Alkali Promotion of Alumina-Supported Cobalt Fischer–Tropsch Catalysts Studied by TPR, TPD and Pulse Chemisorption

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Supported cobalt catalysts are important in several hydrogenation reactions, e.g. hydrodesulfurization and the Fischer–Tropsch synthesis. This work deals with the effect of adding potassium to supported cobalt Fischer–Tropsch catalysts. The catalysts were studied by temperature-programmed reduction (TPR), temperature-programmed desorption (TPD) of hydrogen and by pulse chemisorption of hydrogen. The catalyst activity in the Fischer–Tropsch synthesis was also measured.

The spectrum of unpromoted catalysts shows two peaks, at ca. 675 and 975 K. Low-level potassium addition does not change this much, whereas higher potassium levels give rise to additional TPR peaks.

Owing to the activated nature of hydrogen chemisorption on supported cobalt, hydrogen chemisorption was studied by TPD and by pulse chemisorption at 298, 373 and 473 K. On all catalysts there was only a very small amount adsorbed at 298 K. The hydrogen uptake was highest at 373 K, but lower again at 473 K. This indicates a balance between the activation effect of adsorption and the rate of desorption from the surface.

The catalyst activity and selectivity changed little with low levels of potassium, whereas the highest potassium level gave an almost inactive catalyst.

Promotion of catalysts with alkali metals is a well known method of changing their properties. In the Fischer–Tropsch (FT) synthesis promotion with K is known to increase the activity of unsupported Fe catalysts,[1] whereas on supported FT metals promotion with K lowers the activity and shifts the selectivity towards longer hydrocarbon chains, e.g. on Fe[2], Ni[3] and Ru.[4]

On cobalt catalysts little work has been published on the effect of alkali promotion. Kazansky et al.[5] studied the promotion of Al_2O_3-supported Fe and Co catalysts with alkali by diffuse reflectance IR spectroscopy of adsorbed CO. The catalysts were prepared by decomposition of carbonyls. The authors concluded that the effect of the alkali was to stabilize the metallic form of Co (and Fe), through the formation of surface alkali aluminates. These surface compounds reduce the concentration of surface hydroxyls that can oxidize the metals. Rodriguez-Ramos et al.[6] prepared alumina-supported Co, Fe and Ni catalysts from metal complexes with potassium and cyanide, e.g. from $K_3[Co(CN)_6]$, and reported slightly lower catalytic activities but higher selectivities to alkenes compared to literature data for conventional Co/Al_2O_3 catalysts.

This paper describes some experiments in which a conventional Co/Al_2O_3 catalyst was doped with increasing amounts of K by impregnation with KNO_3 and subsequent calcination. The catalysts were studied by temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) of H_2. The catalyst activity and selectivity in CO hydrogenation (FT synthesis) were also measured.

Experimental

Catalyst preparation. The unpromoted base catalyst was prepared by incipient wetness impregnation of $Co(NO_3)_2 \cdot 6H_2O$ in distilled water on a commercial γ-Al_2O_3 support, ground and sieved to 52-200 mesh before the impregnation. After impregnation, the catalyst was dried (373 K, 24 h) and calcined (723 K, 2 h) in flowing air in a tubular reactor. After calcination, the catalyst had a BET surface area of 180 m^2 g^{-1}, and contained 8.8 wt% Co by analysis. Based on this catalyst, K as KNO_3 was impregnated using the incipient wetness technique with distilled water as the solvent, and the catalyst was dried and calcined as above. The catalyst compositions are given in Table 1.

Temperature-programmed techniques. The TPR, TPD and pulse chemisorption experiments were performed in

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Table 1. Metal composition of the catalysts by analysis and degree of reduction from TPR experiments, assuming all Co as Co_2O_3.[a]

Catalyst	Co (wt%)	K (wt%)	H_2 consumption in TPR (as degree of red. %)
A	8.8	—	83
B	9.0	0.4	74
C	8.8	1.6	82
D	8.1	3.6	122

[a] TPR conditions: 7% H_2 in Ar at a heating rate of 10 K min^{-1}.

the experimental unit shown in Fig. 1. The unit consisted of a reactor made of quartz, a section for feeding and dosing treatment (H_2, O_2, inert) and adsorption gases, a detection unit (the TC detector of a Shimadsu GC-8A gas chromatograph), and a vertical electrical furnace controlled by an electronic temperature-control system (Eurotherm 919P).

