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Transient studies of the elementary steps of Fischer–Tropsch synthesis

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Abstract

The pulse transient method has been used to study the kinetics of several key steps of Fischer–Tropsch (FT) synthesis over cobalt supported catalysts. These elementary steps involve chemisorption of hydrogen and propene, and chemisorption and hydrogenation of carbon monoxide. It is found that at the conditions of Fischer–Tropsch synthesis, hydrogen chemisorption is reversible and quasi-equilibrated, while carbon monoxide adsorption is generally irreversible. Chemisorption of propene on cobalt metal sites results in its rapid autohydrogenation to propane and simultaneous formation of C_xH_y surface species.

The transient response curves produced during hydrogenation of carbon monoxide pulses in a flow of hydrogen have been analyzed using the modified Kobayashi model, which involves irreversible chemisorption and dissociation of carbon monoxide, quasi-equilibrated adsorption of hydrogen and reversible adsorption of water. The kinetic analysis suggests that oxygen-containing species are probably the most abundant surface intermediates. Desorption of water from the catalysts seems to be much slower than hydrogenation of surface carbon species.

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Keywords: Fischer–Tropsch synthesis; Transient kinetics; Cobalt catalysts; Chemisorption

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1. Introduction

The renewed interest to Fischer–Tropsch (FT) synthesis involving cobalt supported catalysts is primarily due to its use in the conversion of natural gas to clean diesel fuels with extremely low content of sulfur and aromatics. Since the reaction proceeds at the conditions far from the equilibrium, the carbon monoxide conversion and hydrocarbon selectivity are principally governed by the reaction kinetics. The mechanism of FT synthesis is rather complex [1,2]. It involves chemisorption of carbon monoxide and hydrogen on cobalt metal sites followed by hydrogenation of adsorbed carbon-containing species to CH_x surface monomers. The hydrocarbons are produced via desorption of surface alkyl fragments formed by linear polymerization of CH_x monomers. The secondary reactions such as olefin readsorption lead to deviations from the polymerization statistics. Little information is available, however, about the rates of elementary steps of FT synthesis. The objective of the present paper is to study the kinetics of several key elementary steps of FT synthesis such as chemisorption of hydrogen, carbon monoxide and olefins in a pulse microreactor. The transient study of carbon monoxide hydrogenation provided new quantitative information about the reaction kinetics.

2. Experimental

2.1. Preparation and characterization of cobalt catalysts

The cobalt monometallic (10%Co) and bimetallic (10%Co-0.2%Ru) catalysts were prepared by impregnation and co-impregnation of silica (Cab-osil M5) using aqueous solution of cobalt nitrate or cobalt acetate and ruthenium nitrosyl nitrate. The $CoPt/Al_2O_3$ catalyst (30%Co-0.07%Pt)

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was prepared by co-impregnation of alumina (Puralox SCCA-5/170) with the aqueous solution of cobalt nitrate and dihydrogen hexachloroplatinate (IV). After impregnation, the catalysts were dried and calcined in air flow at 373–673 K. Prior to the kinetic experiments, the catalysts were reduced in a flow of hydrogen at 673 K for 5 h.

The number of cobalt active metal sites in the reduced catalyst was calculated from cobalt content, cobalt dispersion and cobalt reducibility evaluated, respectively, from X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS). The powder diffraction patterns of oxidized cobalt catalysts were recorded using a Siemens D5000 diffractometer (Cu Kα radiation). The particle size values for cobalt oxide crystallites in these catalysts were calculated using Scherrer equation. These data have been utilized to calculate the corresponding cobalt metal particle size according to the relative molar volumes of metallic cobalt and Co_3O_4 [3]. Cobalt dispersion 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: $D = 96/d$ [3]. XPS surface analyses were performed using a VG ESCALAB 220XL spectrometer. 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. Then the sample was transferred to the vacuum chamber for the XPS measurements. Further information about catalyst preparation and characterization is available from refs. [4,5].

