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Review of recent development in Co-based catalysts supported on carbon materials for Fischer–Tropsch synthesis

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HIGHLIGHTS

- The recent development of Co/carbon catalyst for FT synthesis were concerned.
- O- and N-doping of carbon enhanced the FT performance of Co/carbon catalyst.
- Confinement effect and cobalt size effect affect FT activity of Co/carbon catalyst.
- Feasible methods to control cobalt either inside or outside of CNTs were discussed.

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ABSTRACT

Diminishing petroleum reserves, sharp fluctuations of crude oil prices, increasingly stringent environmental regulations and the global demand for a decreased dependence on petroleum for the production of fuels and chemicals, are the main driving force for the recent renewed interest in Fischer–Tropsch (FT) synthesis in academia and industry. Cobalt catalyst is the preferred catalyst for the production of long-chain paraffins because of its high activity, low water–gas shift activity and comparatively low price. Carbon materials including traditional activated carbons, carbon nanotubes and nanofibres, carbon spheres and mesoporous carbons have been used as the support for cobalt catalyst in the past 10 years for its inert property. The microstructures (e.g., carbon porosity, cobalt particle size, cobalt location and cobalt dispersion) of these carbon supported cobalt catalyst determine the CO conversion and product selectivity. In this paper, we focus on the most recent developments around carbon support structure effect, cobalt intrinsic properties and promoter effect on carbon supported cobalt catalyst for FT synthesis. The nitrogen doping effect, confinement effect and cobalt particle size effect on carbon nanotubes supported Co catalysts are further presented in this review.

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1. Introduction

Fischer–Tropsch (FT) synthesis, a heterogeneous catalytic process, can produce a large variety of products such as paraffins, olefins, alcohols and aldehydes using syngas (CO and H_2) derived from natural gas, coal-bed gas, shale gas, coal or biomass, through steam reforming, partial or autothermal oxidation, or gasification processes (Trépanier et al., 2009a; Zhang et al., 2010; Huffman, 2011; Ma et al., 2011). As a result of diminishing petroleum reserves, sharp fluctuations of crude oil prices, increasingly stringent environmental regulations and the global demand for a decreased dependence on petroleum for the production of fuels and chemicals in the past few years, FT synthesis has been considered as one of the most promising ways to ultra-clean fuel production at economically feasible cost, and also has attracted the renewed interest in academia and industry in recent years (Zhang et al., 2010; Fu et al., 2013). For FT synthesis, cobalt and iron metal have been employed in industry. Compared with cobalt catalysts, iron catalysts can be operated under wider range of temperatures and H_2/CO ratios with low CH_4 selectivity. Especially, Fe catalysts exhibit much higher activity for the water gas shift (WGS) reaction, which is helpful for the conversion of syngas with lower H_2/CO ratios derived from coal or biomass. In addition, linear alkane fuels, alkenes and oxygenates can be obtained through iron catalysts. However, the rapid catalyst deactivation is still a big challenge for Fe catalysts (Khodakov et al., 2007). Comparatively, cobalt catalysts are preferred due to their high activity, high selectivity to long-chain paraffins, low WGS activity and high resistance to deactivation by water (Trépanier et al., 2009a).

For supported cobalt catalysts, both the microstructure and FT performance of the cobalt catalyst has a tight correlation with the support (Borg et al., 2007). The support can disperse cobalt metal particles on the catalyst surface after reduction and further keep these cobalt particles stable during reaction. Also, the support can significantly affect the FT performance due to metal–support interactions, support acidity, porosity and mass transfer limitations (Surisetty et al., 2010; Gardezi et al., 2011). The metal–support interactions could affect the structure and electron density of cobalt metal particles, and also result in the reaction between the support and cobalt species forming cobalt–support mixed compounds. The support acidity could lead to olefin isomerization, lower chain growth probability, and higher selectivity to lighter hydrocarbons. The support porosity, such as average pore diameter, pore volume and surface area, can significantly influence the cobalt dispersion and reducibility, and thus the activity/selectivity for FT synthesis. Also, the support texture modifies diffusion of reactants and products inside the catalyst grains. In addition, the support also dissipate the reaction heat and thus reduce a temperature gradient in a fixed bed reactor.