Two thermocouples were used; one was used for furnace control and one was placed in the well in the catalyst bed. The pulse valve and the loop were placed in the GC furnace, which was thermostatted at 373 K. Before entering the detector, water and other condensibles were frozen out of the gas in the cold trap, kept at 195 K.

The TPR experiments were performed at a heating rate of 10 K min^{-1}, with a gas consisting of 7% H_2 in Ar.

TPD and pulse adsorption experiments were performed after a standard reduction procedure, copied from the activity experiments as described below. The TPD spectra were recorded at a heating rate of 10 K min^{-1} up to 773 K, with a holding time of 30 min. TPD spectra were recorded after reduction and cooling in H_2. A series of pulses (usually 10 pulses) of H_2 (100 μl) were admitted at intervals of 4 min using the valco valve. The exit pulses were detected using the TC detector.

After pulse chemisorption of H_2 the catalyst was flushed in flowing Ar for 15 min at the adsorption temperature before a similar TPD spectrum was recorded. H_2 was pulsed and subsequently desorbed at 298, 373 and 473 K. All gases used were of purity 99.99% or better, and purified in a deoxo unit followed by a molecular sieve trap before use.

Activity measurements. The catalysts were studied in CO hydrogenation in an ordinary microreactor apparatus at 1115 kPa and 523 K with a WHSV (weight hourly space velocity) of 10 h^{-1}. The catalyst was diluted 9:1 with inert material (α-Al_2O_3). The feed gas composition was H_2 : CO = 2 : 1, with a dilution of inert gas (He) of 50%. These conditions secured proper temperature control of the reactor, as measured by the thermocouple in the catalyst bed. Feed and product gases were analyzed by on-line gas chromatography. The CO conversion was determined from TC detection using N_2 as the internal standard. Product composition and mass balances were
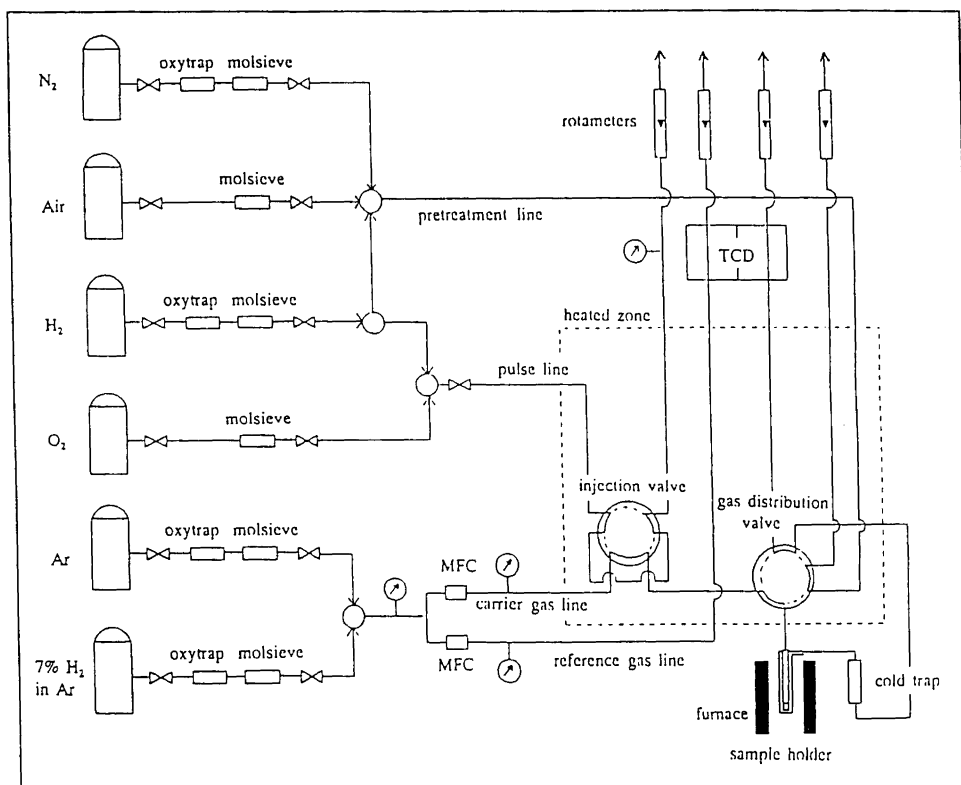

Fig. 1. Apparatus for catalyst characterization by TPR, TPD and pulse chemisorption.

obtained from the FID, using CH_4 to link the two analyses.

