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Silica supported cobalt Fischer–Tropsch catalysts: effect of pore diameter of support

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Abstract

The influence of the effect of average pore diameter of silica support on the physical and chemical properties of supported cobalt catalysts and their performance in the Fischer–Tropsch synthesis was investigated. Silicas with different mean pore diameter (20, 40, 60, 100 and 150 Å) were impregnated with cobalt nitrate to produce catalysts containing 20 wt.% cobalt. The metal crystallite size and degree of reduction was found to increase with increasing pore diameter of the support for supports with an average pore diameter larger or equal to 40 Å, and hence the dispersion decreased. In impregnated catalysts, the metal crystallites seems to appear in clusters on the support. With increasing average pore diameter, the size of these clusters increases. In the Fischer–Tropsch synthesis, the 100 Å supported catalyst proved to be the most active and selective catalyst for hydrocarbon formation. The C_{5+} and methane selectivity passed through a maximum and minimum at the 100 Å supported catalyst, respectively, which can be explained quantitatively using the reactant transport model proposed by Iglesia et al. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fischer–Tropsch synthesis; Cobalt; Silica; Pore diameter; Selectivity; Diffusion limitations

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1. Introduction

Cobalt catalysts are promising catalysts for the synthesis of fuels and chemicals via the Fischer–Tropsch process [1]. To expose as many metal atoms as possible to gaseous reactants, the relatively precious metal cobalt is normally deposited on a high surface area carrier to obtain a high metal dispersion [2]. Commonly used high surface area carriers are silica, alumina, and to a lesser extent, carbon, titania and magnesia. The supported metal catalyst has significant advantages over their bulk metal counterparts. They are drastically cheaper as the activity per weight of active metal is increased due to high dispersions on high surface area carriers that maximise metal usage. They also show enhanced thermal stability due to interaction between the active metal and support which leads to a decrease in sintering and an extended catalyst life [3].

Reuel and Bartholomew [4] showed that the support could significantly influence the extent of reduction, morphology, adsorption and activity/selectivity properties of the active phase, especially in well-dispersed catalysts. Iglesia et al. [5] also reports that hydrocarbon product selectivity depends on a complex interplay between diffusion, reaction and convection processes occurring within the catalyst pellets and reactors. A structural parameter, which includes parameters such as pellet radius, pellet porosity, mean pore radius of support and active metal distribution on support, seems to play a vital role in determining the Fischer–Tropsch activity and selectivity.

In this study, the effect of the pore diameter of the silica support on the physico-chemical properties of supported cobalt catalysts will be investigated in

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detail. Furthermore, the performance of the impregnated catalysts in the Fischer–Tropsch synthesis will be investigated. The validity of the reactant transport model proposed by Iglesia and co-workers [7] will be verified.

2. Experimental

The catalysts were synthesised by the incipient wetness impregnation method using an aqueous solution of cobalt nitrate so as to produce a catalyst containing 20 wt.% of Co metal on silica. The characteristics of the silicas used are given in Table 1. Following impregnation, the catalysts were dried in a rotor evaporator for 30 min at 95 °C and 40 kPa and stored in a desiccator.

The composition of the synthesised catalysts was verified using atomic absorption spectroscopy. The cobalt loading for all samples was found to be within the error of measurement of the after preparation expected loading.

The reduction behaviour of the catalyst precursors was studied using temperature-programmed reduction (TPR) using home-built equipment [6]. The catalyst precursor (0.15 g) was loaded into the quartz TPR cell and heated at 10 K/min up to the final calcination temperature (473 K) in 60 ml (NTP)/min N_2, and held there for 2 h. A calcination step was included to remove all the nitrates from the catalyst. Subsequently, the reactor was cooled to 373 K. Finally, the catalyst was reduced using a linear temperature program (10 K/min up to 1273 K) in 60 ml (NTP)/min reducing gas (6.36% H_2 in N_2). The TPR procedure was calibrated using the reduction of CuO.