2.2. Adsorption and reaction measurements

The adsorption experiments were performed at transient conditions using a pulse tubular reactor. The plug-flow hydrodynamics was checked by the experiments with the microreactor filled with the carborundum of the same granulometry (0.05–0.2 mm) as the catalyst. To remove any chemisorbed hydrogen species prior to hydrogen adsorption, the reduced cobalt catalysts were purged in a flow of helium at temperatures ranging from 373 to 673 K. To reduce the exothermic effects due to the chemisorption and reaction, the catalysts were diluted in carborundum. The pulse volumes were between 0.1 and 1.0 cm^3. Temperature programmed desorption (TPD) measurements coupled with the detection of desorption products by mass-spectrometry were carried using a temperature ramp of 5 K/min. During the transient CO hydrogenation experiments, the pulses of carbon monoxide were periodically injected to a flow of hydrogen over a series of silica and alumina supported cobalt catalysts at 403–593 K. The concentrations of carbon monoxide, methane and water were measured at the reactor outlet as functions of time. Hydrogenation of carbon monoxide pulses was also studied in the presence of water. Water vapor was added to the hydrogen flow by a vaporizer kept at 289 K.

The time-resolved mass-spectra of the reactants and products were recorded using a Quadstar QMS-200 mass spectrometer. The analysis of hydrocarbons produced during propene adsorption–desorption and carbon monoxide hydrogenation was also carried out using gas chromatography. The kinetic modeling and fitting the experimental and simulated transient responses were performed using Matlab software.

3. Results and discussion

3.1. Chemisorption measurements

The conclusions about the reversibility and the relative rates of adsorption and desorption of carbon monoxide, hydrogen and propene were deduced, respectively, from the irreversible uptakes of the adsorbents at different temperatures and from broadening the transient response curves after the contact with the catalyst in the tubular reactor.

At the temperatures below 373 K, irreversible hydrogen uptake (~0.01–0.02 mmol H_2/mol Co at 323 K) was observed over cobalt catalysts. This suggests that hydrogen chemisorption is partially irreversible at these temperatures. TPD experiments showed that the hydrogen irreversibly chemisorbed on cobalt catalysts desorbs at 363–383 K producing a broad H_2 peak in the TPD profiles. A partially irreversible chemisorption of hydrogen at temperatures lower than 373 K over cobalt supported catalysts was previously observed by Reuel and Bartholomew [6]. No irreversible hydrogen uptake was observed at temperatures higher than 423 K. This suggests that at the conditions typical of FT synthesis, the hydrogen chemisorption is mostly reversible. No noticeable broadening of hydrogen pulses was observed after interaction of hydrogen with the cobalt catalysts at these temperatures. This suggests that at the conditions of FT synthesis, the rate of hydrogen desorption is fast relative to the rate of hydrogen adsorption.

Carbon monoxide chemisorption has been found mostly irreversible on cobalt silica and alumina supported catalysts at the whole range of studied temperatures (323–523 K). TPD measurements showed that the cobalt catalysts containing irreversibly chemisorbed carbon monoxide species, desorb some carbon monoxide at about 373 K. Desorption at temperatures higher than 423 K leads selectively to carbon dioxide. Formation of carbon dioxide from chemisorbed carbon monoxide species at temperatures higher than 423 K implies dissociation of chemisorbed carbon monoxide on cobalt catalysts.

Consecutive adsorption of hydrogen and carbon monoxide on cobalt catalysts at 323 K has shown that hydrogen which was pre-adsorbed irreversibly, can be substituted by pulses of carbon monoxide, whereas no substitution of pre-adsorbed carbon monoxide by hydrogen was observed in any experiment. Fig. 1 shows that the chemisorption of the first pulses of carbon monoxide on cobalt catalysts with pre-adsorbed hydrogen results in CO-assisted hydrogen desorption. This suggests that irreversibly chemisorbed hydrogen

