Catalysis Letters Vol. 101, Nos. 1–2, May 2005 (© 2005)
DOI: 10.1007/s10562-005-3759-z

Chemisorption of C3 hydrocarbons on cobalt silica supported Fischer–Tropsch catalysts

Anatoly S. Lermontov, Jean-Sébastien Girardon, Anne Griboval-Constant, Stanislas Pietrzyk, and Andrei Y. Khodakov*

Laboratoire de Catalyse de Lille, Université des Sciences et Technologies de Lille, Bât. C3, Cité Scientifique, 59655 Villeneuve d' Ascq, France

Received 19 October 2004; accepted 10 January 2005

Chemisorption of propene and propane was studied in a pulse reactor over a series of cobalt silica-supported Fischer–Tropsch catalysts. It was shown that interaction of propene with cobalt metal particles resulted in its rapid autohydrogenation. The reaction consists in a part of the propene being dehydrogenated to surface carbon and CH_x chemisorbed species; hydrogen atoms released in the course of propene dehydrogenation are then involved in hydrogenation of remaining propene molecules to propane at 323–423 K or in propene hydrogenolysis to methane and ethane at temperatures higher than 423 K. The catalyst characterization suggests that propene chemisorption over cobalt catalysts is primarily a function of the density of cobalt surface metal sites. A correlation between propene chemisorption and Fischer–Tropsch reaction rate was observed over a series of cobalt silica-supported catalysts. No propane chemisorption was observed at 323–373 K over cobalt silica-supported catalysts. Propane autohydrogenolysis was found to proceed at higher temperatures, with methane being the major product of this reaction over cobalt catalysts. Hydrogen for propane autohydrogenolysis is probably provided by adsorbed CH_x species formed via propane dehydrogenation. Propene and propane chemisorption is dramatically reduced upon the catalyst exposure to synthesis gas ($H_2/CO = 2$) at 323–473 K. Our results suggest that cobalt metal particles are probably completely covered by carbon monoxide molecules under the conditions similar to Fischer–Tropsch synthesis and thus, most of cobalt surface sites are not available for propene and propane chemisorption.

KEY WORDS: cobalt catalysts; Fischer–Tropsch synthesis; olefin readsorption; autohydrogenation; hydrogenolysis.

1. Introduction

Fischer–Tropsch (FT) synthesis produces a wide range of hydrocarbons from synthesis gas. The renewed interest to FT synthesis is primarily due to its use in the conversion of natural gas to more valuable long-chained hydrocarbons. Owing to their high activity and selectivity, cobalt-supported catalysts have been found particularly suitable for the production of higher hydrocarbons [1–3].

The mechanism of FT synthesis represents linear polymerization of adsorbed CH_x monomers formed, by hydrogenation of adsorbed CO molecules [2,3]. It has been suggested [3] that chain growth proceeds via the addition of surface methylene species to adsorbed alkyl groups, which can undergo β-hydrogen abstraction to form linear α-olefins or hydrogen addition to form *n*-paraffins. It has been shown that *n*-paraffins and α-olefins are the primary products of FT polymerization, and that the reaction kinetics and hydrocarbon selectivity normally obey an Anderson–Schulz–Flory (ASF) distribution. The secondary reactions, however, lead to deviations from ASF statistics, which are generally attributed to readsorption of α-olefins produced by the FT reaction. It has been shown that the readsorbed olefins could be either hydrogenated or reinserted into the polymerization sequence. The rate of hydrogenation to the rate of olefin reinsertion ration depends on a number of parameters, e.g. the pressure of carbon monoxide, hydrogen and water [4]. Olefin hydrogenation leads to *n*-paraffins, which are terminal products of FT synthesis, whereas olefin reinsertion into the polymerization network reverses the predominant chain termination pathway by reinitiating the surface chain growth. As the result, the chain termination probability is reduced, while the paraffin to olefin ratio and selectivity to higher hydrocarbons are increased. Readsorption of olefins becomes more influential with increasing bed residence time and carbon monoxide conversion. The effect of olefin readsorption on the selectivity of FT synthesis has been confirmed by olefin co-feeding experiments [5,6] with the highest rate of reinsertion observed for C2 and C3 olefins [7]. Propene hydrogenation as a model reaction of secondary olefin readsorption and hydrogenation has been studied by Aaserud [8] and Schanke [9]. It has been found that lower activity of the catalysts in propene hydrogenation favors propene readsorption and leads to a higher C5+ selectivity in FT reaction.

Only chemisorption of methane and ethene has been extensively studied on transition metals, while studies of propene chemisorption have been mostly limited to

---

* To whom correspondence should be addressed.
E-mail: andrei.khodakov@ec-lille.fr

monocrystals and Pt catalysts. It has been shown that propene adsorption on Pt/SiO_2 catalysts at room temperature leads to a variety of structures, including propylidyne, di-σ-bonded and π-bonded propene [10–13]. Carbon-13 NMR shows [14] that at elevated temperatures propylidyne decomposes over Pt catalysts via dehydrogenation to surface carbon. Besides molecular desorption and hydrogen production from propene dehydrogenation over Pt(111), a small amount of propane was detected over 280 K, which is probably due to self-hydrogenation of the olefin [15].

Overall, despite the fact that olefin readsorption seems to be at the heart of the FT synthesis mechanism, very few studies have addressed the detailed mechanism of C3+ olefins chemisorption and reaction over cobalt-supported catalysts. The present paper is focused on adsorption and reaction of propene and propane over cobalt silica-supported FT catalysts in a pulse reactor. The objective of the work is to obtain new insights into the mechanism of propene and propane interaction with cobalt-supported FT catalysts at different conditions. For a series of cobalt silica supported catalysts, the data on propene chemisorption are discussed alongside with the results of catalyst characterization and compared with the catalytic performance in FT synthesis.

