Preferential chemical vapor deposition of ruthenium on cobalt with highly enhanced activity and selectivity for Fischer–Tropsch synthesis

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A B S T R A C T

Various amount of ruthenium was preferentially deposited on cobalt of Co/γ-Al_2O_3 by chemical vapor deposition (CVD) of ruthenocene and compared with a $CoRu/\gamma$-Al_2O_3 catalyst prepared by the usual impregnation method for Fischer–Tropsch synthesis (FTS). The Co/γ-Al_2O_3 was prepared by wet impregnation of cobalt nitrate aqueous solution, and then dried and calcined at 400 °C for 4 h. Ruthenocene was sublimated, carried by argon, and then mixed with H_2 and passed over γ-Al_2O_3 or calcined Co_3O_4/γ-Al_2O_3 catalyst at various temperatures. The effluent gasses were passed through a gas cell of FTIR to determine the ruthenocene thermo-chemical decomposition products. In a temperature range (window) of 150–200 °C the ruthenocene decomposes on Co_3O_4/γ-Al_2O_3 but not on γ-Al_2O_3. The catalysts were characterized by TPR, EDX, TEM, XRD and BET. The FTS activity and selectivity of the Ru-Co/γ-Al_2O_3 catalysts were investigated in a fixed bed microreactor. The preferential CVD of 0.3 wt% ruthenium onto 15.0 wt% Co/γ-Al_2O_3 (CoRu5-180) catalyst shifted both cobalt TPR peaks by about 120 °C to lower temperatures, showed about 2.8 times higher conversion, 30% more C_{5+} selectivity, and 30% less selectivity of methane. The CoRu5-180 catalyst showed about 81% higher CO conversion and 12% higher selectivity to C_{5+} than the same catalyst composition prepared by the used impregnation of ruthenium chloride onto the 15.0 wt% Co/γ-Al_2O_3.

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1. Introduction

In Fischer–Tropsch synthesis (FTS), mixtures of hydrocarbons (HCs) are produced from synthesis gas (H_2 and CO) in a catalytic reaction. FTS always produces a wide range of light gases and distillates, including olefins, paraffins and oxygenated compounds [1,2]. The synthetic fuel produced from FTS has a high quality particularly in terms of high cetane number and low pollution [2].

The most common catalysts for FTS are cobalt- or iron-based catalysts. Fe-based catalysts are less active than Co-based ones; which requires lower reaction temperature to be active in FTS [3].

Some inorganic supports with high surface area, such as silica and alumina, have been used to increase dispersion of the cobalt. FTS over cobalt on alumina catalysts mainly produces heavy linear hydrocarbons, even at atmospheric pressure [4,5]. Also, less active for the water gas shift (WGS) reaction [4]. The interaction of alumina with cobalt is stronger than that of other supports, such as titania and silica [6]. The formation of irreversible cobalt-aluminates during pretreatments and under reaction conditions decreases the catalysts activity [7,8]. Low degree of reduction of cobalt-aluminates results in decreasing the number of active sites, and thus lowers the catalyst activity [9–11].

The promoting effects of a second metal on supported cobalt catalysts have been reported in numerous studies [5–9,12]. Higher FTS activity, better cobalt oxides reducibility, and higher catalyst stability are the advantage of promoter addition. The promoters also lower the temperature of cobalt oxides reduction to metallic cobalt by the well-known mechanism of hydrogen spillover [3,13]. Also the addition of small amounts of promoters to the catalysts increases the dispersion and reducibility of actives metal and achieves improved FTS conversion and selectivity. Vada et al. [14] have reported that the addition of Pt or Re to Co/γ-Al_2O_3 significantly increased its FTS activity, whereas its selectivity remained unchanged. They suggested that the higher activity was due to an increase in cobalt reducibility and number of surface atoms. Schanke et al. [15] have shown that addition of a small amount of Pt (0.4 wt%) strongly improved the reducibility of Co/γ-Al_2O_3 catalysts, as did Li et al. [16] and Jacobs et al. [17]. Re [13,18], and

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Ru [7,9], also increase the reducibility and the catalytic activity of cobalt on alumina catalysts. It is proposed that hydrogen spillover from Re and Ru improves the reduction of cobalt oxides. Ru promoter has also significantly increased the turnover rates on Co/SiO_2 and Co/TiO_2 catalysts. It was proposed that Ru inhibited the deactivation of cobalt catalysts, by catalyzing the hydrogenolysis of carbonaceous deposits [17].

