Hydrogenation of propene on cobalt Fischer–Tropsch catalysts

Christian Aaserud[a], Anne-Mette Hilmen[b,**], Edvard Bergene[b], Sigrid Eric[c], Dag Schanke[c], and Anders Holmen[a,*]

[a]*Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway*
[b]*SINTEF Applied Chemistry, N-7465 Trondheim, Norway*
[c]*Statoil R&D, Postuttak, N-7005 Trondheim, Norway*

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Hydrogenation of propene to propane has been studied as a model reaction for secondary hydrogenation of olefins in the Fischer–Tropsch (FT) synthesis. The study has involved promoted and unpromoted cobalt FT catalysts supported on different types of supports. The hydrogenation of propene was carried out at 120 °C, 1.8 bar and $H_2/C_3H_6 = 6$. Co and Co–Re supported on alumina with different surface areas gave catalysts with different dispersion of cobalt. The cobalt dispersion for the alumina supported catalysts increased with increasing surface area. The rate of propene hydrogenation (based on exposed Co) also increased with increasing surface area of the alumina support. The rate for CoRe supported on TiO_2 corresponded to the alumina support with equal (low) surface area, but the SiO_2 supported catalyst did not. CO hydrogenation on the same alumina supported catalysts at FT conditions (210 °C, 20 bar and $H_2/CO = 2.1$) has shown that the C_{5+} selectivity increases with decreasing surface area of the alumina support. The increased C_{5+} selectivity fits very well with the decreased importance of olefin hydrogenation on catalysts with low surface area. The olefins will to a larger extent readsorb and participate in further chain growth rather than being hydrogenated to paraffins.

KEY WORDS: Fischer–Tropsch catalysts; propene to propane; olefins.

1. Introduction

The Fischer–Tropsch (FT) synthesis converts synthesis gas to hydrocarbons. Typical catalysts for the FT synthesis are promoted cobalt catalysts on a suitable carrier. Supported cobalt catalysts are preferred in FT synthesis of higher hydrocarbons from natural gas due to their high activity and selectivity, low water-gas shift activity, resistance towards deactivation and comparatively low price. Modern FT technology focuses on maximizing the yield of higher hydrocarbons, which are then hydrocracked to high quality diesel and other products. FT technology makes it possible to convert natural gas reserves to more easily transportable liquid fuels [1].

The FT synthesis is usually described as a chain growth mechanism where a C_1 unit is added to a growing chain. Linear α-olefins and paraffins are the primary products of the FT synthesis. α-olefins can also participate in secondary reactions including readsorption and further chain growth or they can be hydrogenated to paraffins. Formation of paraffins terminates the chain. A simplified reaction network is shown on figure 1. Hydrogenolysis [2] and isomerization [3] are also secondary reactions that can influence the final product composition. The rate of olefin readsorption [4,5] and of hydrogenation [4] is both increasing with increasing chain length.

Secondary reactions have been the subject of several studies involving model catalysts [6,7] and supported catalysts [8–22]. By adding ^{14}C labelled propene during FT synthesis on a cobalt catalyst Schulz et al. [23] found that 93% of the labelled propene reacted. The main part of the converted propene was either hydrogenated (54%) or adsorbed and involved in chain growth (33%). Co-feeding of olefins in FT synthesis has in fact been studied by several groups [2,3,5,7–20] and the conclusion from these studies is that addition of olefins increases the formation of compounds with higher carbon numbers than the added olefin. Iglesia et al. [24] found that the reactivity of added α-olefins in chain initiation increased in the order: ethene $\gg$ propene $>$ 1-butene $\sim$ C_{5+} α-olefins.

Even though the reactants are in the gas phase, the reactions take place in liquid filled pores and relatively slow reactions as the FT synthesis may become diffusion limited. The importance of diffusion in liquid filled pores has been discussed by Iglesia et al. [24].