Before the activity measurements the catalysts were reduced *in situ* for 16 h in flowing H_2 (101 kPa and 623 K). Activity and selectivity data are reported after the initial stabilization of the system (5 h).

Results and discussion

Temperature-programmed reduction. Fig. 2 shows the TPR profiles obtained for the catalysts. The unpromoted catalyst shows two large TPR peaks, at 670 and 900 K, weaker shoulders at 580 and 770 K and a small peak at 1130 K, the end point of the temperature ramp. The latter peak was also observed during experiments with the support alone, and could be linked with reactions involving phase changes in the alumina.

Similar profiles are also observed for the catalysts with 0.4% and 1.6% K. The weak shoulder at 590 K is due to the reduction of residual nitrate.[7] Similar TPR curves of Al_2O_3-supported Co catalysts have been observed by others, e.g. by Guczi et al.,[8] who report significantly lower peak temperatures (460 and 650 K) but a similar shape of the spectrum of a 10 wt% Co/Al_2O_3 catalyst. Arnoldy and Moulijn,[9] and recently Okamoto et al.,[10] suggest up to eight different Co species on Co/Al_2O_3 that can be

observed in TPR measurements. With increasing peak temperature, the peaks correspond to increasing degrees of interaction with the alumina surface. The first large peak probably corresponds to a crystalline cobalt oxide, whereas the second large peak is probably a less reducible cobalt species, possibly a surface oxide.

Wang and Chen[11] studied Co/Al_2O_3 catalysts with increasing Co loading, and found that the size of the first peak increases with cobalt loading. They attribute the second peak, which they observe at very high temperatures (1173 K and above), to the formation of cobalt aluminate, but this could be due to their higher calcination temperature (723 K), which is known to favour the formation of such a species.

The results shown here indicate that potassium in low (<2%) loadings does not influence the reduction of the cobalt in these catalysts. This is supported by the calculated H_2 consumptions during TPR, shown in Table 1. Catalysts A, B and C showed similar H_2 consumptions, corresponding to a reducibility of 74–83% up to 1100 K. It is, however, important to note that a major part of the reduction appears to take place at temperatures above 750 K, which is well above the usual reduction temperature employed in such systems (<650 K). Reuel and Bartholomew[12] reported a degree of reduction of 34% for a similar 10% Co/Al_2O_3 catalyst reduced at 648 K. The choice of reduction temperature is a balance between reduction kinetics, and sintering and formation of cobalt aluminates. It is well known that higher reduction temperatures result in increased formation of such less reducible species.[12]
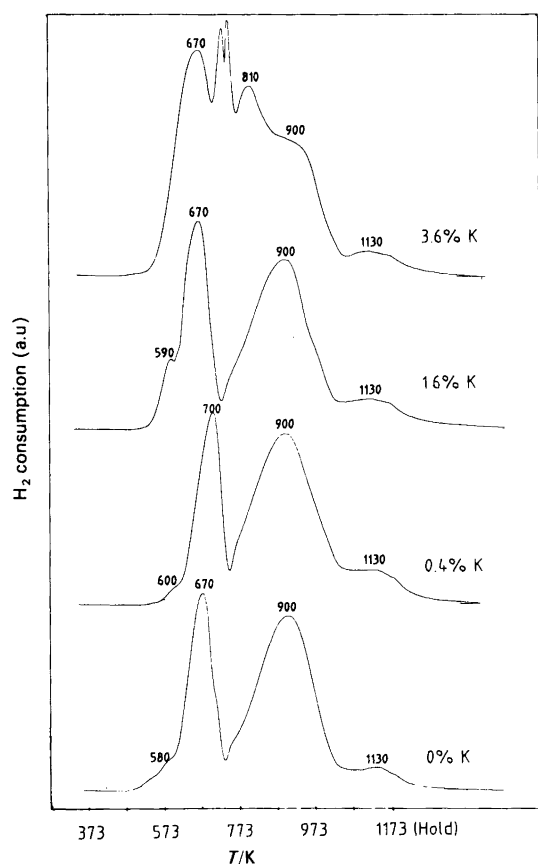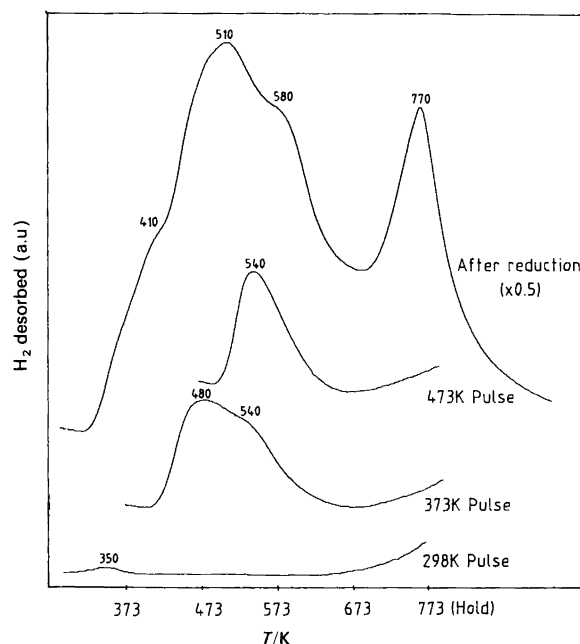

