Co@Ru nanoparticle with core–shell structure supported over γ-Al₂O₃ for Fischer–Tropsch synthesis

Ali Haghtalab[*], *Amir Mosayebi*

Department of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-143, Tehran, Iran

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ABSTRACT

Co@Ru/γ-Al₂O₃ core–shell structure catalysts with Co/Ru different weight ratios are successfully prepared via surface displacement reaction. This novel route including reduction of Co core by NaBH₄ on the surface of γ-Al₂O₃ and then substitution of Co species with Ru species, the resultant of reduction of RuCl₃ precursor with N₂H₄. These catalysts are characterized with techniques X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), high resolution transmission electron microscopy (HRTEM), N₂ adsorption/desorption (BET), temperature programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and Fourier transform infra-red (FTIR) of CO adsorbed. The characterization results confirm a uniform dispersion of Co@Ru nanoparticles with core–shell structure over γ-Al₂O₃. The core–shell Co@Ru/γ-Al₂O₃ catalysts show the remarkable catalytic activity towards Fischer–Tropsch synthesis (FTS) in comparison with Co/γ-Al₂O₃, which is related to special core–shell structure. These catalysts exhibited excellent abilities in the cases of increasing formation of long-chain hydrocarbons and suppressing selectivity to lighter hydrocarbons.

Introduction

The conversion of natural gas to hydrocarbons (GTL) is currently one of the most promising topics in the energy industry due to economic utilization of resources such as natural gas, coal or biomass to environmentally clean fuels, especially waxes. Fischer–Tropsch synthesis (FTS) reaction is a well known way for production of hydrocarbons with different chains from syngas (CO + H₂), that firstly was founded by Fischer and Tropsch in 1925 [1].

The numerous studies on FTS had been carried out, since now. Usually in these studies the influence of different active components, support species, methods of synthesis catalyst, introduction of promoters, etc. had been investigated. Study in the case of effect of catalyst structure on FTS performance was less evaluated. The core–shell structure due to higher catalytic activity was considered in different processes. Nevertheless, in this case few studies on FTS were reported [2–5]. Xie et al. [2] solvothermally synthesized Co₃O₄@m-SiO₂ nanocomposites and obtained better results (higher CO conversion and long-chain hydrocarbon selectivity) in FTS in comparison with Co₃O₄/m-SiO₂. Yang et al. [3] founded the addition of zeolite shell to Co/SiO₂ and formation of a core–shell structure will improve catalytic performance of FTS. Further, Yang et al. in another work [4] achieved the inverse

results when zeolite shell was added to Ru/SiO$_2$ which resulted in synthesis of Ru/SiO$_2$@H-ZSM-5. Jiang et al. [5] prepared a novel catalyst with a core (Fe/SiO$_2$) – shell (silicalite-1), results showed the production of light alkenes from syngas in FTS substantially will increase in comparison with Fe/SiO$_2$, while CO conversion and production of heavier hydrocarbons decreases. All these results should be ascribed to the unique core–shell structure. Core–shell structure have got attracted much attention due to its higher potential in improvement of the core with suitable shell components to reach particular catalytic performance [6]. In the prior studies, a support (silica or zeolite) played the shell role [2–5]. As mentioned, the type of material used as shell has a critical impact in catalytic activity. Thus, using a component as shell with higher catalytic activity would participate in more intensification of FTS performance. All group VIII metals (Fe, Co, Ru, Pt, etc.) have notable activity in the CO hydrogenation [7]. Co (transition metal) is the most common active metal used in FTS due to its higher activity, higher selectivity for heavier hydrocarbons, more resistant to deactivation and lower tendency to water-gas shift reaction [8,9]. The alloy which is composed of transition metal and noble metal has higher catalytic activity than a metal, indicating the synergism effect between two metals [10,11]. Noble metals usually used as promoter and have strong influence on the structure and reducibility of Co, CO conversion and hydrocarbons selectivity in FTS [7]. The results had showed among noble metals, Ru have the most synergism with cobalt species [12]. Hereby, Ru was selected as shell and Co as core. The formation of special core–shell structure and synergism between Co and Ru, led to more advantages in FTS.

In the present investigation, bimetallic Co–Ru nanoparticles with a core–shell structure supported over γ-Al$_2$O$_3$ (Co@Ru/γ-Al$_2$O$_3$) in Co/Ru different weight ratios are synthesized by surface displacement reaction method, which in previous literatures had not been reported. For comparison of the results, Co/γ-Al$_2$O$_3$ and Ru/γ-Al$_2$O$_3$ catalysts are also synthesized. The BET, HRTEM, EDX, XPS and XRD characterization analysis are used to evaluate the catalysts morphology, elemental analysis, surface chemical analysis, and crystal phase structure so that their results are confirmed the formation of core–shell structure. The TPR experiment carries out for consideration catalysts reduction behavior, the reducibility improved strikingly with core–shell structure formation. The FTIR characterization of CO adsorption on the catalysts after reduction treatment is performed and catalysts structural variation, as the resultant of exposure to CO is discussed in details. Finally, effect of the core–shell structure formation is investigated on the efficiency of the FTS catalyst. The FTS reaction performance of the catalysts in terms of CO conversion, CH$_4$ selectivity, long-chain hydrocarbons selectivity and CO$_2$ formation rate are analyzed and compared with the other works.