Metal surface area and cobalt dispersion was determined using hydrogen chemisorption, which was performed using a Micrometrics ASAP 2000C apparatus. The catalyst precursor was heated at 10 K/min up to 623 K under hydrogen (60 ml (NTP)/min), and kept at this temperature for 16 h. After reduction the catalyst was degassed for 2 h at 10^{-5} Torr in order to eliminate chemisorbed hydrogen. The temperature was then lowered to 373 K while maintaining the vacuum. Chemisorption isotherms were measured between 50 and 400 mm Hg. For the calculation of the average particle diameter it was assumed that reduced cobalt and non-reduced cobalt form different phases [7]. Using a density of 8.9 g/cm^3 and assuming spherical metallic cobalt particles, the average particle size was calculated.

Transmission electron microscopy (TEM) employing a JEOL 200CX transmission electron microscope with an acceleration voltage of 200 kV was also used to determine the cobalt crystallite size. The catalysts were reduced in H_2 at 623 K for 16 h. To prevent rapid re-oxidation, the reduced catalysts were stored under *n*-hexane. Following reduction, each sample was crushed using a mortar and pestle in order to obtain finer particles. The finer particles were dispersed in methanol and placed on carbon-coated copper grids. The samples were allowed to dry. At least, three TEM images were taken to evaluate the cobalt crystallite size and the formation of clusters of cobalt particles.

The performance of the catalysts in the Fischer–Tropsch synthesis was tested in a down flow fixed bed reactor. A glass reactor was mounted inside a stainless steel mantle. 1.00 g of catalyst (212–250 μm) was loaded into the isothermal zone of the reactor and the catalyst was reduced using a linear temperature ramp (10 K/min up to 623 K) in 60 ml (NTP)/min hydrogen and held at the final reduction temperature (623 K) for 16 h. After reduction, the catalyst was cooled down to reaction temperature and pressurised. The catalysts

Table 1
Characteristics of the silica used

	Surface area[a] (m^2/g)	Mean pore diameter[a] (Å)	Pore volume[b] (cm^3/g)
Davisil, grade 646	300 (300)	150 (143)	2.3
Davisil, grade 636	400 (312)	100 (101)	2.0
Merck, grade 10181	480 (530)	60 (60)	1.5
Merck, grade	675 (547)	40 (46)	1.35
May & Baker, lot 69554	750 (657)	20 (20)	0.65

[a] As given by supplier and in brackets of the reduced Co/SiO_2 catalyst as measured using BET.
[b] Measured H_2O uptake.

were compared at approximately the same conversion (low CO-conversion (<5%) at 473 K and high CO-conversion ($X_{co} = 30$–50%) at 493 K) using a total reaction pressure of 15 bar and $(H_2/CO)_{inlet} \sim 2.0$.

Argon was added after the reactor to the product stream to maintain the pressure. After the pressure release valve, a flow of cyclohexane in nitrogen was added to the product stream as an internal standard. Samples of the product stream were taken using the ampoule sampling technique [8]. The organic product compounds were separated using a 50 m OV-1 column ($d_i = 0.25$ mm, $d_f = 0.2$ μm) employing a temperature program from 203 to 553 K. The products were detected using an FID. The inorganic gases were separated isothermally at 333 K using a 3 m × 6.4 mm carbosieve column and detected using a TCD.

3. Results and discussion

The influence of pore diameter on the reduction behaviour of the Co/SiO_2 catalysts was studied by TPR. Fig. 1 shows the TPR profiles obtained for the calcined catalyst precursors. Table 2 lists the amount of hydrogen consumed per mole of cobalt for the reduction of the calcined catalyst and the temperature of the first maximum.

