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TAP investigation of hydrogen and carbon monoxide adsorption on a silica-supported cobalt catalyst

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ABSTRACT

A temporal analysis of products (TAP) set-up was applied to investigate the initial elementary steps of the Fischer–Tropsch synthesis over silica-supported cobalt catalysts, i.e., hydrogen and carbon monoxide adsorption. Single-pulse TAP experiments were performed over both reduced and passivated catalysts in order to qualitatively and quantitatively assess the mechanism and kinetics of H_2 and CO adsorption. Multi-pulse experiments were performed to change the state of the catalyst in a predefined way. Only fast and equilibrated physical hydrogen adsorption was observed over a passivated silica-supported cobalt catalyst. Over the reduced catalyst, the surface sites exhibited significant heterogeneity for adsorption. TAP responses were successfully described assuming two different reversible adsorption processes for hydrogen and both irreversible and reversible adsorption for carbon monoxide. Supporting qualitative information about reversibility of the adsorption was also obtained through alternating pulse experiments.

1. Introduction

Fischer–Tropsch (FT) synthesis is an essential catalytic process of gas-to-liquids (GTL), biomass-to-liquids (BTL) and coal-to-liquids (CTL) technologies, which manufacture clean hydrocarbon fuels without sulfur and aromatics [1–4]. FT synthesis typically proceeds at the conditions far from the thermodynamic equilibrium, thus, carbon monoxide conversion and hydrocarbon selectivities are principally governed by chemical kinetics, heat, and mass transfer. Supported cobalt catalysts have proven to be particularly efficient for synthesis of middle distillate and long-chain hydrocarbons. Although FT synthesis has been an extensively studied process, little information is available about the rates of initial elementary steps of the reaction, i.e. hydrogen and carbon monoxide adsorption.

Transient kinetic experiments are particularly helpful in yielding information about reversibility of the elementary steps and allow evaluation of the intrinsic kinetic coefficients [5–11]. Moreover, these experiments can be conducted in the isothermal mode which is usually difficult to attain in steady-state regime for highly exothermic reactions such as FT synthesis. Our previous report [12] addressed the kinetics of the FT synthesis on silica-supported cobalt catalysts in a conventional pulse reactor. Though valuable information about the reaction mechanism and kinetics has been obtained, the conventional pulse method did not provide reliable quantitative kinetic data about the fast carbon monoxide and hydrogen adsorption kinetics because of moderate time resolution. In comparison with conventional pulse methods, a temporal analysis of products (TAP) set-up is particularly suitable for kinetic investigation of adsorption and reaction processes which proceed on a very short time scale.

TAP kinetic studies of carbon monoxide adsorption kinetics involving oxide and noble metal catalysts have been a subject of several reports [13–19]. A few works have addressed the kinetic investigation of hydrogen adsorption mostly on Rh- [20] and Pt-catalysts [21] using TAP. Carbon monoxide and hydrogen adsorption on cobalt catalysts has not been previously investigated using TAP.

The objective of this paper is to investigate the mechanism and kinetics of H_2 and CO adsorption. Throughout this study a TAP

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reactor, a very powerful transient technique combined with transient kinetic modeling and catalyst characterization, was employed. Single-pulse, multi-pulse and alternating pulse experiments have been conducted to qualitatively and quantitatively assess the mechanism and kinetics of H_2 and CO adsorption on a silica supported cobalt catalyst. To the best of our knowledge, this is the first TAP paper which addresses kinetics of carbon monoxide and hydrogen adsorption on cobalt FT catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst was prepared by incipient wetness impregnation of Cab-o-Sil M5 silica (specific surface area of 230 m^2/g) with a solution of cobalt nitrate. After impregnation, the catalyst was dried and calcined at 673 K in air flow. The temperature ramp from room temperature to 673 K was 1 K/min. The catalyst was characterized by low temperature nitrogen adsorption, X-ray diffraction and X-ray photoelectron spectroscopy.

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 [22] using a (4 4 0) peak at $2\theta = 65.344^\circ$.

Cobalt reducibility was evaluated from X-ray photoelectron spectra. XPS surface analysis was performed using a VG ESCALAB 220XL spectrometer. The Al(Kα) non-monochromatized 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 SiO_2 support. In situ catalyst reduction 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, while the spectroscopic measurements were carried out under a vacuum better than 10^{-7} Pa.