The present work deals with secondary reactions in FT synthesis (figure 1). Hydrogenation of propene is used as a model reaction and the hydrogenation is studied on a number of different supported cobalt FT catalysts. Previous studies [25] have shown that the performance of cobalt catalysts during FT synthesis depends on the surface area of the support. The product distribution is influenced by secondary reactions and the focus in this work is on the effect of the support on the

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[*] To whom correspondence should be addressed.
E-mail: holmen@chemeng.ntnu.no
[**] Present address: Shell Technology Norway AS, Drammensveien 147A, N-0277 Oslo, Norway.

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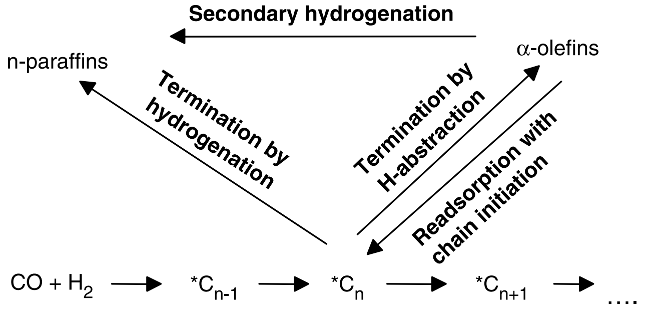

Figure 1. Simplified reaction network of the Fischer–Tropsch synthesis. C_{n-1}, C_n, C_{n+1} represent the growing chain on the catalyst surface.

hydrogenation of propene. Hydrogenation of propene on Co catalysts has not been the subject of many studies. For hydrogenation of propene over Group VIII metals supported on pumice, it was found that the activity of the different metals followed the sequence: Rh > Ir > Ru > Pt > Pd > Ni > Fe > Co. The reaction orders for hydrogen and propene for Co catalysts were 1 and 0, respectively [26].

Most of the supported alumina catalysts used in the present work have previously been tested under FT conditions (210 °C, 20 bar and $H_2/CO = 2.1$) [25]. The C_{5+} selectivity at 50% conversion of CO is given in table 1. It is evident from the results in table 1 that the C_{5+} selectivity depends on the surface area or some other property of the alumina support. The low surface area support gives the highest C_{5+} selectivity. The C_{5+} selectivity decreases from 85% to 81% for unpromoted catalysts with support surface areas of 13 m^2/g and 191 m^2/g, respectively. Adding 0.5 wt% Re to the Co/Al_2O_3 catalysts results in a slight increase in the C_{5+} selectivity. However, the reason for this behaviour of the low surface area supports is still unclear, but secondary reactions may contribute as outlined above.

Table 1
Selectivity of C_{5+} hydrocarbons in Fischer–Tropsch synthesis [28]

Catalyst	CO conversion (%)	C_{5+} selectivity (%)
Co/LSA Al_2O_3	49.2	85.0
CoRe/LSA Al_2O_3	49.8	86.5
CoRe/MSA Al_2O_3	50.0	83.6
Co/HSA Al_2O_3	49.4	81.0
CoRe/HSA Al_2O_3	49.3	82.3

The results are obtained at 20 bar, 210 °C and $H_2/CO = 2.1$ for 12 wt% cobalt catalysts supported on different aluminas [28]. The promoted catalysts contains 0.5 wt % Re and HSA, MSA and LSA are high, medium and low surface area alumina supports, respectively as defined in table 2.

2. Experimental

Propene hydrogenation was studied on supported cobalt catalysts containing 12 or 20 wt% cobalt. The catalysts were prepared by incipient wetness (co)-impregnation of the supports with aqueous solutions of $Co(NO_3)_2 \cdot H_2O$ and/or $HReO_4$ or $Pt(NH_3)_4(NO_3)_2$. The catalysts were dried in air at 100–120 °C for 3 h and then calcined in air at 300 °C for 16 h. The alumina support (Puralox from Condea) was calcined at different temperatures (500–1150 °C) for 10 h prior to impregnation in order to vary the BET surface area. The titania and the silica support were calcined at 700 °C and 500 °C, respectively before impregnation.