The occurrence of multiple reduction peaks indicates the presence of a number of reducible cobalt species present in the catalyst precursor. The first peak has been ascribed the reduction of Co_3O_4 to CoO, followed by the second peak which corresponds to the reduction of CoO to Co. Hydrogen consumption occurring at temperatures larger than 723 K may be

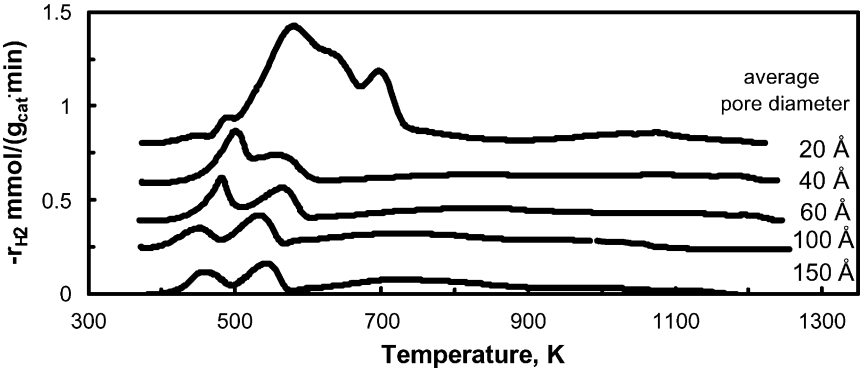

Fig. 1. TPR profiles of calcined catalyst precursors (calcination: 473 K for 2 h in 60 ml (NTP)/min N_2; reduction: 373–1273 K at 10 K/min in 60 ml (NTP)/min in 6.36% H_2/N_2).

Table 2
Hydrogen consumption per mole of cobalt in the TPR[a] of the impregnated Co/SiO_2 catalysts after calcination and after reduction

Support diameter (Å)	Calcined catalysts[b]		Reduced catalysts[c]	
	H_2/Co (mol/mol)	$T_{1st\ maximum}$[d] (K)	H_2/Co (mol/mol)	Degree of reduction[e] (%)
20	2.4	608	0.12	88
40	1.37	505	0.52	48
60	1.2	484	0.34	66
100	1.14	464	0.26	74
150	1.08	457	0.09	91

[a] TPR: 373–1273 K at 10 K/min in 60 ml (NTP)/min 6.36% H_2/N_2.

[b] Calcination prior to TPR: 473 K for 2 h in N_2.

[c] Reduction prior to TPR: 10 K/min up to 623 K in 60 ml (NTP)/min H_2 kept at 623 K for 16 h.

[d] First maximum observed in TPR reduction of calcined catalyst precursor.

[e] Assuming all unreduced cobalt is present as divalent cobalt.

assigned to the reduction of cobalt which has some interaction with the support, since bulk cobalt oxide is reduced completely by 723 K [9]. In general, these peaks are due to the reduction of cobalt silicates [10]. With increasing pore diameter of the support the temperature of the first maximum shifts towards lower temperatures. This might be indicative for the presence of larger cobalt oxide crystallites after calcination on the silica supports with a larger average pore diameter.

The amount of hydrogen consumed per mole of cobalt ranged from 1.08 to 2.4. This is quite surprising since it is known that these values can range from 1 for the reduction of CoO to 1.33 for the reduction of Co_3O_4 [4]. The large hydrogen consumption for the Co/SiO_2 catalyst using silica with an average pore diameter of 20 Å could be reproduced a number of times. The unusual high amount of hydrogen consumed per mole of cobalt might be ascribed to the reductive nitrate decomposition left on the support after calcination. The H_2/Co ratio and the decomposition temperature of Co_3O_4 increased with decreasing pore diameter, i.e. more divalent cobalt and less trivalent cobalt.

The degree of reduction of the reduced cobalt catalysts was determined using TPR of the reduced catalysts. Prior to TPR, the samples were reduced in situ (reduction conditions: 10 K/min up to 623 K in 60 ml (NTP)/min hydrogen and kept at 623 K for 16 h). TPR was performed using a linear temperature program (10 K/min up to 1273 K) in 60 ml (NTP)/min 6.36% H_2 in N_2. Table 2 lists the hydrogen to cobalt molar ratios and the degree of reduction of the reduced catalysts.