Conventionally, silica and alumina have been mainly used as the support of cobalt catalyst (Ma et al., 2011; Trépanier et al., 2009b; Jacobs et al., 2003; Zhang et al., 2003; Bechara et al., 2001; Belambe et al., 1997; Girardon et al., 2005; Jung et al., 2012; Lögdberg et al., 2010; Dinse et al., 2012; Espinosa et al., 2011; den Breejen et al., 2010; Bai et al., 2012; Zhou et al., 2011; Xiong et al., 2009; Enache et al., 2004; Xiong et al., 2005, 2008; Fischer et al., 2013). However, the main problem of these type of catalysts is the limitation on the FT synthesis activity, due to the formation of mixed compounds (Trépanier et al., 2009a, 2009b; Bahome et al., 2005; Bezemer et al., 2006a; Den Breejen et al., 2009; Tavasoli et al., 2008a, 2008b; Xiong et al., 2011, 2010; Zaman et al., 2009; Abbaslou et al., 2009). These compounds are reducible only at hightemperature because of the strong interaction between Co species and support. For example, Al_2O_3 has been one of the mostly used supports for cobalt FT catalysts. The relatively strong interaction between the cobalt particles and the Al_2O_3 support results in the formation of hardly reducible $CoAl_2O_4$ species. So the cobalt reducibility is an important problem for Co/Al_2O_3 catalysts. Although the interaction between support and cobalt is relatively weak in silica-supported catalyst, a hardly reducible material Co_2SiO_4 was also formed and to get high cobalt dispersion is the major challenge for Co/SiO_2 catalysts. So it is hard to get a Co catalyst with both high Co dispersion and high cobalt reducibility for conventional oxide supported cobalt catalyst.

Compared with conventional oxide supports, carbon materials such as carbon nanofibers (CNFs), nanotubes (CNTs), carbon spheres (CSs) and mesoporous carbons display unique properties such as high purity, high mechanical strength, good electrical conductivity, high thermal stability and large surface area, and they are increasingly attracting more and more attention as potential supports for cobalt-based FT catalysts (Tavasoli et al., 2010; De Jong and Geus, 2000). It is unlikely to form aforementioned hardly reducible compound since carbon has an inert surface, which can enhance the reducibility of cobalt oxide. Meanwhile, carbon pore structure can be controlled to promote the cobalt dispersion on the catalyst surface for the pore size has a direct influence on the cobalt size. Also, different functional groups can be introduced onto carbon surface, which is helpful for tuning the metal–support interaction for immobilization of cobalt active sites and further increasing the cobalt dispersion. So it is easy to get a cobalt catalyst with high Co dispersion but without compromising the cobalt dispersion when carbon is used as the support. In addition, carbon material can be used as support to allow study of the intrinsic properties of the cobalt particles and the effect of the support structure on the FT performance. This is possible since carbon is chemically inert, in contrast to oxide supports where poorly reducible mixed oxides may interfere the discussion of these intrinsic properties, which is much helpful for the rational design of Co-based catalyst for

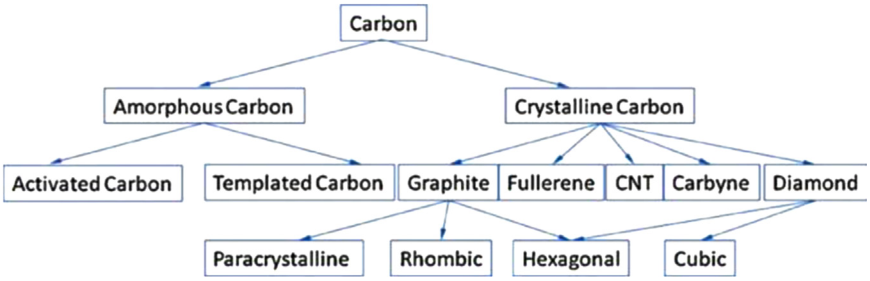

Fig. 1. Polymorphs of carbon (Trogadas et al., 2014; Yang et al., 2011).

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