Fig. 2. TPR profiles of the catalysts described in Table 1. TPR conditions: 7% Ar in H_2 at a heating rate of 10 K min^{-1}.

Fig. 3. TPD profiles of catalyst A (Co/Al_2O_3). Prior to TPD measurements the catalyst was reduced for 16 h at 623 K. TPD conditions: Heating rate of 10 K min^{-1} with a holding time of 30 min. Flushing in Ar for 15 min after pulse chemisorption before TPD measurements.

The catalyst with the highest potassium loading (3.6% K, catalyst D), shows a completely different and very complex TPR profile. Two very sharp peaks at 740 and 755 K are overlayered on two broad peaks similar to those discussed above. In addition, a large shoulder appears at 900 K. This sample also shows a very high H_2 consumption, corresponding to a reduction degree larger than 100%, assuming all the cobalt as Co_3O_4 after calcination. The reason for this behaviour is not known, but in a related system $(Ni-Na/Al_2O_3)$ Lemaitre[13] suggests the possible formation of a reducible Ni species (niccolate) of a higher oxidation state (Na_2NiO_4) during calcination.

Hydrogen chemisorption and TPD. Figs. 3–6 show the results from a series of H_2 chemisorption and desorption experiments. The H_2 chemisorption data are summarized in Table 2. The H_2 uptake measured by TPD after reduction and cooling in H_2 is much higher for all the catalysts compared to pulse adsorption of H_2. The values decrease slightly with increasing potassium contents, and, as shown in Table 2, the apparent dispersion (H : Co ratio) was calculated from these data to decrease from 0.079 for the unpromoted catalyst A, to 0.056 for catalyst D with 3.6% K. If it can be assumed that the impregnation of KNO_3 and subsequent calcination does not change the actual particle size of cobalt on the catalyst surface,[13] this effect is due to site blockage or poisoning of the adsorption process by K. Hoost and Goodwin[14] studied the effect of adding K to a 3% Ru/SiO_2 catalyst, and found reduced H_2 chemisorption, which they attributed to site blockage due to K adspecies situated on the surface of the Ru particles. It is, however, important to point out that
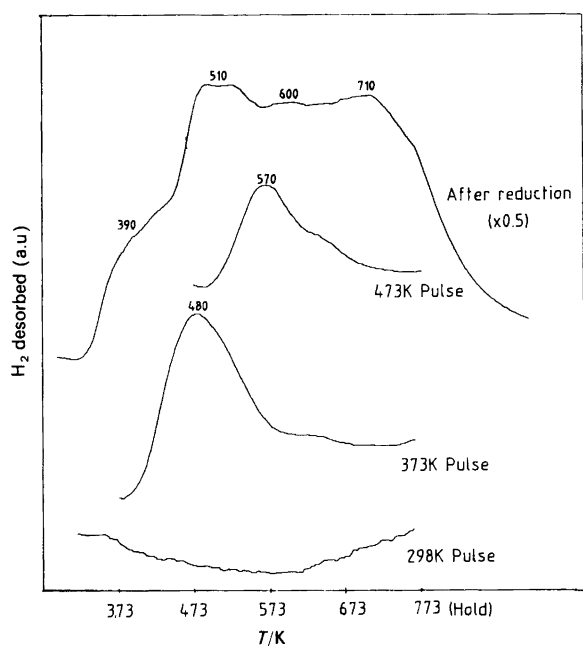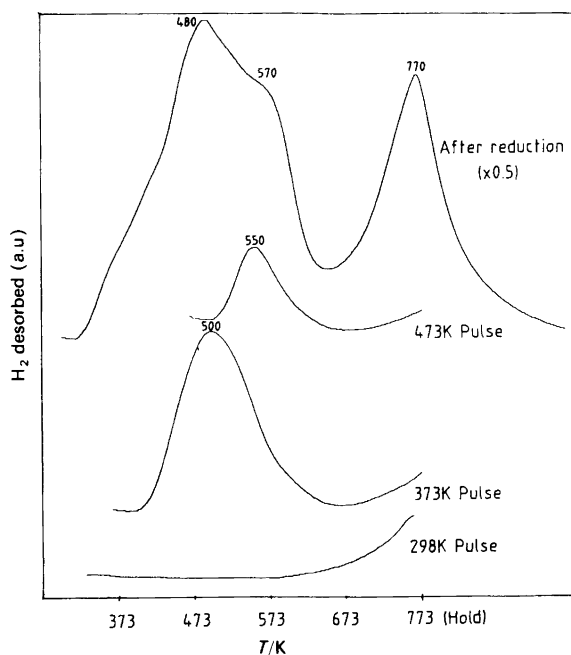