The catalysts were characterized by BET surface area measurements and by H_2 chemisorption. Hydrogen adsorption isotherms were measured at 40 and 125 °C with Micromeritics ASAP 2010. The catalysts (~0.5 g) were reduced *in situ* in flowing hydrogen at 350 °C for 16 h (1 °C/min to 350 °C). The sample was then evacuated for 1 h at 330 °C before cooling to 40 or 125 °C and further evacuated for 0.5 h before the adsorption isotherm between 10 and 500 Torr was measured. The total amount of chemisorbed hydrogen was used to calculate the dispersion assuming a H:Co ratio of 1 [27]. It is assumed that Re does not contribute to the amount of hydrogen chemisorbed when calculating the dispersion. The properties of the catalyst samples are given in table 2.

Table 2
Dispersion and BET surface area of the supported cobalt catalysts

Catalyst	Co (%)	Promoter (wt%)	Dispersion (%)	Calcination temperature of support (°C)	Support surface area (m^2/g)
CoRe/TiO_2	12	0.5 Re	3.7	700	34
CoRe/HSA Al_2O_3	12	0.5 Re	9.1	500	191
CoRe/MSA Al_2O_3	12	0.5 Re	9.1	1100	68
CoRe/LSA Al_2O_3	12	0.5 Re	5.9	1150	16
Co/HSA Al_2O_3	12	–	6.9	500	190
Co/LSA Al_2O_3	12	–	4.2	1150	13
CoPt/HSA Al_2O_3	20	0.1 Pt	7.9	500	185
CoRe/HSA Al_2O_3	20	1.0 Re	9.2	500	191
CoRe/SiO_2	20	1.0 Re	5.5	500	351

HSA, MSA and LSA are high, medium and low surface area alumina supports, respectively. H_2 adsorption has been carried out at 40 °C except for the TiO_2 supported catalyst and the 20% Co catalysts where adsorption was carried out at 125 °C.

Propene hydrogenation was studied in a conventional fixed bed microreactor. The flow rates were regulated by Hi-Tec mass flow controllers, each feed line was equipped with a separate mass flow controller. The reactor was made of stainless steel with 10 mm inside diameter. The reactor temperature was measured by a thermocouple (type K) located just above the catalytic bed. The temperature was regulated by an Eurotherm controller linked to the thermocouple in the reactor, and the reactor pressure was controlled by a Hi-Tec electronic pressure controller.

For the supported catalysts containing 12% Co, 15 mg of catalyst (53–90 μm) was mixed with 1185 mg SiC (75–150 μm) and loaded in the reactor. For the catalysts containing 20% Co, 10 mg catalyst and 1190 mg SiC were used. The amount of catalyst was varied in order to obtain an appropriate degree of propene conversion. The catalyst was reduced in a flow of hydrogen (80 N ml/min, 1 °C/min from ambient to 350 °C and held at 350 °C for 16 h). After reduction the temperature was decreased to 120 °C, the reactor flushed with He (400 N ml/min, 0.5 h) and the reactant mixture (1 N ml/min C_3H_6, 6 N ml/min H_2 and 463 N ml/min He) was then introduced at 120 °C. The reaction pressure was 1.8 bar. The reactor effluent was analyzed on-line by GC using a Hewlett Packard 6890 gas chromatograph equipped with a FID detector (0.53 mm i.d. GS-Q capillary column).

3. Results and Discussion

3.1. Dispersion of cobalt

As shown in table 2 and on figure 2 the dispersion of cobalt depends on the surface area of the support. The dispersion of the rhenium promoted catalyst on the low surface area alumina is in fact only two-third of the dispersion obtained for the two alumina supports with higher surface area. The same trend is also observed for the unpromoted cobalt catalysts although the dispersions are lower. It is well-known that rhenium promotes the reduction of cobalt oxide [28], and the rhenium promoted catalysts are having clearly higher dispersions of cobalt than the unpromoted ones as illustrated in figure 2. Co–Re supported on titania has the lowest dispersions of all the catalysts, even slightly lower than the unpromoted cobalt on low surface area alumina. The results in figure 2 also indicate that the effect of the surface area is most pronounced at surface areas below 70 m^2/g.