The amount of hydrogen consumed for the complete reduction of the reduced catalyst samples ranged from 0.12 to 0.54 mol H_2 consumed per mole Co. Assuming that all unreduced cobalt is present in the divalent form, the degree of reduction of the catalyst samples varies between 88 and 46%. The amount of hydrogen consumed for the reduction of cobalt, which could not be reduced during the applied reduction procedure, increased as the pore diameter decreased for catalysts on supports with a pore diameter larger than 20 Å. Hence, the degree of reduction increased with increasing pore diameter. This has been reported previously by Puskas et al. [7]. They concluded that the degree of reduction increased with pore diameter as a result of a decrease in surface area of support. Silica gel has approximately a constant number of silanol groups per unit surface area and therefore it might be postulated that the increase in silanol groups might cause an increase in the formation of cobalt species, which can only be reduced at high temperatures [11].

The resulting size of the cobalt crystallites after reduction in hydrogen for 16 h at 673 K was determined using chemisorption and TEM (see Table 3). The crystallite size determined using these two techniques concur well. Using a silica support with an average pore diameter of 20 Å results in the formation of large cobalt crystallites, which do not fit in the pores of the support. Hence, the cobalt crystallites are on the external surface of the silica particles. For the supports with an average pore diameter larger than 20 Å, the cobalt crystallite size increases with increasing the average pore diameter of the support. Although, the cobalt crystallite diameter for the supports with an average pore diameter of 40 and 60 Å, seems to be blocking the pores, it must be realised that a significant fraction of the pore volume has a pore diameter larger than the average pore diameter. During the drying of the catalyst precursor, small droplets containing cobalt nitrate will be formed, from which the cobalt

Table 3
Physical–chemical characteristics of reduced catalysts (reduction conditions: 10 K/min up to 623 K in 60 ml (NTP)/min hydrogen for 16 h) as determined by H_2 chemisorption, CO chemisorption and TEM

Pore diameter of support (Å)	H_2 chemisorption		TEM	
	Uptake ($cm^3/g_{red.,cat.}$)	Crystallite size (nm)	Crystallite size (nm)	Cluster size (nm)
20	1.8	19.8	26	169–220
40	2.5	5.9	3.0	54–85
60	3.5	6.0	6.7	68–100
100	3.3	7.3	6.9	100–150
150	3.0	10.6	8.3	200–233

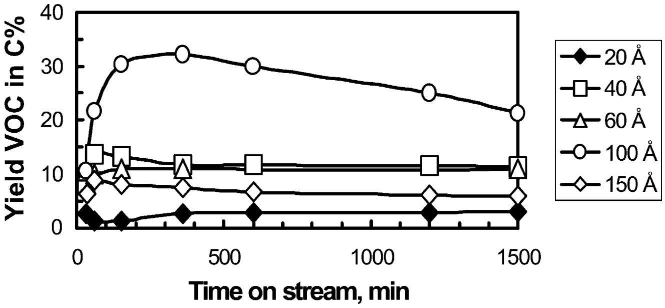

Fig. 2. Yield of the VOC in the Fischer–Tropsch synthesis as a function of time on stream ($T_{\mathrm{reaction}} = 473\,\mathrm{K}$, $p = 15\,\mathrm{bar}$, $(\mathrm{H_2/CO})_{\mathrm{inlet}} = 2$, GHSV = 1.8 l (NTP)/h g).

crystallites are formed. If the droplets are in the pores of the support, the pore diameter will have a dominant effect on the resulting droplet size and hence the final cobalt crystallite size.

The TEM images show that cobalt crystallites on the silica support are present in clusters (as reported previously [12]). With increasing pore diameter, the cluster size was found to increase except for the 20 Å supported catalyst, which can be related to the influence of the pore diameter of the support on the droplet size.