Fig. 5. TPD profiles of catalyst C $(Co,1.6K/Al_2O_3)$. Conditions as in Fig. 3.

Hoost and Goodwin[14] added K to their catalyst in the reduced state, whereas in this work K was added and the sample was subsequently calcined and reduced.

The chemisorption of H_2 on cobalt is an activated process, and is too slow to be monitored by pulse chemisorption at room temperature, as described by Reuel and Bartholomew,[12] and also observed here; 373 K is close to the optimum for H_2 adsorption on such catalysts, as
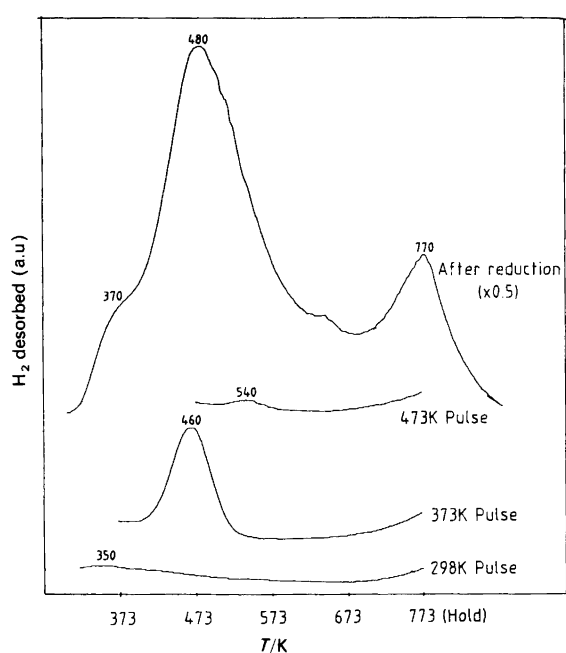

Fig. 4. TPD profiles of catalyst B $(Co,0.4K/Al_2O_3)$. Conditions as in Fig. 3.

Fig. 6. TPD profiles of catalyst D $(Co,3.6K/Al_2O_3)$. Conditions as in Fig. 3.

Table 2. Hydrogen adsorption and desorption [in µmol (g catalyst)$^{-1}$] after reduction in H_2 at 623 K for 16 h.[a]

Catalyst	K (wt%)	TPD after reduction (H_2 desorption) (H : Co)	Pulse chemisorption		
			298 K	373 K	473 K
A	—	58.7 (0.079)	0.5	10.6	4.0
B	0.4	51.3 (0.067)	0.6	10.2	9.8
C	1.6	43.2 (0.058)	0.4	9.4	8.0
D	3.6	38.1 (0.058)	1.1	7.1	5.5

[a] TPD conditions: Heating rate of 10 K min^{-1} to 773 K with a holding time of 30 min.

reported by Zowtiak and Bartholomew.[15] Even though the adsorbed amounts are highest at this temperature, the adsorbed amounts are much lower compared to the amount desorbed after reduction and cooling. At 373 K the pulse adsorption data shown the same trend between the catalysts as the first TPD data. At 298 K the H_2 uptake is very low, and increases with increasing K content. At 473 catalyst B shows the highest uptake. However, the TPD after pulse chemisorption on catalyst D at 473 shows virtually no desorption. This indicates a very rapid desorption from this catalyst. All the adsorbed H_2 is desorbed during the flushing of the system before the TPD experiment. For the other K-promoted catalysts, this effect is less pronounced, but compared to the adsorption data at 473 K, the desorption peaks are smaller than expected.

