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Fischer–Tropsch synthesis on a model Co/SiO_2 catalyst

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ABSTRACT

A model Co/SiO_2 catalyst was prepared by depositing cobalt on silica films in ultrahigh vacuum conditions. Fischer–Tropsch synthesis was carried out at a total pressure of carbon monoxide and hydrogen between 0.33 and 1.0 bar. The effects of reaction temperature and pressure on kinetics and chain growth probability were investigated. The turnover frequency, activation energy, and product distributions were found in good agreement with those obtained on real catalysts. The formation of cobalt oxide or cobalt carbide was not detected after Fischer–Tropsch reaction at the low conversions and low water partial pressures of this work.

1. Introduction

The world has seen the adverse effect caused by our dependence on crude oil, and much effort has been made to develop renewable energy technologies, such as solar, wind, and biofuels. However, it seems that none of these technologies can meet the huge energy requirements of our society. For example, in 2007, solar, wind, and biofuels combined only to contribute 1.5% of the energy consumption of USA [1]. On the other hand, the huge reserves of natural gas and coal exceed those of crude oil by factors of about 1.5 and 25, respectively [2]. Therefore, Fischer–Tropsch technology, although made vulnerable by the dramatic changes in crude oil prices, is still one of the few technologies that can replace oil in the future.

Supported cobalt catalysts have been extensively studied for Fischer–Tropsch synthesis (FTS) because of their higher activity compared to commercially used iron catalysts [2–7]. However, some fundamental questions remain controversial. For example, the oxidation of metallic cobalt to cobalt oxide or other cobalt compounds (such as cobalt silicate and cobalt aluminate) has been proposed to be a possible cause of deactivation for FTS on supported cobalt catalysts [8,9]. Kogelbauer et al. [9] reported the formation of cobalt silicates in Co/SiO_2 as determined by TPR following FTS (493–513 K, $P = 31$ bar, $H_2/CO = 2$). Similarly, Huber et al. [10] reported that Co/SiO_2 catalysts deactivated rapidly during FTS at high water partial pressures due to the formation of stable, inactive cobalt silicates. On the contrary, van de Loosdrecht et al. [11] studied the deactivation of an industrial Co/Al_2O_3 catalyst by X-ray diffraction, magnetic measurements and X-ray absorption near-edge spectroscopy, and the oxidation of cobalt was ruled out as a major deactivation mechanism.

FTS has also been studied using single crystal model catalysts. Structure sensitivity of FTS was observed on different surfaces of cobalt single crystals [12,13]. After reaction, longer chain hydrocarbon fragments were observed on the $Co(1\,1\,\bar{2}\,0)$ surface, whereas on the stepped $(1\,0\,\bar{1}\,2)$ and close-packed $(0\,0\,0\,1)$ surfaces, mainly CH_x ($x = 1–3$) species were present on the surface. Beitel et al. [14] studied the co-adsorption of CO and H_2 on $Co(0\,0\,0\,1)$ at pressures up to 300 mbar, and in situ polarization modulation reflection absorption infrared spectroscopy (PM-RAIRS) results suggested that defects were the active sites for hydrocarbon formation. Johnson et al. [15] reported that submonolayer cobalt deposited on $W(1\,0\,0)$ and $W(1\,1\,0)$ surfaces had similar activity for FTS, and the after-reaction AES spectra showed formation of carbidic species.

The model studies mentioned above were performed on metal single crystal surfaces. Real cobalt catalysts, on the other hand, are small metal particles supported on oxide materials, such as Al_2O_3, TiO_2 and SiO_2. Therefore, the conclusions drawn from these model studies may not apply to industrial applications. So far there have been very limited studies on oxide supported model catalysts. Saib et al. [16] studied the oxidation of a planar $Co/SiO_2/Si(1\,0\,0)$ model catalyst using in situ NEXAFS and found no surface oxidation of cobalt particles (4–5 nm) under model FTS conditions ($P_{Total} = 0.4$ mbar, 423–673 K).

In this study, a model Co/SiO_2 catalyst was prepared and studied under FTS conditions. The effects of reaction temperature and total pressure on FTS activity and product distribution were investigated, and the kinetic results were compared with those on real catalysts.

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2. Experimental

The experiments were carried out in a modified commercial PHI 5500 system consisting of a surface analysis chamber, a preparation chamber, and a high-pressure cell. The surface analysis chamber, which is equipped with a dual Mg/Al anode X-ray source, a hemispherical energy analyzer, and a differential ion gun, allows the characterization and cleaning of catalyst samples. The stainless steel, high-pressure cell (0.2 L) is used as a batch reactor and separated from the preparation chamber by a gate valve, which allows other parts of the system to maintain ultrahigh vacuum (UHV) while Fischer–Tropsch synthesis is carried out in the reactor.

A tantalum foil (9 × 9 mm) was spot-welded to two tungsten wires mounted on a bellows manipulator, which allows translation of the sample to various positions. The sample was heated resistively and temperature was measured by a C-type thermocouple spot-welded to the back of the foil. SiO_2 films [17,18] were prepared by evaporating Si onto the Ta foil in a background of 1.3×10^{-8} bar oxygen, followed by annealing at 850 K. Cobalt was vapor-deposited on SiO_2 films from a cobalt wire wrapped with a tantalum filament, which was resistively heated. The Si and Co dosers were calibrated on a Mo(1 1 0) surface using XPS [19,20].