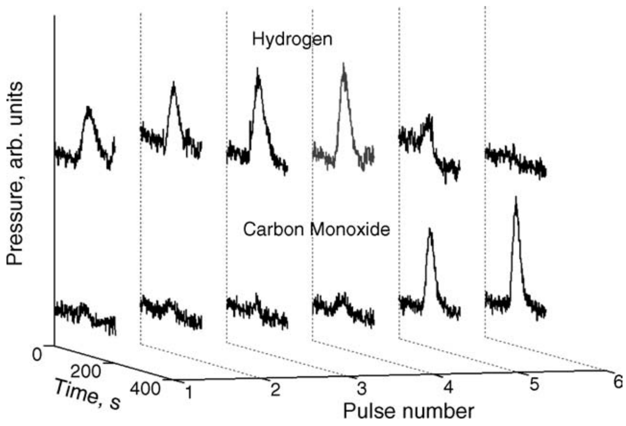
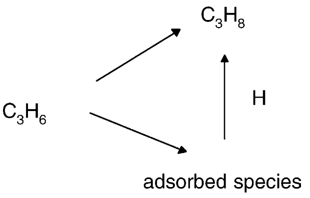


Fig. 1. Variation of hydrogen and carbon monoxide pressures at the outlet of the reactor during the pulse chemisorption of carbon monoxide on a catalyst with pre-adsorbed hydrogen (Co/SiO_2, temperature of hydrogen pre-adsorption and carbon monoxide chemisorption = 323 K). The curves are offset for clarity.

and carbon monoxide adsorbs on the same surface metal sites. In agreement with previous reports [6,7], this observation also confirms that the chemisorption of carbon monoxide is much stronger that that of hydrogen and that at the conditions of FT synthesis, the surface coverage with carbon monoxide could be much higher that that with hydrogen.

Our experiments show that propene undergoes autohydrogenation at 323–373 K over the surface of both unpromoted and promoted cobalt catalysts. During propene autohydrogenation, a part of propene dehydrogenates and chemisorbs over cobalt catalysts. The released hydrogen atoms do not desorb but are involved in hydrogenation of remaining propene molecules to propane in the autohydrogenation reaction:



Previously, propene autohydrogenation was only observed over monocrystals of noble metals and Pt catalysts [8,9].

The kinetic data obtained in pulse mode indicate no delay or broadening of propene or propane transient responses. This suggests that propene autohydrogenation over cobalt catalysts is a very fast reaction. Propane was the only reaction product detected in gaseous phase after interaction of propane with the catalysts at 323–373 K. Some quantities of methane and traces of ethane were also found especially when the reaction was carried out at higher temperatures (423–523 K).

To identify the nature of chemisorbed species, the catalysts after propene chemisorption were treated with the pulses of hydrogen. Only small amount of propene (10–20%) remains as C3 species on the surface of cobalt particles. These species can be easily hydrogenated to propane in the presence of hydrogen. A large part of chemisorbed propene undergoes C–C bond cleavage and produces surface C_xH_y groups ($x = 1$–6), which could be involved in the mechanism of FT chain growth.

Propene adsorption on a series of cobalt silica supported catalysts has shown [5] that the amount of adsorbed propene was always comparable with the number of cobalt metal sites estimated from the measurements of the extent of cobalt reduction and dispersion by other characterization techniques.

3.2. Carbon monoxide hydrogenation

Methane and water were the principal products of hydrogenation of carbon monoxide pulses in a flow of hydrogen over Co/SiO_2, CoRu/SiO_2 and CoPt/Al_2O_3 catalysts at the temperatures higher than 403 K. C_{2+} hydrocarbons were not detected at these conditions. As expected, carbon monoxide conversions were lower at higher hydrogen flow rates. Similar transient responses were observed on silica and alumina supported catalysts. The typical experimental transient curves of carbon monoxide, methane and water on the CoRu/SiO_2 catalyst are shown in Fig. 3.

The chemisorption experiments discussed above suggest irreversible chemisorption and dissociation of carbon monoxide and quasi-equilibrated adsorption of hydrogen on cobalt catalysts at the conditions of FT synthesis. Additional suggestions about adsorption–desorption of water were made from the kinetic measurements of FT synthesis in the presence of water. It was found that water addition to the hydrogen flow resulted in an imminent decrease in the rate of carbon monoxide hydrogenation over cobalt catalysts. This observation is consistent with previous reports [10,11], which show that addition of small amounts of water during FT reaction could result in a reversible decrease in the reaction rate. The most plausible interpretation of the observed phenomenon could be related to reversible adsorption of water on cobalt metal sites. This suggests that the readsorption of water on cobalt sites could be competitive with adsorption of carbon monoxide and hydrogen and, thus, would slow down the reaction rate.