Jacobs et al. [19] have reported that the addition of small amounts of group IB metals (Cu, Ag, Au) to $Co/\gamma-Al_2O_3$ improved the reducibility of cobalt oxides and, in the case of Ag and Au, increased the density of surface cobalt sites. The proposed mechanisms for the promoting effects include hydrogen spillover and formation of bimetallic particles. Among the promoters, ruthenium has been reported [20] to be a structural promoter for Co-based catalysts. Ru also prevents the agglomeration of cobalt oxide particles during calcinations and show high activity in Fischer–Tropsch synthesis.

Song et al. [21] reported the promoting effect of varying amounts of ruthenium, i.e. 0.2–2 wt%, on $Co/\gamma-Al_2O_3$ and Co/SiO_2 catalysts. The SiO_2 supported Co catalysts have shown sustainable reducibility and CO hydrogenation activity in the entire range of Ru contents, whereas its alumina analog displays a maximum reducibility at 0.42 wt% of Ru. Segregation of Ru on the alumina support surface seems to be responsible for decreased activity as reflected by the reduction in the reducibility of Co species.

Most of the promoted cobalt catalysts for FTS have been prepared by a traditional impregnation method [17,18,21–23]. Park et al. [24] have reported the preparation of $RuCo/\gamma-Al_2O_3$ catalyst by impregnation method. Uniformly sized cobalt oxide nanoparticles with different amounts of ruthenium promoter have been prepared by solvothermal method using oleic acid as capping agent. Pre-synthesized $CoRuO_x$ nanoparticles were then impregnated on $\gamma-Al_2O_3$ support. The catalysts prepared by the solvothermal method have shown less-agglomerated spherical particles even after calcination. By adopting the above methodology, it is expected that the dispersion of cobalt on the catalyst support will be higher due to the intimate contact between Co and Ru, and the presence of ruthenium promoter will reduce cobalt oxide at lower reduction temperatures. Intimate contact between the promoter element and the active metal is most essential to acquire the advantage of bimetallic synergy.

Preparation of promoted catalysts using traditional impregnation methods may result in promoters impregnation on both active phase and support. The highest promoting role of ruthenium may occur when the ruthenium is only impregnated onto the cobalt active phase with close contacts, but not onto the alumina. Chemical vapor deposition (CVD) is used for selective addition of a promoter on the active phase surface of a catalyst with high bimetallic interaction. Organometallic complexes can be used as CVD precursors or atomic layer deposition (ALD) precursors to deposit metal clusters on various substrates, such as metals, oxides, and zeolites [25–28]. Because of the weak binding between metal atoms and organic ligands in the organometallic precursors, metal atoms will be deposited on the substrates, with organic ligands escaping in the gas, after heating organometallic adsorbates at elevated temperature.