Experimental

Preparation of Co/γ-Al$_2$O$_3$ nanoparticle

Cobalt nanocrystals deposited on γ-Al$_2$O$_3$ are prepared by cobalt chloride reduction with NaBH$_4$ solution in the presence of water-ethanol. In detail, 0.5 g of γ-Al$_2$O$_3$ (Merck) is dispersed in 60 ml ethanol–water (Volume ratio = 1:1) solution by ultrasonic at 323 K for 30 min. Then, 0.025 g of CoCl$_2$.6H$_2$O (Sigma Aldrich) aqueous solution was added into the suspension, stirred and purged by N$_2$ for 90 min. Suspension is saturated by N$_2$, NaBH$_4$ prepared solution (0.005 g in 10 ml of 0.5 M NaOH solution), as reducing, is added drop wise into the solution under stirring at room temperature. After mixing of the suspension for 12 h, a clear change from pink to brown was observed, indicating the reduction process is taking place as

$$CoCl_2 \cdot 6H_2O + 2NaBH_4 \rightarrow Co\downarrow + 2NaCl + 2BH_3 + 6H_2O + H_2 \quad (1)$$
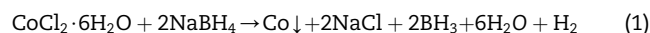
Hereby, Co nanocrystals are formed over γ-Al$_2$O$_3$ support.

Preparation of Co@Ru/γ-Al$_2$O$_3$ catalyst

The Co@Ru/γ-Al$_2$O$_3$ nano-structure catalysts are synthesized using a surface displacement reaction. Briefly, the solution including Co/γ-Al$_2$O$_3$ nanoparticles was heated to 513 K. 10 ml of RuCl$_3$ (Sigma Aldrich) aqueous solution is added into suspension under stirring for 1 h. At this time, a color change from brown to black is taken place. Afterward, 3 mL of hydrazine hydrate solution as a reducing is added drop wise under stirring. After 6 h, the solution is left to settle. Then, the solid sample is filtrated using circle filtration paper and washes several times with ethanol and deionized water. The catalysts are dried in vacuum condition at 373 k for 12 h. In order to remove impurities and residuals, the catalysts are calcined at 773 k for 6 h. The schematic illustration of the preparation method of Co@Ru nanoparticles on γ-Al$_2$O$_3$ is shown in Fig. 1.

In this study to comparing, the Co@Ru/γ-Al$_2$O$_3$ catalysts at the different Co/Ru ratios (from 9 to 1) are synthesized so that the cobalt loading is 5 wt% for all the catalysts. To synthesis the Co/γ-Al$_2$O$_3$ catalyst, a solution containing Co/γ-Al$_2$O$_3$ is washed with DDI water and ethanol for several times, then, dried at 373 k and finally calcined at 773 K for 6 h. The Ru/γ-Al$_2$O$_3$ catalyst is prepared directly in γ-Al$_2$O$_3$ suspension slurry through reducing the RuCl$_3$ using hydrazine hydrate. Co/γ-Al$_2$O$_3$ and Ru/γ-Al$_2$O$_3$ catalysts were noted as CA and RA, respectively.

The loading of cobalt and ruthenium in the calcined catalysts is verified by an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) system after complete dissolution of the catalysts (5 mg) in 5 ml of HNO$_3$/HCl solution (1/3 volume ratio). The theoretical Co and Ru contents in the CA and RA catalysts are targeted as 5 and 0.55 wt%, respectively. The ICP analysis shows the actual contents of Co and Ru are 4.93 and 0.64 wt%, respectively. The Co@Ru/γ-Al$_2$O$_3$ catalysts nomenclature and compositions are summarized in Table 1.
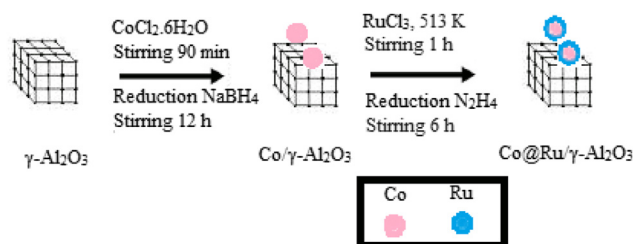

Fig. 1 – The schematic diagram of the preparation of Co@Ru nanoparticles on γ-Al$_2$O$_3$.