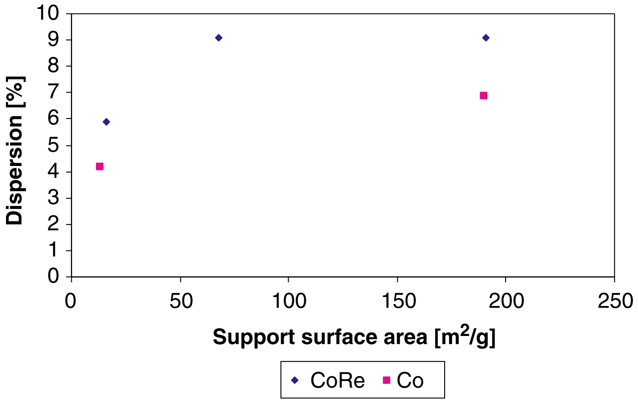

Figure 2. Dispersion of unpromoted and Re promoted cobalt catalysts supported on alumina with different surface area. Catalyst properties as given in table 2.

The dispersions of the catalysts containing 20% cobalt are shown in table 2. The rhenium promoted cobalt catalyst on silica has about half the dispersion of a similar catalyst supported on alumina.

The dispersion of the platinum and rhenium promoted cobalt catalyst on high surface area alumina is high for both systems as shown in table 2. However, the platinum promoted catalyst contains only 0.1 wt% Pt and a direct comparison is therefore difficult. However, it has been found that both Pt and Re addition increases the cobalt dispersion for alumina supported catalysts due to increased reducibility [29,30]. It has also been found that the selectivity does not change as a result of Pt or Re addition [30].

3.2. Propene hydrogenation

Blank runs without any catalyst present were performed at the same conditions as used for propene hydrogenation in order to verify that the reactor wall is catalytically inactive for hydrogenation of propene or other possible reactions. Only propene was detected in the product gas indicating that the reactor system can be regarded as inert and that no gas phase reactions occur. The alumina supports and the silicon carbide particles which are used as diluent in the catalyst bed, were also checked for possible catalytic activity but no activity was observed. The different supports were also tested for possible hydrogenation activity at similar conditions as the catalysts, but propene was the only product detected in the product gas. Cobalt oxide was also found to be inactive at the conditions used in this study.

Hydrogenation of propene over cobalt is a very rapid reaction. In order to carry out the hydrogenation at conversions less than 100%, a very diluted propene feed was used and the temperature had to be reduced to 120 °C.

The initial rate of propene hydrogenation to propane as a function of the alumina surface area for catalysts containing 12% Co is shown in figure 3. The experiments have all been carried out at constant GHSV (~31 000 N mL/g, min). The rate is clearly a function of the surface area of the support and the rate (*g*/*g*$Co_{(surface)}$, h) increases with increasing surface area. At surface areas below 70 m^2/g the rate increases almost linearly with the surface area, but the rate seems to approach a constant value at higher surface areas.

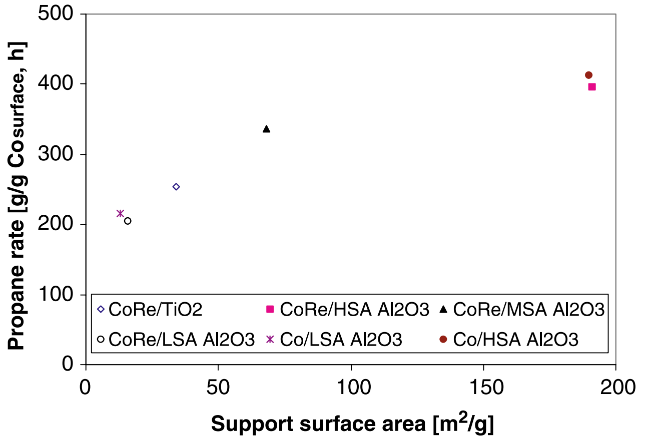

Figure 3. Initial rate of propene hydrogenation to propane as a function of the surface area of catalysts containing 12 wt% Co. LSA, MSA and HAS are low, medium and high surface area aluminas, respectively as defined in table 2. Conditions: 120 °C, 1.8 bar, $H_2/C_3H_6 = 6$ and GHSV = 31 000 N mL/g min.

