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Particle Size and Crystal Phase Effects in Fischer-Tropsch Catalysts

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ABSTRACT

Fischer-Tropsch synthesis (FTS) is an increasingly important approach for producing liquid fuels and chemicals via syngas—that is, synthesis gas, a mixture of carbon monoxide and hydrogen—generated from coal, natural gas, or biomass. In FTS, dispersed transition metal nanoparticles are used to catalyze the reactions underlying the formation of carbon-carbon bonds. Catalytic activity and selectivity are strongly correlated with the electronic and geometric structure of the nanoparticles, which depend on the particle size, morphology, and crystallographic phase of the nanoparticles. In this article, we review recent works dealing with the aspects of bulk and surface sensitivity of the FTS reaction. Understanding the different catalytic behavior in more detail as a function of these parameters may guide the design of more active, selective, and stable FTS catalysts.

1. Introduction

Due to higher price levels of crude oil, Fischer-Tropsch synthesis (FTS), which converts coal, natural gas, and biomass to chemicals and liquid fuels, has attracted increasing attention in recent years as a way to diversify both the feedstock base for obtaining liquid transportation fuels and the monetization of natural gas and coal resources [1,2]. The principal reaction was discovered by Fischer and Tropsch [3] about 90 years ago. FTS reactions involve the strongly exothermic hydrogenation of carbon monoxide (CO) to paraffins and olefins according to the following chemical equations:

$$(2n+1)\,H_2 + nCO \longrightarrow C_nH_{2n+2} + nH_2O \qquad (1)$$

$$2nH_2 + nCO \longrightarrow C_nH_{2n} + nH_2O \qquad (2)$$
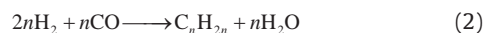
Aside from alkanes and alkenes, oxygenated hydrocarbons and carbon dioxide (CO_2) are obtained as by-products in industrial FTS. The mechanism underlying the FTS reaction is complex and involves many steps such as CO dissociation, carbon (C) hydrogenation, CH_x

coupling reactions, and hydrogenation and dehydrogenation reactions that lead to hydrocarbon product desorption as well as oxygen (O) removal reactions [4]. There continues to be considerable debate about many of these steps, most notably the nature of the active site and the way CO is dissociated, which is closely linked to the question of which is the growth monomer in FTS. From a practical point of view, the main drivers for the improvement of FTS catalysts are higher activity, improved selectivity to targeted product classes such as long-chain hydrocarbons or light olefins, and improved lifetime.

In heterogeneous catalysis, it is well accepted that catalytic performance is governed by the electronic structure of the catalyst [5]. Tunable parameters are active phase composition, particle size, crystal structure, crystal morphology, and the formation of the interface between the transition metal nanoparticles and the support of the catalysts [6–11]. Typical transition metals for catalyzing the FTS reaction are ruthenium (Ru), cobalt (Co), and iron (Fe). All of these present high activity and selectivity toward liquid hydrocarbons in the low-temperature FTS reaction [12]. Although Ru is usually deemed to be too expensive for this purpose despite its high activity, Co and Fe

have been the main components of industrial FTS catalysts. Nickel (Ni)-based catalysts generally produce too much methane (CH_4) under practical reaction conditions [13]. Here, we review recent developments in the field of Co-, Ru-, and Fe-based catalysts for the production of alkanes, alkenes, and alcohols via the FTS process. The focus of this review is on the influence of particle size and crystal phase, in which catalyst synthesis, modern characterization techniques, and density functional theory calculations are playing increasingly important roles. This review consists of three main parts: first, a discussion of the particle size effects of Co-, Ru-, and Fe-based catalysts in FTS; second, a description of the crystal structure effect of Co, Ru, Fe, and Ni metals in FTS; and finally, conclusions and a brief perspective.

2. Particle size effect of FTS over Co-, Ru-, and Fe-based FTS catalysts

A general approach to increase catalytic activity is to improve the active phase surface area by decreasing the size of the particles that make up the active phase [7,11,14]. Increasing the number of exposed surface sites works well for structure-insensitive reactions [11]. However, many catalytic reactions are structure sensitive, implying that the specific activity depends on the dispersion in a more complex manner [7,11,15–17]. This becomes particularly evident when metal nanoparticles become smaller than 10 nm, as specific surface sites such as corners, edges, and step edges then become dominant over terrace sites. As the FTS reaction is a well-known structure-sensitive reaction, it is no wonder that many researchers have focused on resolving optimum particle size for high activity and selectivity. Given their importance in commercial operation, we limit our discussion of particle size effects to Co, Ru, and Fe nanoparticles.