2. Experimental

2.1. Catalyst preparation

Cobalt-supported catalysts were prepared using impregnation of silica (Cab–o–Sil M5, $S_{BET} = 230$ m^2/g) with aqueous solutions of cobalt nitrate or acetate and are labeled as CoN and CoAc, respectively. Prior to impregnation, silica support was agglomerated by wetting in distilled water. Following the impregnation stage, the catalysts were dried overnight at 373 K and then calcined in flowing air at 373–673 K. The temperature ramp was 1 IC/min. The cobalt content and temperatures of catalyst calcination are shown in table 1. Prior to chemisorption experiments and FT catalytic tests, the catalysts were reduced in a flow of hydrogen at 673 K for 5 h. Further details of catalyst preparation and characterization are available from Ref. [16].

2.2. Catalyst characterization

The surface area of the catalysts was measured by nitrogen adsorption using BET method. Cobalt dispersion was measured by X-ray diffraction, the powder diffraction patterns of oxidized cobalt catalysts were recorded using a Siemens D5000 diffractometer (Cu(Kα) radiation). The average crystallite size of Co_3O_4 was calculated according to the Scherrer equation [17] using a (440) peak at $2\theta = 65.344°$.

Cobalt reducibility was evaluated from X-ray photoelectron spectra (XPS). XPS surface analyses were performed using a VG ESCALAB 220XL spectrometer. The Al(Kα) nonmonochromatized line (1486.6 eV) was used for excitation with a 300 W-applied power. The analyzer was operated in a constant pass energy mode ($E_{pass} = 40$ eV) and the binding energies were referenced to the Si 2p core level (103.6 eV) of the SiO2 support. The powdered catalyst was pressed as thin pellets onto a steel block. *In situ* reduction of the cobalt catalysts was carried out in pure hydrogen at 673 K for 5 h in the reactor cell of the preparation chamber attached to the analysis chamber of the spectrometer, whilst the spectroscopic measurements were carried out under vacuum better than 10^{-7} Pa.

2.3. FT catalytic measurements

The carbon monoxide hydrogenation was carried out in a fixed bed microreactor at atmospheric pressure. The catalyst was crushed and sieved to obtain catalyst grains between 0.05 and 0.2 mm in diameter. After the reduction, a flow of premixed synthesis gas with the molar ratio of $H_2/CO = 2$ was introduced into the reactor. The reaction temperature was 463 K. The carbon monoxide contained 5% of nitrogen, which was used as an internal standard for calculating carbon monoxide conversion. The gas transfer lines were kept at 423 K to avoid possible condensation of the reaction products. The reaction products were analyzed on-line by gas chromatography using a Hewellet-Packard 5890 Series II Gas Chromatograph with a 13X molecular sieve column and a thermal conductivity detector for the analysis of H_2, N_2, CO, CO_2 and CH_4. C_1–C_{18} hydrocarbons were separated on a packed 10% CP-Sil5 column on Chromosorb WHP and analyzed by a flame-ionization detector.

Table 1
Cobalt silica-supported FT catalysts

Catalyst	Cobalt content, wt.%	S_{BET}, m^2/g	$T_{calination}$, K	dCo_3O_4 (XRD), nm	Cobalt dispersion, %	Relative amount of metallic cobalt after reduction (XPS), %	Estimated number of cobalt metal sites, μmol/g
CoNl	12.0	–	673	21	6.0	~65	79.3
CoN2	9.9	180	423	12.3	10.4	~60	104.7
CoN3	9.9	128	373	9.6	13.3	~20	44.6
CoAcl	9.5	162	673	–	–	~11	–
CoAa	9.5	163	443	–	–	~26	–

Propene and propane chemisorption

Reaction and adsorption experiments were performed at transient conditions using a pulse reactor with helium as the carrier gas, whereas argon was used as the carrier gas in all experiments involving deuterium. Following reduction in hydrogen, the studied catalysts were purged for about 20 min in a flow of helium at temperatures ranging from 373 to 673 K. The reactor loading was usually 0.1 g of the catalyst diluted in 0.5 mL carborundum. The pulse volume was typically 0.1 cm^3. The product analysis was carried out using gas chromatography with a Chrompack Plot 0.53-mm capillary column, a flame-ionization and thermoconductivity detectors. Time-resolved mass-spectra of the reaction products were also recorded using a Pfeiffer QMS analytical system equipped with a Quadstar QMS-200 mass spectrometer.

3. Results and discussion

3.1. *Catalyst characterization*

3.1.1. *X-ray diffraction*

In agreement with previous reports [16,18–20], XRD patterns of the oxidized catalysts prepared from cobalt nitrate (not shown) indicate the presence of Co_3O_4 crystalline phase. The width of the XRD peaks is a function of catalyst calcination temperature with the broader XRD peaks observed for the catalysts calcined at lower temperature. The particle size values for cobalt oxide crystallites in these catalysts calculated using Scherrer equation [17] are presented in the table 1. These data have been utilized to calculate to the corresponding cobalt metal particle size according to the relative molar volumes of metallic cobalt and Co_3O_4. The resulting conversion factor for the diameter of a given Co_3O_4 particle being reduced to metallic cobalt is: $d(Co^0) = 0.75\ d(Co_3O_4)$ [18,21]. Cobalt dispersion (D, %) was calculated from the average metal particle sizes (nm) assuming spherical uniform particles with site density 14.6 atoms/nm^2, by the use of formula: $D=96/d$ [18,21].

Only very broad low intensity XRD peaks are observed in the oxidized catalysts prepared from cobalt acetate, indicating low concentrations of cobalt oxide crystalline phases. In agreement with earlier data [22–26], this observation suggests the presence of relatively high concentration of hardly reducible amorphous cobalt silicate. Our previous report showed [16] that higher concentration of hardly reducible cobalt silicate in the catalysts prepared from cobalt acetate could be primarily attributed to the exothermicity of cobalt acetate decomposition. A more efficient heat flow control at the stage of cobalt acetate decomposition significantly increases the concentration of easily reducible Co_3O_4 in the oxidized catalysts and thus, the number of cobalt metal active sites after the catalyst reduction. It is known that amorphous cobalt silicate can be reduced only at temperatures in excess of 973 K. Therefore, it is expected that these catalysts would not produce any considerable concentration of cobalt metal sites after reduction in hydrogen at 673 K.