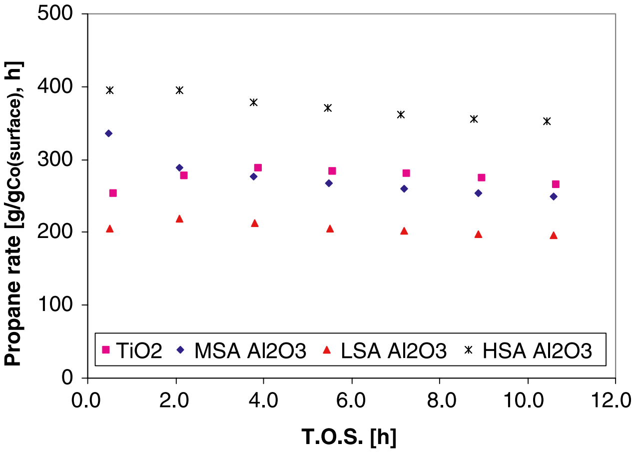

Figure 4. Rate of propene hydrogenation to propane as a function of time on stream (TOS) for Re promoted (0.5 wt%) catalysts with 12 wt% Co. LSA, MSA and HSA are low, medium and high surface area alumina, respectively as defined in table 2. Conditions: 120 °C, 1.8 bar, $H_2/C_3H_6 = 6$ and GHSV = 31 000 N mL/g min.

Promotion with rhenium possibly results in a small decrease in olefin hydrogenation rates for both low and high surface area alumina supported catalysts, but the differences are very small. Therefore, the addition of rhenium does not seem to influence the hydrogenation activity of the cobalt catalysts to any great extent. However, rhenium has a large effect on the dispersion of cobalt. On figure 3 the alumina supports are also compared with TiO_2 on otherwise similar catalysts and TiO_2 fits very well with the results obtained for the alumina supports.

The initial rate for propane formation for the 20 wt% catalysts is given in table 3. The Re (1.0 wt%) promoted catalyst was somewhat more active than the Pt (0.1 wt%) promoted catalyst, but the rate of deactivation was higher.

The above results are initial values. It is observed, however, that the rates change as a function of time on stream (TOS) and that the behaviour during the first hours depends on the support as shown on figure 4. The rate increases during the first hours for TiO_2 and the low surface alumina (LSA), but decreases for the medium (MSA) and high surface area alumina (HSA). For the two supports giving the lowest initial rates for propene hydrogenation to propane, the rate increases during an initial period. After about 10 h on stream when a pseudo steady-state is obtained, the relation between the alumina supports is still HAS > MSA > LSA, but the TiO_2 supported catalyst is now becoming more active than the medium surface area alumina.

Table 3
Rate of propene hydrogenation on 20 wt% cobalt catalysts

Catalyst	Support surface area (m^2/g)	Propane formation rate ($g/gCo_{(surface)}$, h)
CoPt/HSA Al_2O_3	185	418
CoRe/HSA Al_2O_3	191	467
CoRe/SiO_2	351	244

Experimental conditions: 120 °C, 1.8 bar, $H_2/C_3H_6 = 6$ and sGHSV = 47 000 N mL/g min. The amount of promoter is 1.0 wt% Re and 0.1 wt% Pt. HSA is high surface area alumina support. Details of the catalysts are given in table 2.

The results indicate that it is not only the surface area which is of importance, but also the type and/or structure of the support. This is further supported by the use of SiO_2 as support. As shown in table 3 the rate of propene hydrogenation to propane on the SiO_2 supported catalyst is much lower than on the high surface area support for otherwise equal catalysts. Although the surface area of silica is much higher than for alumina, the rate is lower. The catalyst supported on silica seems to be more stable than the catalyst supported on high surface area alumina (figure 5), but it should be kept in mind that the lower deactivation rate with silica is obtained at a lower conversion of propene.