Fig. 2 shows a typical time-on-stream in the Fischer–Tropsch synthesis behaviour for the catalysts investigated. After 25 h on stream steady state for the formation of products was reached for all the catalysts except the catalyst supported on silica with an average pore diameter of 100 Å. All the catalysts except the 20 Å show an initial increase in the yield of volatile organic product compounds (VOCs), followed by a decrease before steady state is reached. This initial increase in activity is very pronounced for the catalyst supported on silica with an average pore diameter of 100 Å. Its activity increases from 10 C% at 30 min to 32 C% at 250 min. However, this catalyst also shows strong deactivation after the initial increase in activity.

The activity of the catalysts in the Fischer–Tropsch synthesis were compared at 473 K ($X_{\mathrm{CO}} < 5\%$) and at 493 K ($X_{\mathrm{CO}} = 30$–60%) (see Table 4). CO conversions less than 5% were achieved by using high gas flow rates. CO conversions of 30–60% at 493 K were established by using the lowest possible gas flow rate. A high conversion could not be achieved with the cobalt catalyst supported on silica with an average pore diameter of 20 Å (maximum CO-conversion of only 16% could be achieved). It has been reported that the turnover frequency should be independent of the cobalt crystallite size [13]. The turnover frequency varies significantly for the investigated catalysts. The variation can be ascribed to the different degree of deactivation of the different catalysts, since the turnover frequency is based on the metal dispersion of the fresh catalyst.

Table 4
Comparison of the activity of the cobalt catalysts supported on silica with differing average pore diameter ($T_{\mathrm{reduction}} = 623\,\mathrm{K}$; $t_{\mathrm{reduction}} = 16\,\mathrm{h}$; $(\mathrm{H_2/CO})_{\mathrm{inlet}} = 2$; $p_{\mathrm{reaction}} = 15\,\mathrm{bar}$)

Support pore diameter (Å)	$T_{\mathrm{reaction}} = 473\,\mathrm{K}$			$T_{\mathrm{reaction}} = 493\,\mathrm{K}$		
	GHSV (l (NTP)/h g)	X_{CO} (C%)	TOF[a] ($\mathrm{s^{-1}}$)	GHSV (l (NTP)/h g)	X_{CO} (C%)	TOF[a] ($\mathrm{s^{-1}}$)
20	1.8	2.0	0.71	–	–	–
40	6.0	2.6	0.38	0.9	44	0.91
60	6.0	3.5	0.31	0.9	41	0.83
100	12.6	6.0	0.84	0.9	60	1.72
150	6.0	3.0	0.32	0.9	30	0.95

[a] Turnover frequency of the number of CO molecules converted per cobalt, which was in the zero-valent state before the Fischer–Tropsch synthesis.

Table 5
Comparison of the selectivity and the chain growth probability α (in the range C_7–C_{12}) of the cobalt catalysts supported on silica with differing average pore diameter ($T_{\mathrm{reduction}} = 623\,\mathrm{K}$; $t_{\mathrm{reduction}} = 16\,\mathrm{h}$; $(H_2/CO)_{\mathrm{inlet}} = 2$; $p_{\mathrm{reaction}} = 15\,\mathrm{bar}$)

Support pore diameter (Å)	$T_{\mathrm{reaction}} = 473\,\mathrm{K}$				$T_{\mathrm{reaction}} = 493\,\mathrm{K}$			
	X_{CO} (C%)	S_{CH_4} (C%)	$S_{C_{5+}}$ (C%)	α	X_{CO} (C%)	S_{CH_4} (C%)	$S_{C_{5+}}$ (C%)	α
20	2.0	44.0	32.3	0.72	–	–	–	–
40	2.6	18.7	60.4	0.77	44	12.1	71	0.80
60	3.5	28.5	54.8	0.81	41	17.5	69.4	0.83
100	6.0	19.2	61.8	0.80	60	11.2	74	0.85
150	3.0	37.6	43.7	0.84	30	13.7	72.1	0.84

The selectivity of the Fischer–Tropsch synthesis over the cobalt catalysts supported on silicas with different average pore diameter is given in Table 5. With increasing pore diameter of the support the C_{5+}-selectivity seems to pass a maximum as predicted by the transport model proposed by Iglesia et al. [5]. According to this model, the selectivity of the Fischer–Tropsch synthesis may be characterised by the structural parameter χ

$$\chi = \frac{R_0^2 \varepsilon \theta_{\mathrm{CO}}}{r_{\mathrm{P}}}$$

The structural parameter χ depends only on the number of sites available for chain desorption and re-adsorption and on the average distance molecules must travel by diffusion within the intra-pellet liquid phase before they are removed by convective gas flow within intra-pellet bed interstices.