3.1.2. *X-ray photoelectron spectroscopy*

The Co2p XPS spectra of the reduced cobalt silica supported catalysts are shown in figure 1. The energy (777–778 eV) of $Co2p_{3/2}$ lines and spinorbital splitting (15.0 eV) are typical of cobalt metal phase in CoN1 and CoN2 samples [27–29]. This suggests a higher relative concentration of cobalt metal phase, and therefore a higher extent of cobalt reduction. The XPS Co2p spectrum of CoN3 indicates the presence of both Co^{2+} species ($Co2p_{3/2}$ binding energy of 782 eV and spin-orbital splitting of 15.7 eV [30]) and Co metal phase. The lower extent of reduction observed in CoN3 may be related to the smaller sizes of the supported Co_3O_4 crystallites detected in these samples by XRD (table 1). Indeed, the lower degree of reduction of smaller particles of supported cobalt oxide, as compared to the larger ones, has been reported previously [31–35].

The relative intensities of XPS lines characteristic of cobalt metal phase are much lower in the reduced CoAc1 and CoAc2, indicating a lower relative concentration of cobalt metal phase in these catalysts. The lower extent of cobalt reduction in these catalysts can be attributed to the presence of significant concentrations of hardly reducible cobalt silicate species. In line with this finding, the extent of cobalt reduction is slightly higher in CoAc2 sample than in CoAc1. This might be due to a higher concentration of reducible Co_3O_4 crystallites in the catalyst prepared from cobalt acetate, which has been calcined at a lower temperature (443 K).

More quantitative information about relative concentration of cobalt metal phase in the catalysts reduced at 673 K has been obtained using simulation of XPS spectra by the Eclipse software (ThermoVG Scientific). Following the Shirley background subtraction and binding energy alignment, the sum of areas of Co2p XPS peaks in the catalysts and in the reference compounds has been normalized. The sets of linked parameters for Co^{2+} and Co metallic species (energy center separation, width and height ratio, Gaussian/Lorentzian form, asymmetry) have been determined from the XPS spectra of Co^{2+} ions in oxidized CoAcl sample and of Co^0 atoms in the reference sample of Co metal [29]. The relative amount of Co metal phase (table 1) has been estimated from fitting the experimental and simulated XPS profiles.

The number of cobalt surface sites in the reduced catalysts is calculated by multiplying the total concentration of cobalt in the catalysts by the value of cobalt metal dispersion measured from XRD data and by the relative amount of cobalt metal phase after catalyst

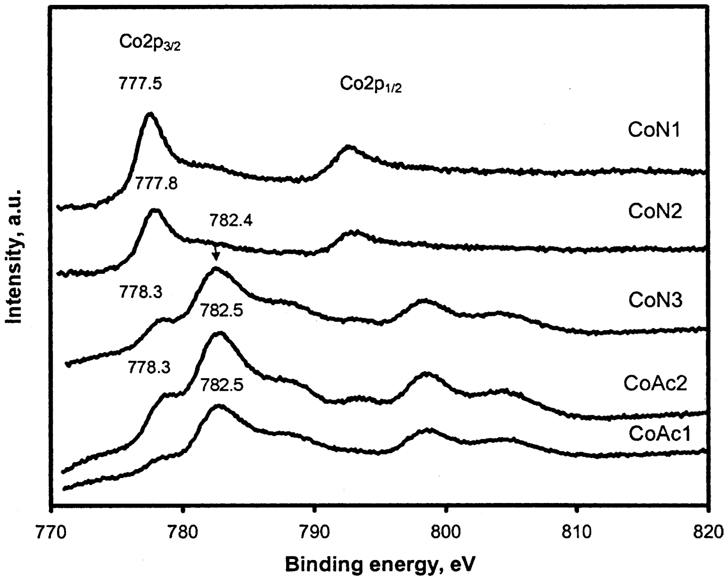

Figure 1. Co 2p XPS spectra of cobalt catalysts reduced in hydrogen at 673 K.

reduction evaluated from XPS data. Our data (table 1) demonstrate that the maximal number of cobalt metal sites in the catalysts prepared from cobalt nitrate can be obtained, when decomposition of the cobalt precursor was conducted at 423 K.

3.2. Fischer–Tropsch reaction

The evaluation of FT catalytic behavior has been carried out at 463 K in a differential catalytic reactor with a plug-flow hydrodynamics. In agreement with previous data [20,36], FT reaction rates are decreasing slowly during the first 4–5 h of the reaction, and quasistationary conditions are generally attained after 24 h. The reaction rates measured at quasi-stationary conditions are, presented in figure 2.

Notably, higher FT reaction rates are observed over the catalysts prepared from cobalt nitrate, which have a greater concentration of cobalt metal sites as estimated from XRD and XPS data (table 1). A somewhat lower FT catalytic activity found over the cobalt catalysts prepared from cobalt acetate is probably due to the presence of hardly reducible cobalt silicate. Methane and C5+ selectivities, calculated on carbon basis, are between 13–18 and 62–70%, respectively.

3.3. Chemisorption of C3 hydrocarbons on freshly reduced cobalt catalysts

The propene chemisorption results for freshly reduced cobalt-supported catalysts are shown in figure 3 and table 2. It should be noted that no propene

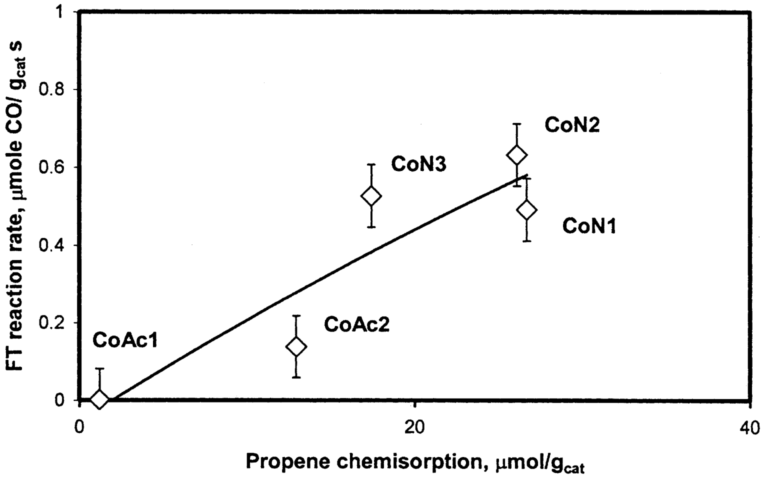

Figure 2. Fischer–Tropsch reaction rates as a function of propene chemisorption at 323 K over a series of cobalt-supported catalysts.