Miura and Itoh [29] have reported the preparation of Pt–Sn bimetallic catalysts by a CVD technique, in which Sn was selectively deposited onto Pt by passing volatile organometallic compounds over $Pt/ZnAl_2O_4$ in an H_2 flow. Mixed Pt–Sn sites improve the activity of isobutane dehydrogenation, while Sn on the support improves the selectivity. In addition, Miura [30] has reported the preparation of supported bimetallic catalysts by selective deposition of metal complex precursors on the surface of other metal particles. This technique was applied for the preparation of the Pt–Ru bimetallic catalyst supported on silica, using ruthenocene as a precursor for ruthenium.
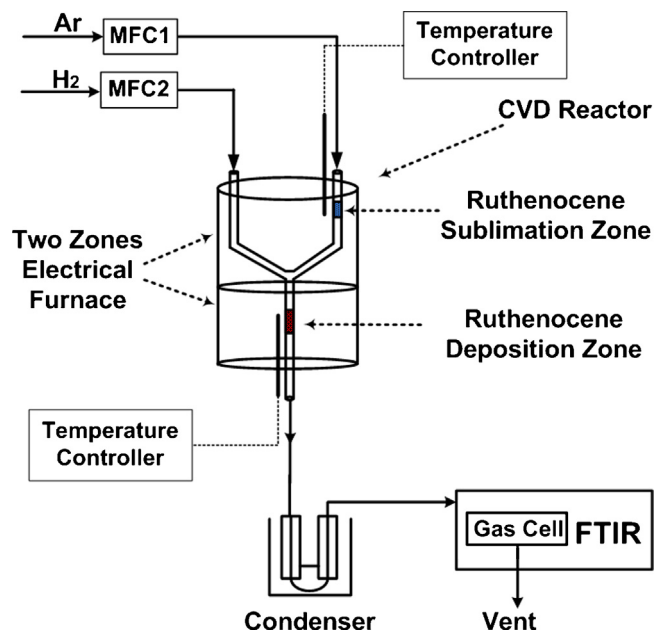

Fig. 1. Schematic diagram of the chemical vapor deposition experimental setup.

In this study, chemical vapor deposition of ruthenocene is applied for preferential deposition of ruthenium onto the cobalt of FTS catalyst. The close contact between cobalt and ruthenium greatly enhances the reducibility of the Ru-promoted cobalt catalysts and improves their FTS activity and selectivity.

2. Materials and methods

2.1. $Co/\gamma-Al_2O_3$ preparation

The alumina supported cobalt catalyst was prepared by impregnation of $\gamma-Al_2O_3$ (Sasol with a BET surface are of $200\,m^2/g$ and a pore volume of $0.76\,cm^3/g$) with a cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$ from Merck) aqueous solution. The alumina support was calcined in air, while the temperature was increased from 25 to $500\,°C$ at a rate of $1.5\,°C/min$ and kept at this temperature for 10 h. 12 g of the alumina was immersed in 20 mL solution containing 22.9 g $Co(NO_3)_2 \cdot 6H_2O$ for 1 h, and then filtered. The 12 g alumina had 9.12 mL pore volume and took up the same amount of the solution, which contained 10.46 g $Co(NO_3)_2 \cdot 6H_2O$, corresponding to 15 wt% cobalt on alumina. The sample was then dried at $120\,°C$ overnight and calcined at $400\,°C$ for 4 h in air. The preferential chemical vapor deposition of various amounts of ruthenium on cobalt of $Co/\gamma-Al_2O_3$ is presented in Section 3.1.

2.2. CVD setup for Ru deposition on $Co/\gamma-Al_2O_3$

Fig. 1 shows the CVD experimental setup used for preferential deposition of ruthenium on the $Co_3O_4/\gamma-Al_2O_3$. It consists of an Ar and H_2 feeding section, a ruthenocene sublimation zone, a ruthenocene deposition zone, and a gas cell in an FTIR for analysis of ruthenocene decomposition products in effluent gases.

The feeding section consists of two mass flow controllers (MFCs) used to adjust the flow rates of Ar and H_2, already passed through two sets of moisture and oxygen traps. Quartz CVD reactor consists of two lines for feeding the carrier gas (Ar) and reactant gas (H_2). Also the furnace provides two different temperature zones for the ruthenocene sublimation and decomposition. Ruthenocene was loaded into the sublimation zone of the CVD reactor with Ar as the carrier gas. The temperature of this zone was sufficient