Fig. 3 shows the C_{5+}-selectivity as a function of the structural parameter χ for both the experiments at 473 K ($X_{CO} < 5\%$) and the experiments at 493 K ($X_{CO} = 30$–60%). In addition to our experimental data, a curve showing the trend observed by Iglesia et al. [5] (for conversion levels between 55 and 65%) is given. The pore diameter has only a small effect on the structural parameter, although a wide variation in the C_{5+}-selectivity was obtained. The quantitative agreement with the data obtained by Iglesia et al. [5] is excellent for the experiments carried out at 493 K and conversion levels between 30 and 60%. At 473 K and low conversion, very low C_{5+}-selectivities were obtained with a larger deviation from the proposed correlation with the structural parameter χ, although the principal trend can still be observed, i.e. an increase in the C_{5+}-selectivity with increasing value for the structural parameter χ. The maximum C_{5+}-selectivity,

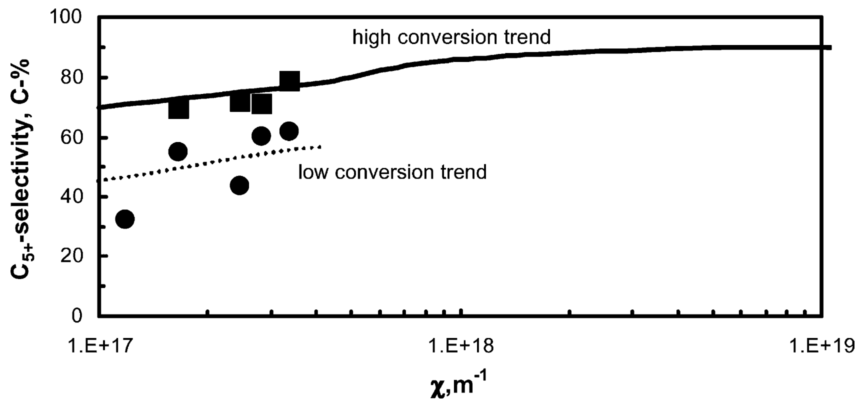

Fig. 3. The effect of structural parameter (χ) on the C_{5+}-selectivity in the Fischer–Tropsch synthesis ($p = 15\,\mathrm{bar}$, $(H_2/CO)_{\mathrm{inlet}} = 2$, GHSV adjusted to obtain desired conversion—see Table 4; (solid line) redrawn from Iglesia et al. [5]; (●) $T_{\mathrm{reaction}} = 473\,\mathrm{K}$ and $X_{CO} < 5\%$; (■) $T_{\mathrm{reaction}} = 473\,\mathrm{K}$ and $X_{CO} = 30$–60%).