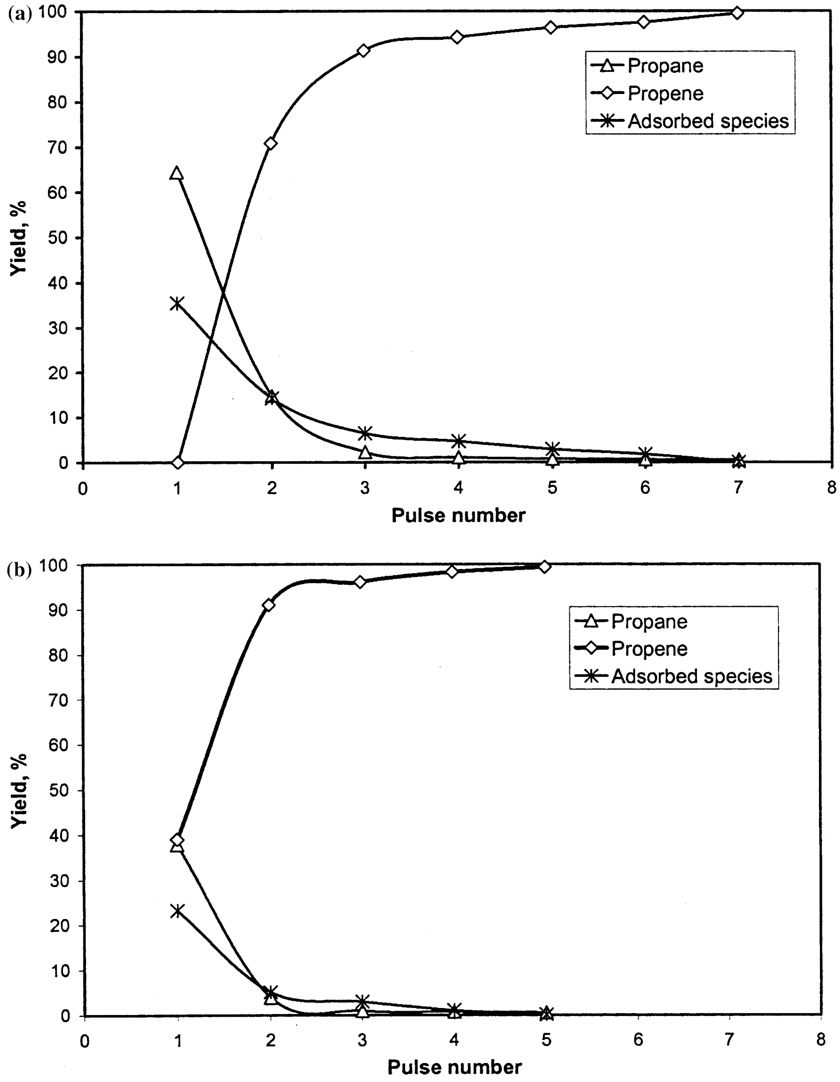

Figure 3. Adsorption and reaction of propene in a pulse reactor on CoN1 (a) and CoAc2 (b) catalysts at 323 K.

Table 2
Propene adsorption and reaction over freshly reduced cobalt catalysts

Catalyst	Cobalt content, %	Temperature of propene chemisorption, K	Propene adsorbed, μmol/g	Propene produced, μmol/g	Propene converted to methane and ethane, μmol/g
CoN1	12.0	323	26.7	34.7	~0.0
		323[a]	20.8	29.2	~0.0
		373	20.2	36.8	~0.0
		423	28.1	26.9	0.3
		473	32.0	17.8	4.7
		523	31.7	6.6	8.6
CoN2	9.9	323	26.1	42.8	~0.0
		473	36.6	18.1	6.9
CoN3	9.9	323	17.4	30.5	~0.0
CoAcl	9.5	323	1.2	1.0	~0.0
CoAc2	9.5	323	12.9	18.0	~0.0
		373	10.7	13.2	~0.0
		423	14.4	19.6	~0.0
		473	23.1	20.8	5.7

[a] After reduction with hydrogen at 673 K the catalyst was purged with He at the same temperature and then cooled in He to 323 K.

chemisorption has been observed in the pulse reactor over pure silica support. At 323–373 K, propane is the major product detected in the gas phase after the cobalt catalyst exposure to the first 2–3 pulses of propene (figure 3). Some quantities of methane and traces of ethane and hydrogen are also detected, especially when the reaction is carried out at higher temperatures (423–523 K).

The material balance calculations show, however, that a part of propene is retained by the catalyst. The quantity of the chemisorbed propene is much higher at temperatures over 373 K (table 2). Propene conversion only slightly depends on the reciprocal gas flow rates, suggesting that propene autohydrogenation is a very rapid chemical reaction.

The formation of propane observed for cobalt supported catalysts in the pulse reactor can be explained by the hydrogenation of C_3H_6 with reactive hydrogen chemisorbed on cobalt particles or by propene autohydrogenation. Two sets of experiments have been carried out to verify these two possibilities.

