been deposited on the Co foil model catalyst surface to measure the promotion effects in CO hydrogenation at atmospheric pressures. We observed that both additives shifted the product distribution towards C^{3+} hydrocarbons. The main product of the reaction was in every case methane. With potassium, the deposition of carbonous species on the surface during the reaction was inhibited and we conclude that the main promotion effect of potassium on cobalt surfaces is due to the increased resistivity towards graphite formation.

Acknowledgements

References

[1] R.B. Anderson, The Fischer–Tropsch Synthesis, Academic Press, 1984.
[2] C.H. Bartholomew, Catal. Lett. 7 (1990) 303.
[3] L. Guczi (Ed.), New Trends in CO Activation, Elsevier, 1991.
[4] R.L. Palmer, D.A. Vroom, J. Catal. 50 (1977) 244.
[5] J. Lahtinen, T. Anraku, G.A. Somorjai, J. Catal. 142 (1993) 206.
[6] J. Lahtinen, G.A. Somorjai, J. Mol. Catal. 91 (1994) 387.
[7] J. Lahtinen, T. Anraku, G.A. Somorjai, Catal. Lett. 25 (1994) 241.
[8] J.J.C. Geerlings, M.C. Zonnevylle, C.P.M. de Groot, Surf. Sci. 241 (1991) 302.
[9] J.J.C. Geerlings, M.C. Zonnevylle, C.P.M. de Groot, Surf. Sci. 241 (1991) 315.
[10] B.G. Johnson, C.H. Bartholomew, D.W. Goodman, J. Catal. 128 (1991) 231.
[11] D.A. Wesner, G. Linden, H.P. Bonzel, Appl. Surf. Sci. 26 (1986) 335.
[12] J. Vaari, J. Lahtinen, P. Hautojärvi, Appl. Surf. Sci. 78 (1994) 255.
[13] J. Vaari, J. Lahtinen, T. Vaara, P. Hautojärvi, Surf. Sci. 346 (1996) 1.
[14] J. Lahtinen, J. Vaari, A. Talo, A. Vehanen, P. Hautojärvi, Surf. Sci. 245 (1991) 244.
[15] J. Vaari, J. Lahtinen, A. Talo, P. Hautojärvi, Surf. Sci. 251–252 (1991) 1096.
[16] J. Vaari, T. Vaara, J. Lahtinen, P. Hautojärvi, Appl. Surf. Sci. 81 (1994) 289.
[17] J. Nakamura, I. Toyoshima, K. Tanaka, Surf. Sci. 201 (1988) 185.
[18] J. Vaari, J. Lahtinen, P. Hautojärvi, Catal. Lett. 44 (1997) 43.
[19] D.A. Wesner, F.P. Coenen, H.P. Bonzel, Langmuir 1 (1985) 478.
[20] D.J. Dwyer, J.H. Hardengergh, Appl. Surf. Sci. 19 (1984) 14.
[21] C.T. Campbell, D.W. Goodman, Surf. Sci. 123 (1982) 413.
[22] A.L. Cabrera, N.D. Spencer, E. Kozak, P.W. Davies, G.A. Somorjai, Rev. Sci. Instrum. 53 (1982) 1888.
[23] R. Davis, D.P. Woodruff, O. Schaff, V. Fernandez, K. Schindler, P. Hoffmann, K. Weiss, R. Dippel, V. Fritzsche, A.M. Bradshaw, Phys. Rev. Lett. 74 (1995) 1621.
[24] M. Kiskinova, G. Pirug, H.P. Bonzel, Surf. Sci. 133 (1983) 323.
[25] G.A. Somorjai, Surf. Sci. 89 (1979) 496.
[26] J. Vaari, J. Lahtinen, P. Hautojärvi, Surf. Sci. 277 (1992) 253.