2.2. FT catalytic test

The carbon monoxide hydrogenation was carried out in a fixed bed microreactor (inner diameter = 9 mm) at atmospheric pressure. First, the catalyst was crushed and sieved to obtain catalyst grains between 0.05 and 0.2 mm in diameter. The catalyst loading was 0.5 g. Then, the catalyst was heated until 673 K and reduced at this temperature with a flow of hydrogen. After the reduction, a flow of premixed synthesis gas with the molar ratio of $H_2/CO = 2$ was introduced into the reactor at 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 Hewlett-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. C1–C18 hydrocarbons were separated on a packed 10% CP-Sil5 column on Chromosorb WHP and analyzed by a flame-ionization detector. The FT reaction rates are expressed as cobalt-time yields; they were calculated from carbon monoxide conversion, inlet carbon monoxide partial pressure, gas-space velocity and amount of cobalt in the reactor. Hydrocarbon selectivity was calculated on carbon basis.

2.3. TAP experiments

Before the TAP experiments, the catalyst was first reduced in a fixed bed reactor described in Section 2.2 in hydrogen flow at 673 K and then passivated at room temperature by injecting small pulses of air to helium flow. The passivated catalyst was removed from the fixed bed reactor and loaded into the TAP reactor. In the TAP reactor, the catalyst was reduced by multi-pulses of hydrogen at 673 K.

The TAP reactor applied in this study is a TAP-1 instrument, consisting of three vacuum chambers in line. The first chamber contains a microreactor in quartz, 45 mm long, with an inner diameter of 4.86 mm. In single-pulse experiments, the reactor contained a pre-bed filled with quartz (length 3.37 mm), a catalyst bed containing 0.1 g of catalyst (13.85 mm) and a post-bed filled with quartz (13.54 mm). The catalyst and quartz particle size are in the range of 250–500 μm. The reactor is connected via a small entrance volume (0.0218 cm^3) with two high-speed pulse valves and two continuous-feed valves. The background pressure in the reactor chamber varies between 10^{-4} and 10^{-5} Pa. The second chamber is the differential chamber. This chamber also acts as a pre-vacuum chamber for the analysis chamber. The pressure in the differential chamber is about 10^{-6} Pa. The responses of the reactant and products at the exit of the reactor are measured with a UTI 100C quadrupole mass spectrometer located in the third chamber, the analysis chamber. The pressure in the analysis chamber is 10^{-7} Pa. This ensures that the signal detected with the mass spectrometer is proportional to the flow rate at the outlet of the reactor. The time resolution at which the evolution of the outlet flow rate can be measured is far less than 1 ms. Preliminary experiments with Ar pulses were performed over an inert bed consisting of the quartz particles of 250–500 μm which were also used in other TAP experiments to determine Knudsen diffusion coefficients. Single-pulse experiments were carried out with the catalyst sample at 423–493 K temperature range.

H_2/Kr (9:1) and CO/Kr (9:1) mixtures were used for the experiments in which Kr was present as internal standard. The number of molecules admitted per pulse was in the range of 10^{14}–10^{15} molecules, allowing the transport in the reactor to occur through Knudsen diffusion. The amount of surface sites in 0.1 g of catalyst was estimated as 4×10^{18}, therefore the number of molecules per pulse was considerably lower that the number of surface sites in the catalyst. In alternating-pulse experiments, the reactors load consisted in a pre-bed of quartz (length 2.77 mm), a mixture of 0.0496 g of catalyst and 0.0506 g of quartz (length 9.34 mm), and a post-bed of quartz of 18.54 mm. The gas mixtures used were H_2/Kr (2/8) and CO/Ar (1/9).

For mass spectroscopic quantification of the different compounds leaving the TAP reactor, the following m/e values were chosen, based on sensitivity and specificity for each component: 2 for hydrogen, 15 for methane, 18 for water, 27 for C2 and C3 hydrocarbons, 28 for carbon monoxide, 44 for carbon dioxide and 84 for krypton. The fragmentation patterns were experimentally determined. The absolute sensitivities for the above ions have been measured in separate experiments. Preliminary data analysis was performed using the theory of the TAP reactor as presented in [10], and the detailed modeling was done using COMSOL and MATLAB software packages.

3. Results and discussion

3.1. Catalyst characterization

Characterization data for the Co/SiO_2 catalyst are displayed in Table 1. The catalyst has a BET surface area of 168.6 m^2/g and pore volume of 1.06 cm^3/g. The pore size distribution in mesopore range is relatively broad with a maximum at 200–300 Å. Co_3O_4 was the major phase in the calcined catalyst as identified by XRD and XPS. The average size of the Co_3O_4 crystallites calculated using the Scherrer equation [12] was about 21 nm. The fraction of cobalt metal phases in the catalyst reduced at 673 K was estimated as 65%