In the first series of experiments, CoN1 catalyst reduced in hydrogen at 673 K has been purged with helium at two different temperatures (323 and 673 K) prior to propene chemisorption. If propane produced on cobalt catalysts is due to propene hydrogenation by prechemisorbed hydrogen, the quantity of propane should be a function of the temperature of the helium purge. Since the surface hydrogen coverage on metal catalysts is a function of temperature, the quantity of reactive chemisorbed hydrogen would significantly decrease when the catalysts are purged with helium at elevated temperatures. However, table 2 shows that the helium purge at 673 K has little effect on the amount of propane produced from propene. This suggests that hydrogen for propene autohydrogenation is largely provided by an alternative source, rather than by the hydrogen atoms chemisorbed on cobalt metal particles.

The second set of experiments involves propene chemisorption over deuterated cobalt catalysts. Prior to propene adsorption at 323 K, CoN1 catalyst has been pretreated with deuterium at the same temperature. H_2 and HD were observed at the reaction outlet during this treatment. These products are probably due to the exchange of deuterium with hydroxyl groups of silica catalyzed by cobalt metal sites:

$$\mathrm{D2} + 2\mathrm{SiOH} \rightarrow 2\mathrm{SiOD} + \mathrm{H}_2$$

A rapid exchange of hydroxyl groups with deuterium is usually observed over metal-supported catalysts [37,38]. The quantity of hydrogen exchanged with deuterium can provide information about the concentration of hydroxyl groups in the catalysts. The measured hydroxyl group coverage of cobalt silica supported catalyst is 0.5 $\mathrm{OH/nm^2}$ which is consistent with the previous data obtained for different silicas [39]. Following the completion of H–D exchange, the deuterated catalyst has been exposed to propene pulses at 323 K. The propene chemisorption over a completely deuterated CoNI sample selectively yields C_3H_8 propane molecules, with only ~1% of mono-deuterated propane (C_3H_7D) was observed under these conditions. This suggests that at 323 K the rate of H–D exchange is considerably slower than the rate of propene autohydrogenation, confirming that the hydrogen atoms for propene hydrogenation are principally provided by the adsorbed propene molecules and not by the surface of the catalyst.

The relatively high molar ratio (> 1) of hydrogenated to adsorbed propene observed at lower temperatures of chemisorption (323–373 K, table 2) suggests a rather deep dehydrogenation of the adsorbed species. Indeed, if propylidyne (CCH_2CH_3) is the dominant species present on the catalyst surface after propene chemisorption, the ratio of hydrogenated to chemisorbed propene should be close to 0.5:

$$3C_3H_6 \rightarrow C_3H_8 + 2CCH_2CH_3$$

Therefore, dehydrogenated surface carbon and chemisorbed species with the H/C ratio lower than that in propylidyne should be the most abundant species generated by propene chemisorption:

$$4C_3H_6 \rightarrow 3C_3H_8 + 3C_{\mathrm{surface}}$$

Tables 1 and 2 show that propene chemisorption is a function of the number of cobalt metal sites in the reduced catalysts. Much lower chemisorption is observed for hardly reducible CoAc1 and CoAc2 samples, and no propene chemisorption is detected under these conditions on the pure silica support, confirming that propene chemisorption proceeds on cobalt metal sites. Therefore, propene chemisorption could be considered as an efficient tool for characterization of cobalt metal sites in the reduced silica-supported catalysts.

Surface species generated by propene chemisorption over a series of cobalt supported catalysts have been hydrogenated by hydrogen in a pulse mode. A typical product distribution is shown on figure 4. Only a relatively small amount of propene remains as C3 species on the surface of cobalt particles, while most of chemisorbed propene undergoes C–C bond cleavage producing a range of different surface polymerized C_nH_{nx} species. Methane selectivity observed in the hydrogenation of the surface species obtained by propene chemisorption is only 5–15%. Methane could be produced by hydrogenation of either monomer CH_x groups, surface carbon or via hydrogenolysis of long chain polymeric species. Figure 4 shows that methane selectivity steadily increases with the number of hydrogen pulses, indicating that long chained C_nH_{nx} species

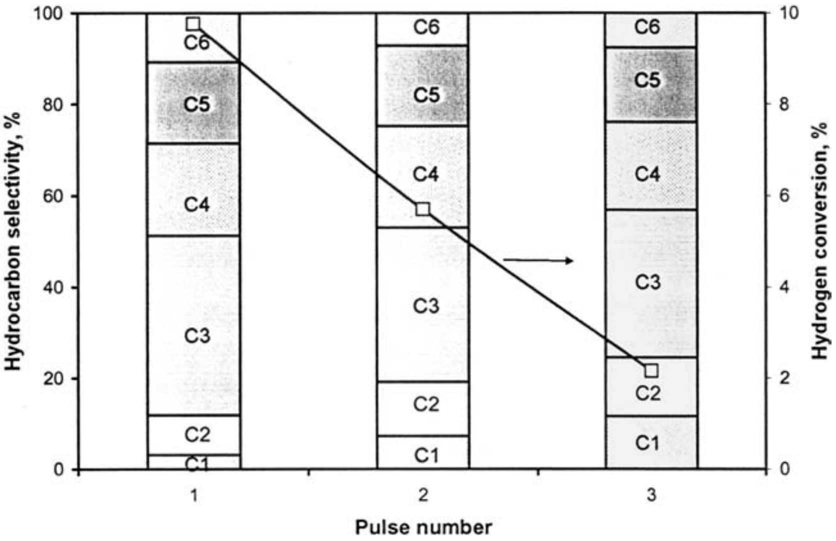

Figure 4. Hydrocarbon distribution during hydrogenation of chemisorbed propene species on CoN1 catalyst by pulses of hydrogen (temperature of propene chemisorption −373 K, temperature of hydrogenation −373 K, catalyst weight, 0.1 mg, pulse volume, 0.1 mL).

are much more reactive and easier to hydrogenate than monomer CH_x groups and surface carbon.