The transient response curves obtained on cobalt silica and alumina supported catalysts have been fitted using the modified Kobayashi method [12,13]. The following system of partial differential equations (PDE) with predetermined initial conditions was written for gaseous components (CO, H_2, CH_4 and H_2O):

$$\frac{\partial p_i}{\partial t} = -\frac{u_0}{\varepsilon}\frac{\partial p_i}{\partial x} + \frac{RT\rho_b}{\varepsilon}\sum_{j=1}^{m} r_{i,j}$$

and for adsorbed species (H^*, CO^*, C^* and O^*):

$$\frac{\partial \theta_i}{\partial t} = \frac{1}{n_i}\sum_{j=1}^{m} r_{i,j}.$$

In these equations, ε is the void fraction of the catalyst bed, ρ_b the bed bulk density, u_0 the superficial velocity of the feed, x the catalyst bed coordinate, n_i the number of sites (mmol/g) and θ_i is site coverage. The $\frac{u_0}{\varepsilon}\frac{\partial p_i}{\partial x}$ terms represent gas transport in the reactor by convection, while the $\frac{RT\rho_b}{\varepsilon}\sum_{j=1}^{n} r_{i,j}$ term is due to chemical kinetics. The number, n_i, of cobalt metal sites in the catalysts was calculated from cobalt dispersion measured by XRD and extent reduction evaluated by XPS. In agreement with Hinz et al. [13], the catalytic reactor can be projected by a set of tank-reactors (tank-in-series model). In this case, the set of PDE is transformed into a set of ODEs by the following approximations:

$$\frac{\mathrm{d}p_{i,l}}{\mathrm{d}t} = -\frac{u_0}{\varepsilon}\,\frac{p_{i,l} - p_{i,l-1}}{x_l} + \frac{RT\rho_b}{\varepsilon}\sum_{j=1}^{m} r_{i,j,l}$$

$$\frac{\mathrm{d}\theta_{i,l}}{\mathrm{d}t} = \frac{1}{n_i}\sum_{j=1}^{m} r_{i,j,l}$$

where $p_{i,l}$ and $p_{i,l-1}$ are the pressure of gas component, i, in the reactors, l and $l-1$.

In the present work, a set of 30 tanks has been used in the modeling of transient response. Several possible reaction mechanisms, which involve irreversible chemisorption and dissociation of carbon monoxide, quasi-equilibrated adsorption of hydrogen and reversible adsorption of water, have been evaluated. A better fit (Fig. 2) was obtained with the reaction network shown below:

$$H_2 + 2^* \leftrightarrow 2H^*, \quad \text{quasi-equilibated,} \quad K\ (\text{equilibrium constant}), \tag{1}$$

$$CO + {}^* \rightarrow CO^*, \quad \text{irreversible,} \quad k_1\ (\text{kinetic constant}), \tag{2}$$

$$CO^* + {}^* \rightarrow C^* + O^*, \quad \text{irreversible,} \quad k_2\ (\text{kinetic constant}), \tag{3}$$

$$C^* + 4H^* \rightarrow CH_4 + 5^*, \quad \text{irreversible,} \quad k_3\ (\text{kinetic constant}), \tag{4}$$

$$O^* + 2H^* \leftrightarrow H_2O + 3^*, \quad \text{reversible,} \quad k_4 \text{ and } k_{-4}\ (\text{kinetic constants}). \tag{5}$$

In this model, the fitting experimental and calculated transient responses involved six adjustable parameters (K, k_1, k_2, k_3, k_4 and k_{-4}).

Fig. 2 shows that the tank-in-series modeling represents adequately the shape of methane and carbon monoxide transient curves. The tanks-in-series model, however, does not describe satisfactorily the observed water lag phenomenon. The more recent data obtained in our laboratory suggest that the observed water lag could be reproduced much better using a more advanced kinetic modeling, which describes the concentration profiles in the reactor as a function of time and involves solving PDEs instead of ODEs.