Carbon monoxide was first passed through an oxygen trap, and then a quartz tube, which was filled with quartz chips and kept at 573 K, to remove metal carbonyls. CO and H_2 with various ratios were premixed in an aluminum cylinder to ensure complete mixing. Before reaction, the H_2/CO mixtures were passed through a liquid-nitrogen trap before entering the reactor to remove other impurities. The products were analyzed with a HP 5890 gas chromatograph equipped with a flame ionization detector and a HP-PLOT Al_2O_3 capillary column. Blank experiments were carried out at various temperatures with clean tantalum foils and no reactions were observed at up to 573 K.

XPS spectra were collected using an Mg Kα X-ray source and a precision PHI hemispherical analyzer operated at a pass energy of 58.7 eV. The binding energies were referenced to the Si 2p line in SiO_2 at 103.4 eV.

3. Results and discussion

3.1. Activity and selectivity

The Co/SiO_2 model catalyst used in this study was prepared by depositing three equivalent monolayers of cobalt onto a 10 nm thick SiO_2 film, followed by annealing to 800 K in ultrahigh vacuum. The nominal Co/Si atomic ratio was 1:4, as estimated from the XPS peak areas and atomic sensitivity factors. The relative small Co/Si ratio suggests that cobalt was present as nanoparticles on the SiO_2 surface, instead of as continuous cobalt layers. In addition, the Co/Si XPS ratio decreased considerably after the annealing, indicating the sintering of cobalt particles. Other studies [16,21] by STM and AFM also showed that metals exist in the form of nanoparticles on amorphous silica films.

FTS was carried out on this catalyst at temperatures from 493 to 573 K using 1:1 H_2/CO mixtures at a total pressure of 1.0 bar. The products were mainly methane, ethylene, propylene, and butenes. A small amount of ethane and propane were also detected. For example, after an hour of reaction at 513 K, the concentrations of CH_4, C_2H_4, C_3H_6, and C_4H_8 were 20.7, 2.6, 1.8, and 0.8 ppm, respectively. The reaction rates, expressed as CO molecules converted per second, as a function of reaction time are shown in Fig. 1. The activity decreased in the first hour, particularly at higher temperatures, and then became relatively stable. The selectivities, on the other hand, did not show a similar steady state, as shown in Fig. 2 for the reaction at 513 K. The selectivity to C_2–C_4 products decreased almost linearly with time, as the CH_4 selectivity kept increasing. This suggests that the active sites for chain growth were poisoned by carbonaceous depositions, whereas the formation of methane on non-specific sites was not as affected [22].

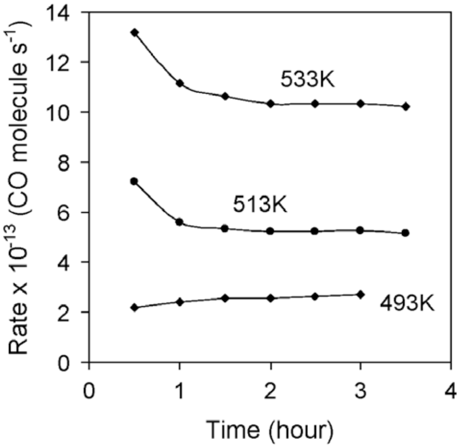

Fig. 1. FTS activity as a function of reaction time at various temperatures (1.0 bar, $H_2/CO = 1$).

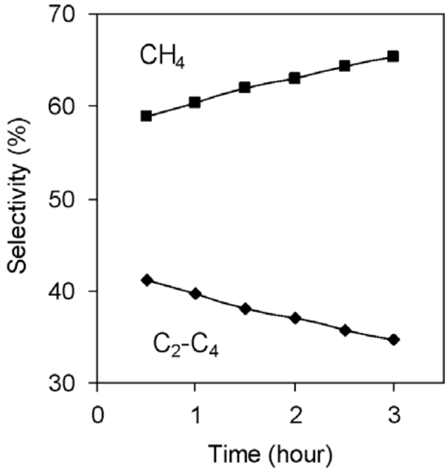

Fig. 2. Selectivity to CH_4 and C_2–C_4 products as a function of reaction time at 513 K, 1.0 bar, and $H_2/CO = 1$.

The Arrhenius plot of CO conversion rate (Fig. 3a) showed a straight line, giving an apparent activation energy of 93 kJ/mol. This value is consistent with the apparent activation energies of 93–103 kJ/mol from previous studies on cobalt-based FTS catalysts [23,24]. The formation rates of C_2–C_4 products apparently did not follow the Arrhenius law at higher temperature (>533 K), as shown in Fig. 3b, and their yields were lower than expected. This means that high temperature favors chain termination or desorption reactions since desorption is an endothermic process, so increasing temperature shifts selectivity to methane.

The reported turnover frequency of FTS (number of CO molecules per active site per second, or TOF) varies greatly in the literature. Recent studies [25,26] have shown that the TOF was strongly affected by cobalt particle sizes. More specifically, cobalt particles smaller than 6–8 nm were much less active than larger ones. Ribeiro et al. [27] reviewed kinetic studies of FTS and selected 36 sets of data on well-reduced cobalt catalysts from 12 different studies. The average TOF at 473 K, 10 bar, and $H_2/CO = 2$ was $0.017 \pm 0.014\ s^{-1}$. The reaction rate on our Co/SiO_2 catalyst was