No significant adsorption or decomposition of propane has been found at 323 and 373 K over cobalt-supported catalysts (table 3). At higher temperatures, however, mostly methane (and a very low concentration of ethane) is detected (figure 5). Note that methane production is always associated with some propane chemisorption. Propane autohydrogenolysis is likely to be the most plausible interpretation of the observed propane chemisorption and methane production over cobalt-supported catalysts at temperatures higher than 423 K. In this reaction, hydrogen atoms for hydrogenolysis are probably provided by the chemisorbed propane molecules.

3.4 *Chemisorption of C3 hydrocarbons over cobalt-supported catalysts exposed to synthesis gas at different temperatures*

Propene and propane adsorption and reaction have been also studied over cobalt catalysts reduced in hydrogen at 673 K and then pretreated with synthesis gas ($H_2/CO = 2$) at different temperatures. The results are presented in table 4. In contrast to the data for a freshly reduced catalyst, only very low adsorption of propene is observed at lower temperatures over the catalysts exposed to synthesis gas. This suggests that most of cobalt metal sites are not available for adsorption and probably blocked by either chemisorbed carbon monoxide and hydrogen molecules or by the intermediates of carbon monoxide hydrogenation. No carbon monoxide hydrogenation is expected when synthesis gas is in contact with the catalyst at relatively lower temperatures (323–423 K). Note that pretreatment of the catalysts with hydrogen at a wide range of temperatures does not significantly affect propene chemisorption.

Previous reports have shown significantly higher chemisorption of carbon monoxide than hydrogen on cobalt catalysts. Moreover, it has been suggested that cobalt surface is predominately covered with adsorbed CO during FT synthesis [40,41]. Therefore, the observed decrease in propene adsorption capacity should be attributed to the blockage of cobalt metal surface sites by carbon monoxide molecules. At higher temperatures (473 K), some propene adsorption coincides with the release of small amounts of propane (table 4). No propane adsorption or hydrogenolysis is observed at the whole range of temperatures when the catalysts are pretreated with the synthesis gas ($H_2/CO = 2$).

Table 3
Propane adsorption and reaction over freshly reduced cobalt catalysts

Catalyst	Temperature of propane chemisorption, K	Propane chemisorbed, μmol/g	Propane converted to methane, μmol/g
CoNl	323	~0	~0
	373	~0	0.07
	423	2.1	2.0
	473	12.5	14.0
	523	18.8	26.0
CoAc2	473	~0	2.5

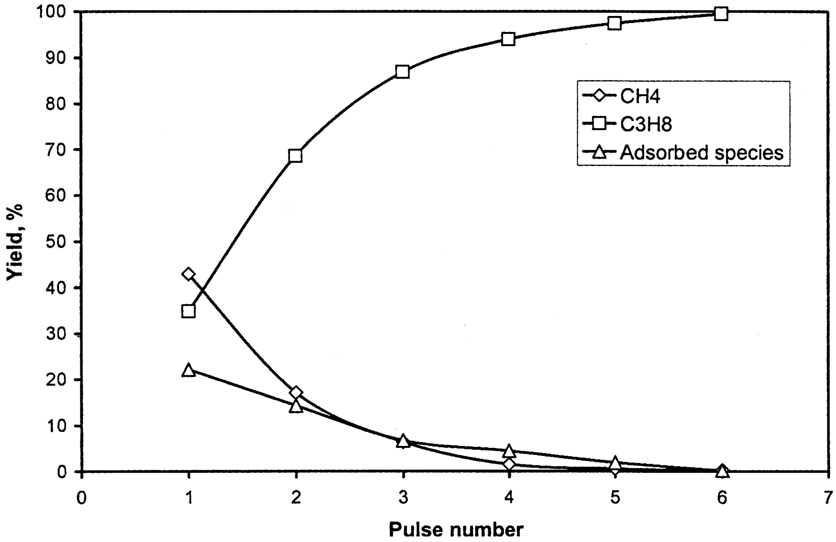

Figure 5. Adsorption and reaction of propane in a pulse reactor on CoN1 catalyst at 523 K.

3.5. Mechanistic aspects of C3 hydrocarbon chemisorption

The results obtained in this work indicate very rapid propene chemisorption on cobalt metal catalysts at temperatures ranging from 323 to 523 K. Propene chemisorption appears to be dissociative and irreversible, probably resulting in breaking of C–H and C–C bonds.

The scheme below summarizes possible reaction pathways of propene conversion over cobalt silica supported catalysts. When interacting with cobalt silica-supported catalysts in the pulse regime at relatively low temperatures (323–423 K), propene molecules undergo partial dehydrogenation and adsorption. Mass-spectroscopic measurements have shown that only very small amounts of hydrogen are released to gaseous phase. Most of hydrogen produced by propene dehydrogenation and chemisorption seems to be involved in hydrogenation of the remaining propene molecules to propane. At higher temperatures propene is also converted to methane via autohydrogenolysis.

To the best of our knowledge, the present paper represents the first work in which propene autohydrogenation is experimentally observed over cobalt-supported catalysts. The suggestion that propene undergoes autohydrogenation over cobalt catalysts is consistent with the literature data. Indeed, propene autohydrogenation has been reported for Pt and Ni catalysts [15,42]. This reaction network seems to be very similar to that found for ethene and propene adsorption on single crystals [10,14,15,43,44]. It is known for example, that upon chemisorption, ethene losses one or more hydrogen atoms forming ethylidyne (CCH_3), vinylidyne (CCH_2) or acetylidyne (CCH) surface species. At low temperature, these hydrogen atoms do not desorb but are used to hydrogenate other ethene molecules to ethane.

Zaera *et al.* [15] have studied propene chemisorption on Pt(111) single crystals surfaces. Propene has been found to dehydrogenate first to propylidyne and then to surface carbon, which is accompanied by hydrogen production. A small amount of propane from autohydrogenation has also been detected. IR studies [10] confirm that partially dehydrogenated propylidyne

Table 4
Propene chemisorption over cobalt catalysts exposed to synthesis gas for 15 h

Catalyst	Temperature of propene chemisorption, K	Propene adsorbed, μmol/g	Propene produced, μmol/g	Propene converted to methane and ethane, μmol/g
CoNl	323	~0	1.9	~0
	373	~0	2.9	~0
	423	~0	1.4	~0
	473	~0	0.7	~0
CoAc2	323	~0	~0	~0
	373	~0	~0	~0
	423	~0	< 1	~0
	473	4.8	2.8	~0

The catalysts were exposed to synthesis gas at the temperature of propene chemisorption.