Hydrogenation of olefins on metal surfaces is usually believed to be structure insensitive reactions [31], but in this case the rate (turnover frequency) is different on different supports. figure 3 shows that the rate of propene hydrogenation increases with increasing surface area of the support and from figure 2 it is obvious that the dispersion increases with increasing surface area for the two series of catalysts. However, promoting the 12 wt% cobalt catalysts with Re increases the dispersion, but it does not affect the hydrogenation activity (figure 3). Silica with very high surface area gave a catalyst with cobalt dispersion of 5.5%. The rate of propene hydrogenation for the silica supported catalyst is slightly higher than the low surface area catalyst with a comparable dispersion. Therefore, it does not seem to

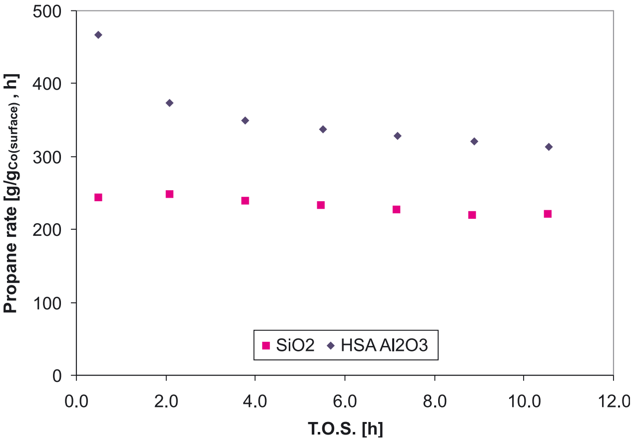

Figure 5. Rate of propene hydrogenation to propane as a function of time on stream (TOS) for Re (1.0 wt%) promoted catalysts with 20 wt% Co. HSA is high surface area alumina as defined in table 2. Conditions: 120 °C, 1.8 bar, $H_2/C_3H_6 = 6$ and GHSV = 47 000 N mL/g min.

exist a clear relationship between dispersion and the hydrogenation activity.

It has been discussed that hydrogen spillover from the metal to the support can do the support active or the spillover hydrogen may hydrogenate olefins [32,33]. It could therefore be that the observed increase in olefin hydrogenation activity with increasing support surface area is due to the ability of the support to store spillover hydrogen from the metal. The supports themselves have no catalytic activity. The different aluminas have been prepared by treating Puralox (γ-alumina) at different temperatures. The low surface alumina (LSA) consists of 86% α-alumina [25]. The idea of hydrogen spillover is therefore according to the experimental findings: The low surface alumina (LSA) gave the lowest activity for propene hydrogenation and the high surface area alumina (HSA) gave the highest activity. This is further supported by the use of silica as a support. Better ability to store hydrogen on alumina compared to silica could explain why the silica supported catalyst has a lower activity for hydrogenation of propane even though the surface area of silica is quite large.

The partial pressure of hydrogen is very important. By increasing the hydrogen to propene ratio from 3 to 6, it was observed that the conversion of propene increased from 50% to 95% (12% CoRe/HSA, doubling of the partial pressure of hydrogen by increasing the flow of hydrogen and decreasing the flow of He correspondingly). Increasing the hydrogen/propene ratio from 3 to 6 also changed the product composition, the amount of C_4 and in particular of C_{5+} decreased and the amount of ethane and methane increased.

The selectivity for propane is high for all catalysts, between 80% and 85%. The product selectivities after 30 min on stream for the 12 wt% cobalt catalysts are given in table 4 and for the 20 wt% cobalt catalysts in table 5. C_5 and higher hydrocarbons are the most important by-products. The C_{5+} selectivity for Re promoted samples is about 10–11% except for the SiO_2 supported catalyst on which a higher C_{5+} selectivity was observed (15.6%). The unpromoted catalysts (Co/LSA and Co/HSA) gave somewhat lower C_{5+} as shown in table 4.

The selectivity for C_4 compounds, the second most important by-product, was about 5% for all the catalysts except for CoRe/TiO_2 and Co/LSA which had a selectivity of C_4 below 3%. Ethene, ethane and methane were only minor products with selectivities below 1%. Coking was not observed as a problem at the low temperature used in this work.