Catalyst activity. Table 3 shows the results from hydrogenation of CO over the catalysts. The main products detected were hydrocarbons for all the catalysts. The selectivity to CO_2 due to the water-gas shift reaction was low in all cases. The catalyst with the highest potassium loading was virtually inactive, giving only a very weak trace of hydrocarbons in the analysis. The products detected were mainly light gases, as indicated by the low growth probability found for catalyst D.

The unpromoted catalyst A showed a typical behaviour for Co catalysts. The methane selectivity was higher and the C_2 selectivity was lower than expected from Schulz–Flory kinetics, while the CO_2 selectivity was low. A thorough description of CO hydrogenation over this catalyst will be given elsewhere.[16]

The catalyst with the lowest potassium loading showed a similar activity to the unpromoted sample, but with significantly less C_1–C_4. The catalyst with 1.6% K was an order of magnitude less active, with a low selectivity to gases and apparently a high selectivity to alkenes. This could, however, be linked with the low CO conversion, as alkenes are primary products of the FT synthesis.

Effect of potassium. The effect of K on these catalysts and on other Ni- and Ru-based FT catalysts can be discussed in terms of the H_2 chemisorption and TPD results. Bartholomew[17] states in his review of CO hydrogenation that the reaction rate will be proportional to the fractional coverage of H on the surface. This is based on the assumption that the rate-determining step involves hydrogen adsorption or hydrogenation of surface intermediates, as indeed many suggested mechanistic models indicate.

Brown *et al.*[18] studied the chemisorption of D_2 on a Pt(111) single crystal promoted with K. They found that K in this case acted as a poison, leading to a lower rate of D_2 dissociation, and explained this as a long-range electronic effect. K is then a poison for H_2 adsorption due to electronic effects. Studying K promotion of Fe and Pt catalysts with XPS, Bonzel *et al.*[19] suggested that the changes they observed in the acitivity in CO hydrogenation were due to electronic effects. As noted above, Hoost and Goodwin[14] discuss the effect of K on Ru/SiO_2 in terms of site blockage, a purely geometric effect.

The differences in acitivity observed for these catalysts are much more dramatic than the changes in the adsorption properties. Catalyst D, which is virtually inactive, chemisorbs almost as much hydrogen as the unpromoted sample. The only change that is as dramatic is the increase in the H_2 desorption rate at the high temperature (473 K).

Table 3. Fischer–Tropsch synthesis data for the catalysts.[a]

Catalyst	CO conversion (%)	Growth probability, α	Selectivities				
			CH$_4$	C$_{2-4}$	C$_{5+}$	CO$_2$	C$_{2=}$/Σ C$_2$
A	17	0.70	26	23	50	1.2	27
B	16	0.78	20	19	60	1.1	28
C	2	0.80	12	20	64	4.4	92
D	n.d.[b]	0.33[c]	—	—	—	—	—

[a] Reaction conditions: $P = 1115$ kPa, $T = 523$ K, WHSW = 10 h^{-1} and H_2 : CO = 2 : 1. Feed dilution: 50% He, catalyst dilution with α-Al_2O_3 : 9 : 1. [b] Not delectable. [c] From weak hydrocarbon trace.

For the other K-promoted catalysts (B and C) the TPD profiles also indicated more rapid desorption of H_2. This could be a subtle clue to the cause of the strong effect of K on catalyst activity: The activity is reduced owing to reduced availability of H on the surface. This would also explain the higher alkene selectivity that is often observed over K-promoted catalysts.[2] As a consequence of the lower coverage of H on the surface, the rate of hydrogenation of adsorbed alkenes is reduced, and the selectivity of alkenes increases. Indirect evidence to the same effect can be found from work on noble-metal-promoted catalysts.[7,20] Although the exact mechanism of the activity increase found when Co catalysts are promoted with noble metals like Pt is unclear, one suggested explanation[20] is that the noble metal dissociates H_2 and acts as a source of spillover hydrogen to the hydrogenation sites on the Co surface. This effect would be the opposite of the one observed with K as the promoter.

Conclusions

K addition to a Co/Al_2O_3 catalyst has been shown to induce small changes in the properties of the catalyst with respect to H_2 chemisorption and desorption, while a very large K loading was neccessary to have any profound influence on the TPR spectrum. The CO hydrogenation activity and selectivity changes followed similar patterns as seen for other FT metals, i.e. reducing the activity and increasing the olefin selectivity. These changes were discussed in terms of reduced availability of adsorbed H on the surface caused by K.

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