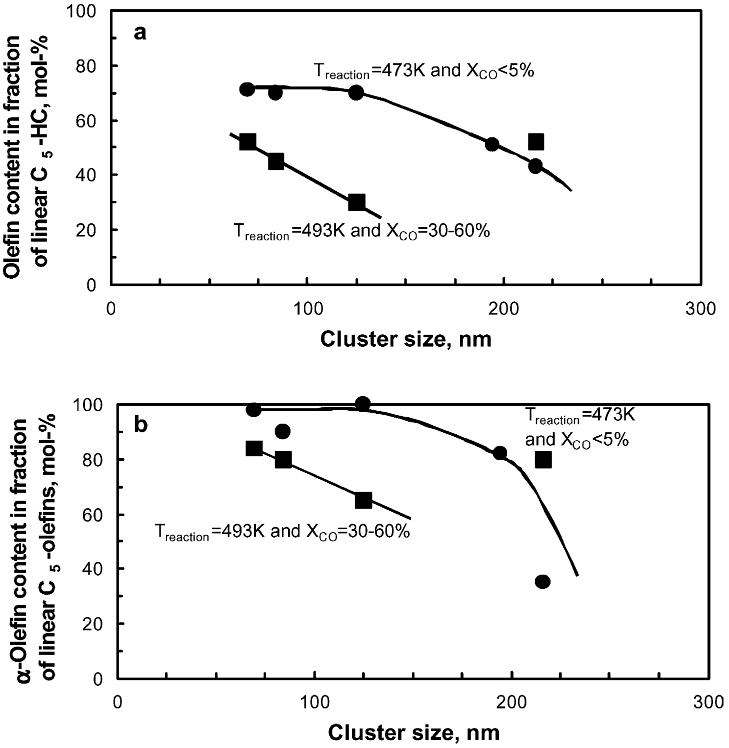

Fig. 4. The effect of size of cluster of cobalt crystallites on the extent of secondary reactions in the Fischer–Tropsch synthesis ($p = 15\,\text{bar}$, $(H_2/CO)_{\text{inlet}} = 2$, GHSV adjusted to obtain desired conversion—see Table 4; (solid line) redrawn from Iglesia et al. [5]; (●) $T_{\text{reaction}} = 473\,\text{K}$ and $X_{CO} < 5\%$; (■) $T_{\text{reaction}} = 473\,\text{K}$ and $X_{CO} = 30–60\%$). (a) Olefin content in the fraction of linear C_5-hydrocarbons, (b) α-olefin content in the fraction of linear C_5-olefins.

which can be achieved at low conversion, seems to be lower. This can be rationalised based on the expected lower local partial pressures of the reactive olefins, since their re-incorporation in the chain growth process will enhance the C_{5+}-selectivity. The extent of secondary reactions does not correlate well with the structural parameter χ.

Feller et al. [12] stressed the importance of the clusters in impregnated cobalt catalysts. With increasing cluster size, they observed a strong increase in the extent of secondary reactions, i.e. olefin re-adsorption. Fig. 4a shows the olefin content in the fraction of linear C_5-hydrocarbons as a function of the cluster size. With increasing cluster size, a decrease in the olefin content in the fraction of linear C_5-hydrocarbons is observed. Thus, the extent of secondary hydrogenation increases with increasing size of the cobalt cluster caused by the enhanced probability for re-adsorption of the primarily formed olefins.

Fig. 4b shows the effect of cluster size on the secondary double bond isomerisation. With increasing cluster size, the α-olefin content in the fraction of linear C_5-olefins decreases. Thus, the extent of double bond isomerisation increases with increasing size of the cobalt cluster caused by the enhanced probability for re-adsorption of the primarily formed olefins.

4. Conclusions

The pore diameter of the support has a strong effect on the obtained cobalt crystallite size using the incipient wetness technique for the preparation of silica supported cobalt catalysts using cobalt nitrate. With supports with a very small average pore diameter (ca. 20 Å), cobalt crystallites formed are too big to fit in the pore. They will be located on the external surface of the support. With supports with a larger average pore diameter, the obtained cobalt crystallite size increases with increasing pore diameter. The distribution of cobalt crystallites over the support is inhomogeneous, i.e. clusters with cobalt crystallites can be found on the support.

The obtained activity of the supported cobalt catalysts in the Fischer–Tropsch synthesis seems to be a function of the metal dispersion and the extent of deactivation during the Fischer–Tropsch synthesis. The C_{5+}-selectivity can be described using the reactant transport model proposed by Iglesia et al. [5]. The maximum C_{5+}-selectivity is, however, a function of conversion. The extent of secondary reactions is a function of the size clusters with cobalt crystallites.

Acknowledgements

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