3.3. C_{5+} selectivity in Fischer–Tropsch synthesis

It has been shown previously [25] that the C_{5+} selectivity in Fischer–Tropsch synthesis on similar catalysts depends on the surface area of the support. Since the C_{5+} selectivity in Fischer–Tropsch synthesis depends on the conversion, the selectivities given in table 1 are obtained at the same conversion. It is also evident from figure 2 that the dispersion depends on the surface area of the support. The dispersion increases with the support surface area.

A possible mechanism for explaining the effect of surface area could involve secondary reactions. Accord-

Table 4
Product distribution for 12 wt% Co catalysts after 0.5 h on stream

Selectivity /conversion (%)	CoRe/TiO_2	CoRe/HSA Al_2O_3	CoRe/MSA Al_2O_3	CoRe/LSA Al_2O_3	Co/LSA Al_2O_3	Co/HSA Al_2O_3
Conversion of C_3H_6	16.8	66.5	56.1	22.5	15.5	51.7
C_{5+}	11.5	10.1	10.1	10.3	8.4	7.6
C_4	2.2	5.0	5.0	5.4	2.9	5.7
Propane	85.1	82.6	83.1	83.3	87.3	84.0
Ethene	0.5	–	0.2	0.3	0.8	0.2
Ethane	0.6	2.2	1.6	0.8	0.7	2.4
Methane	–	0.1	–	–	–	0.1

Experimental conditions: 120 °C, 1.8 bar, $H_2/C_3H_6 = 6$ and GHSV = 31 000 N mL/g min. HSA, MSA and LSA are high, medium and low surface area supports, respectively. The promoted catalysts contain 0.5% Re. Details of the catalysts are shown in table 2.

Table 5
Product distribution for 20 wt% Co catalysts after 0.5 h on stream

Selectivity/ conversion (%)	CoPt/HSA Al_2O_3	CoRe/HSA Al_2O_3	CoRe/ SiO_2
Conversion of C_3H_6	66.1	88.1	29.0
C_{5+}	7.1	10.1	15.6
C_4	5.7	6.0	4.2
Propane	84.7	81.7	79.2
Ethene	–	–	0.2
Ethane	2.5	2.1	0.8
Methane	0.1	0.1	–

Experimental conditions: 120 °C, 1.8 bar, $H_2/C_3H_6 = 6$ and GHSV = 47 000 N mL/g min. HSA is high surface area alumina and the promoted catalysts contain 1.0 wt% Re or 0.1 wt% Pt. Details of the catalysts are shown in table 2.

ing to the simplified picture given in figure 1, hydrogenation of desorbed olefins will terminate the growing chain. As shown on figure 3 the catalysts with low surface area supports have the lowest activity for propene hydrogenation and hence an increased probability for olefin readsorption. Readsorbed olefins will participate in the chain growth resulting in an increased selectivity of higher hydrocarbons. The low surface area alumina catalysts also give the highest C_{5+} selectivity in Fischer–Tropsch synthesis.

It is important to emphasise that this is a model study and that no CO has been added to the feed. However, it gives a clear indication that secondary hydrogenation of olefins may contribute to the observed effect of surface area on the C_{5+} selectivity during Fischer–Tropsch synthesis.

4. Conclusions

Alumina supports with different surface areas were obtained by air treatment of γ-alumina at different temperatures. The cobalt dispersion increased with increasing surface area for both Co/Al_2O_3 and $CoRe/Al_2O_3$. The Re promoted catalysts have always higher dispersion compared with the unpromoted samples.

The rate of propene hydrogenation increases with increasing surface area for alumina supported catalysts. The TiO_2 supported catalyst followed the same relationship, but the SiO_2 supported catalyst did not. Differences in the supports ability to store hydrogen can be a reason for the observed differences in the propene hydrogenation activity.

Promoting the 12 wt% cobalt catalyst with Re increases the dispersion, but it did not affect the rate of hydrogenation. However, rhenium promotion leads to a slightly improved selectivity for C_{5+} products in the Fischer–Tropsch synthesis.

A higher C_{5+} selectivity in Fischer–Tropsch synthesis is obtained for cobalt catalysts supported on a low surface area support compared to catalysts on high surface alumina. This correlates well with the low olefin hydrogenation activity on low surface area alumina supports.

Acknowledgments

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