(CH_3CH_2C) is the predominant surface species after propene adsorption over Pt/SiO_2 catalysts. The structure labeled propylidyne (CH_3CH_2C) is also supported by secondary mass spectrometry and thermal desorption [45]. Propylidyne has been also detected by Bent *et al.* [10] as the most abundant species formed from chemisorbed propene at temperatures up to 270 K on Rh(111) single crystal surface, whereas at room temperature, all the C3 hydrocarbons decompose to ethylidyne (CCH_3) and polymerized C_xH_{nx} fragments. Our data show that chemisorption of propene over cobalt catalysts leads to C_nH_{nx} species with relatively low H/C ratio. Therefore, the surface carbon could be one of the dominant species formed over the catalysts after propene chemisorption. At the same time hydrogenation of chemisorbed species formed from propene over cobalt supported catalyst (figure 4) indicates the presence of a wide range of polymerized hydrocarbon fragments. Indeed, in addition to propane, a range of hydrocarbons up to C6 has been detected as the catalyst with the chemisorbed species is treated with hydrogen pulses at 373 K. This observation is consistent with the data reported by Aaserud *et al.* [8] demonstrating that propene hydrogenation over cobalt supported silica catalysts in addition to propane, leads to the formation of C5+ hydrocarbons. These results suggest that a part of chemisorbed propene is involved in polymerization and that the C_nH_{nx} chemisorbed species forming from propene could be similar to the intermediates of FT synthesis.

Hydrogenolysis of propane is also observed over cobalt supported catalysts at the temperatures higher than 373 K with methane being the major product of the reaction (table 3, figure 5). Notably, the methane production always coincides with some propane chemisorption, indicating that as in the case of propene autohydrogenation, the hydrogen atoms for propane hydrogenolysis are generated by dehydrogenation of propane during its chemisorption over cobalt catalysts.

It should be noted that propane conversion over cobalt silica supported catalysts is low compared to that of propene, which is probably due to the lower reactivity of saturated hydrocarbons relative to olefins.

3.6. *Propene chemisorption and Fischer–Tropsch reaction*

Figure 2 displays FT reaction rates observed over a series of cobalt catalysts as a function of propene chemisorption. Higher FT reaction rates are generally measured over the catalysts chemisorbing more propene and thus having a higher density of cobalt metal sites. It is generally accepted that FT turnover rate only slightly depends on catalyst support or cobalt dispersion [2,3], suggesting that FT synthesis is a structure insensitive reaction by the definition of Boudart [3]. The observed correlation between FT reaction rates and propene chemisorption is consistent with that suggestion. Thus, propene chemisorption could provide valuable information about the density of cobalt metal sites in the cobalt silica-supported catalysts and their catalytic activity in FT synthesis.

It has been shown [2,3,46] that hydrocarbon selectivities obtained in FT synthesis over cobalt supported catalysts depend on both CH_x polymerization kinetics and olefin readsorption. Iglesia *et al.* [46] have demonstrated that the intrinsic chain growth kinetics is not affected by the changes in catalyst support or cobalt dispersion, suggesting that the surface reaction and site activity are independent of metal particle size. Therefore, different hydrocarbon selectivities observed over catalysts with different cobalt dispersion can be attributed to the different rates of olefin readsorption. In the present work, most of our propene chemisorption data have been obtained for freshly reduced catalysts. Although propene chemisorption is very rapid on all studied samples, it is difficult to suggest any direct correlation between the amount of chemisorbed propene and, for example, C5+ selectivity observed at the conditions of FT synthesis. This is likely to be due to the very different condition of catalyst surface in the freshly reduced and working FT catalysts. Our results show that most of cobalt surface sites, which are available for propene chemisorption in freshly reduced catalysts, are blocked by strongly adsorbed carbon monoxide molecules in the working FT catalysts (compare tables 2 and 4). Therefore, the rate of propene readsorption in the course of FT synthesis would not depend on the total density of cobalt metal sites measured after catalyst reduction, but on the number of sites, which are still available for propene at a given partial pressure of carbon monoxide and reaction temperature.

4. Conclusion

A combination of characterization techniques and chemisorption experiments allowed new information about the mechanism of propene and propane chemisorption over cobalt supported FT catalysts to be obtained. In the pulse regime, propene chemisorbs mostly irreversibly on cobalt silica-supported catalysts. The propene chemisorption was found to be a function of the density of cobalt metal sites. Catalytic measurements in FT synthesis showed higher catalytic activity of cobalt catalysts chemisorbing more propene.

The mechanism of propene chemisorption on cobalt catalysts involves its dissociation and dehydrogenation to surface carbon and probably propylidyne (CH_3CH_2C) type species. Hydrogen produced by propene dehydrogenation is not released to any greater extent to the gaseous phase but is involved in hydrogenation of remaining propene molecules to propane at relatively lower temperatures (323–373 K) and at higher temperatures (>423 K) in hydrogenolysis of propene molecules to methane.

Propane was found not to adsorb to any noticeable extent over freshly reduced cobalt catalysts at temperature below 423 K. At higher temperatures propane autohydrogenolysis proceeds with hydrogen atoms for hydrogenolysis being probably provided by chemisorbing propane molecules.

Only very low propene and propane chemisorption was observed over cobalt catalysts after their exposure to synthesis gas at the conditions similar to FT synthesis. The results suggest that most of cobalt metal surface sites are blocked by chemisorbed carbon monoxide during FT synthesis, and thus are not available for chemisorption and reaction with C3 hydrocarbons.

References

[1] M.E. Dry, Catal. Today 71 (2002) 227.

[2] E. Iglesia, S.C. Reyes, R.J. Madon and S.L. Soled, Adv. Catal. 39 (1993) 221.