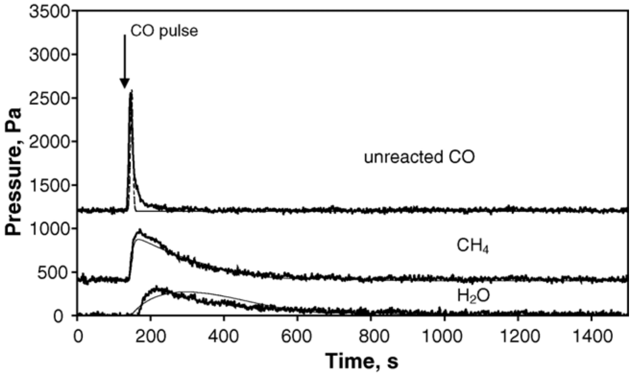


Fig. 2. Experimental and simulated transient response curves obtained at 423 K during hydrogenation of a pulse of carbon monoxide in a flow of hydrogen over a CoRu/SiO_2 catalyst (m_{cat} = 0.5 g, H_2 flow rate = 50 cm^3/min, catalyst and reactor parameters n = 0.136 mmol/g, ε = 0.45 and ρ_b = 1.8 g/cm^3). The transient curves are offset for clarity.

Though the water transient response seems to be rather complex, the observed lag relative to methane could be attributed to a desorption of water, which is much slower than hydrogenation of C^* surface species and water readsorption on metal sites. This indicates that the k_4 kinetic constant is much smaller than the k_3. Indeed, the fitting of the transient kinetic data obtained at 423 K yields, respectively, k_4/k_3 ratio of about 0.1–0.3 for both CoRu/SiO_2 and CoPt/Al_2O_3 catalysts. The evolution with time of the concentrations of the surface intermediates calculated from the transient kinetic data is shown in Fig. 3. The analysis indicates that oxygen species, which could be produced on carbon monoxide chemisorption and water readsorption, are the most abundant surface intermediates. Higher water pressure would lead to the increase in the concentration of surface oxygen due to the enhanced water readsorption. The observed decrease in carbon monoxide hydrogenation rate in the presence of water could be therefore, attributed to a decrease in the concentration of available cobalt metal sites due to the competitive water readsorption, which leads to higher concentrations of surface oxygen containing species.

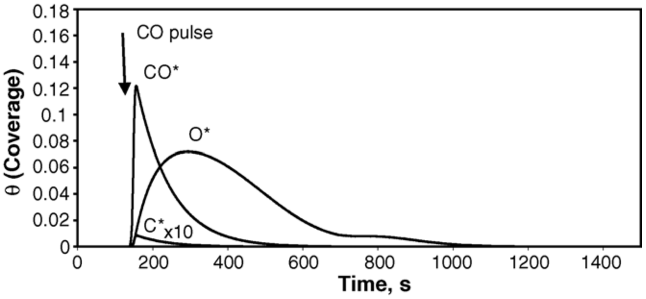


Fig. 3. Variation with time of the simulated surface coverage near the outlet of catalyst bed (30th tank in a series of 30 tank-reactors) during hydrogenation of a carbon monoxide pulse (for experimental conditions see Fig. 2).

4. Conclusion

The pulse transient method allowed new information about the key elementary steps of FT synthesis to be obtained. The experimental data indicate the high rate, low activation barrier and irreversibility of carbon monoxide adsorption on cobalt silica and alumina supported FT catalysts. Hydrogen adsorption was found fast and reversible at the temperatures of the reaction. Adsorption of propene on cobalt metal sites lead to its autodehydrogenation. A part of adsorbed propene is dehydrogenated over catalyst surface. The hydrogen produced by propene dehydrogenation is then involved in hydrogenation of the remaining propene molecules to propane.

The carbon monoxide and hydrogen chemisorption data were used for the quantitative analysis of the transient responses obtained during hydrogenation of carbon monoxide pulses in the flow of hydrogen over cobalt silica and alumina supported catalysts. It was shown that desorption of water from the catalysts seems to be much slower than hydrogenation of chemisorbed carbon species. Oxygen-containing species appear to be the most abundant surface intermediates. This supports the proposal that at steady-state conditions, water desorption could be one of the kinetically relevant steps of carbon monoxide hydrogenation on cobalt silica and alumina supported catalysts.

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