2.1. Co particle size effect in FTS

Iglesia [18] showed that Co site-time yields are independent of Co particle size in the 10–210 nm range using aluminium oxide (Al_2O_3), silicon dioxide (SiO_2), and titanium dioxide (TiO_2) as supports. Bezemer et al. [15] contended that CO hydrogenation activity is insensitive when the (carbon-nanofiber-supported) Co nanoparticles are larger than 6 nm, but demonstrated that smaller Co nanoparticles (< 6 nm) have lower CO hydrogenation activity and higher CH_4 selectivity (Fig. 1). Steady-state isotopic transient kinetic analysis (SSITKA) measurements suggested that the lower CO consumption rates of small Co nanoparticles can be attributed to blocking of the active edge/corner sites by CO [7]. Higher hydrogen coverage on smaller particles explains the higher CH_4 selectivity that is observed for smaller Co nanoparticles. These trends have been confirmed by other groups for silica-supported Co catalysts [19,20]. An alternative interpretation offered is that smaller Co nanoparticles
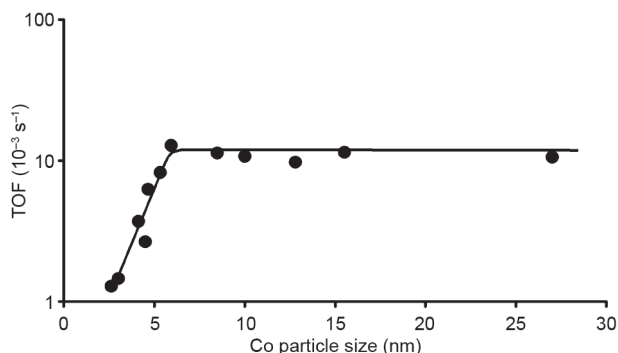
(< 2.5 nm) can be easily oxidized by water [19]. Different points of view on the effects of particle size may originate from different reaction conditions.

Herranz et al. [21] showed that Co nanoparticles remain metallic under methanation conditions. While CO methanation activity (i.e., the turnover frequency, TOF) of Co/SiO_2 catalysts decreases when particles become smaller than about 10 nm, the apparent activation energy for CO methanation is insensitive to Co particle size (Fig. 2). Hydrogen-deuterium exchange experiments indicate that the dissociation of H_2 is difficult on small Co nanoparticles, a reason that is used to explain lower rates for smaller particles. Further research provided evidence that CO activation is facilitated by the presence of hydrogen on Co nanoparticles, and that the ability to dissociate hydrogen is the key parameter determining FTS activity [22]. However, Holmen et al. [23] provided an alternative view on the Co particle size effect in FTS. Their SSITKA experiments showed that the number of surface CH_x intermediates increased with particle size, while the intrinsic activity remained constant when the Co particle size varied from 4 nm to 15 nm. They suggested that the site-based activity does not change in the 4–15 nm range, but that smaller particles have comparatively less active sites than larger ones.

Regarding FTS selectivity, quite small Co nanoparticles generally display increased CH_4 selectivity. There is a volcano-like curve for C_{5+} selectivity that varies with the particle size of Co/γ-Al_2O_3 catalysts, and the maximum selectivity was found for 7–8 nm Co nanoparticles [24]. This finding was confirmed by Holmen's [25] lateral work showing that the C_{5+} selectivity does indeed increase with Co particle size below 8–9 nm, and approaches a constant value for even larger Co particles. It is interesting that the lowest CH_4 selectivity as well as the highest olefin-to-paraffin ratio were obtained at maximum C_{5+} selectivity. Recently, Melaet et al. [26] found that the FTS reaction exhibited obvious changes with Co particle size (3.2–11 nm) in the product distribution at 250 °C. Fig. 3 shows that CH_4 selectivity increases with decreasing Co particle size, and is ac-
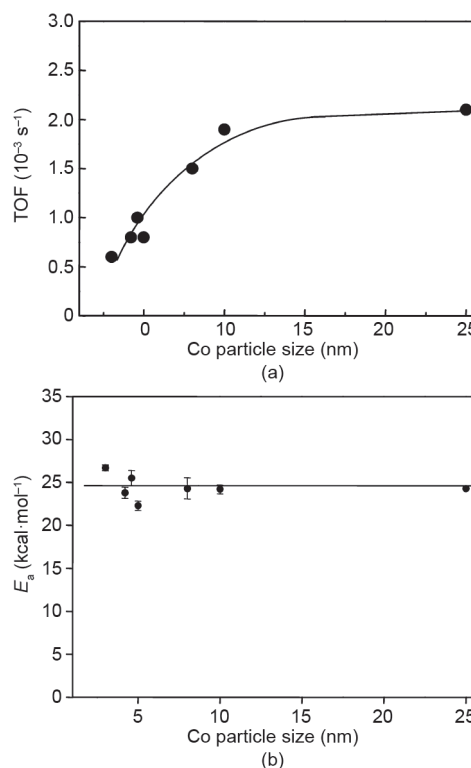

Fig. 1. Co particle size effect in the turnover frequency (TOF) of FTS (220 °C, $H_2/CO = 2$, 1 bar (1 bar = 10^5 Pa)) [15].

Fig. 2. CO methanation activity as a function of particle size. (a) TOF of CO hydrogenation at 240 °C; (b) activation energy (E_a) of CO hydrogenation varying with particle size [21]. 1 kcal = 4184 J.