[3] E. Iglesia, Appl. Catal. A: Gen. 161 (1997) 59.

[4] E.W. Kuipers, I.H. Vinkenburg and H. Oosterbeek, J. Catal. 152 (1995) 137.

[5] H. Schulz and M. Claeys, Appl.Catal. A 186 (1999) 71.

[6] R.J. Madon, S.C. Reyes and E. Iglesia, J. Phys.Chem. 95 (1991) 7795.

[7] E. Iglesia, S.C. Reyes and R.J. Madon, J. Catal. 129 (1991) 238.

[8] C. Aaserud, A.-M. Hilmen, E. Bergene, S. Eric, D. Schanke and A. Holmen, Catal. Lett. 94 (2004) 171.

[9] D. Schanke, S. Eri, E. Rytter, C. Aaserud, A.-M. Himen, O.A. Lindvag, E. Bergene and A. Holmen, Stud. Surf. Sci. Catal 147 (2004) 301.

[10] B.E. Bent, C.M. Mate, J.E. Crowell, B.E. Koel and G.A. Somorjai, J. Phys. Chem. 91 (1987) 1493.

[11] R.J. Koestner, J.C. Frost, P.C. Stair, M.A.V. Hove and G.A. Somorjai, Surf. Sci. 116 (1982) 85.

[12] H. Steininger, H. Ibach and S. Lehwald, Surf. Sci. 117 (1982) 685.

[13] G. Shahid and N. Sheppard, Spectrochim. Acta 46 (1990) 999.

[14] J.M. Griffiths, A.T. Bell and J.A. Reimer, J. Phys. Chem. 98 (1994) 1918.

[15] F. Zaera and D. Chrysostomou, Surf. Sci. 457 (2000) 89.

[16] A.Y. Khodakov, A. Girardon, A. Griboval-Constant, S. Lermontov and P.A. Chernavskii, Stud. Surf. Sci. Catal 147 (2004) 295.

[17] B.D. Cullity, *Elements of X-Ray Diffraction* (Addision-Wesley, London, 1978).

[18] S. Sun, N. Tsubaki and K. Fujimoto, Appl. Catal. A: Gen. 202 (2000) 121.

[19] A.Y. Khodakov, A. Griboval-Constant, R. Bechara and F. Villain, J. Phys. Chem. B 105 (2001) 9805.

[20] A.Y. Khodakov, A. Griboval-Constant, R. Bechara and V.L. Zholobenko, J. Catal. 206 (2002) 230.

[21] D. Schanke, S. Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff and A. Holmen, J. Catal. 156 (1995) 85.

[22] I. Puskas, T.H. Fleisch, J.B. Hall, B.L. Meyers and R.T. Roginski, J. Catal. 134 (1992) 615.

[23] K.E. Coulter and A.G. Sault, J. Catal. 154 (1995) 56.

[24] E. Steen, G.S. Sewel, R.A. Makhothe, C. Micklethwaite, H. Manstein, M. Lange and C.T. O'Connor, J. Catal. 162 (1995) 220.

[25] A. Khodakov, O. Ducreux, J. Lynch, B. Rebours and P. Chaumette, Oil Gas Sci. Technol. – Rev IFP 54 (1999) 525.

[26] J.M. Jablonski, M. Wolcyrz and L. Krajczyk, J. Catal. 173 (1998) 530.

[27] C.R. Brundle, T.J. Chuang and D.W. Rice, Surf. Sci. 60 (1976) 286.

[28] D.G. Castner, P.R. Watson and I.Y. Chan, J. Phys. Chem. 94 (1990) 819.

[29] A. Griboval-Constant, J.-M. Giraudon, G. Leclercq and L. Leclercq, Appl. Catal. A: Gen. 260 (2004) 35.

[30] S.W. Ho, M. Horialla and D.M. Hercules, J. Phys.Chem. 94 (1990) 6396.

[31] H.F.J. van't Blik and R. Prins, J. Catal. 97 (1986) 210.

[32] R. Bechara, D. Balloy, J.-Y. Dauphin and J. Grimblot, Chem. Mater. 11 (1999) 1703.

[33] D.G. Castner, P.R. Watson and I.Y. Chan, J. Phys. Chem. 94 (1990) 819.

[34] A.Y. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson and P. Chaumette, J. Catal. 168 (1997) 16.

[35] B. Ernst, A. Bensaddik, L. Hilaire, P. Chaumette and A. Kiennemann, Catal. Today 39 (1998) 329.

[36] A.Y. Khodakov, R. Bechara and A. Griboval-Constant, Appl. Catal. A: Gen. 254 (2003) 273.

[37] A. Khodakov, N. Barbouth, Y. Berthier, J. Oudar and P. Schulz, J. Chem. Soc. Faraday Trans. 91 (1995) 569.

[38] S. Stolle, L. Sümmchen, U. Roland, K. Herzog and R. Salzer, J. Mol. Struct. 349 (1995) 93.

[39] C.G. Armistead, A.J. Tyler, F.H. Hambleton, S.A. Mitchell and A. John Hockey, J. Phys. Chem. 73 (1969) 3947.

[40] S. Krishnamoorthy, M. Tu, M.P. Ojeda, D. Pinna and E. Iglesia, J. Catal. 211 (2002) 422.

[41] P. Winslow and A.T. Bell, J. Catal. 94 (1985) 385.

[42] R. Kleyna, S. Fickert, D. Borgmann and G. Wedler, Langmuir 14 (1998) 5464.

[43] T. Koerts, P.A. Leclercq and R.A. van Santen, J. Am. Chem. Soc. 114 (1992) 7272.

[44] M. Salmerõn and G.A. Somorjai, J. Phys.Chem. 86 (1982) 341.

[45] K.M. Ogle, J.R. Creighton, S. Akhter and J.M. White, Surf. Sci. 169 (1986) 246.

[46] E. Iglesia, S.L. Soled and R.A. Fiato, J. Catal. 137 (1992) 212.