Ru promoted cobalt catalyst on γ-Al₂O₃: Influence of different catalyst preparation method and Ru loadings on Fischer–Tropsch reaction and kinetics


A C T I V E N E W S

ABSTRACT

Ruthenium promoted cobalt catalysts supported on γ-Al₂O₃ were prepared by stepwise and co-impregnation methods. The effects of impregnation order on activity and selectivity of the Fischer–Tropsch synthesis (FTS) were investigated using fixed bed microreactor. The catalysts were characterized by TPR, XRD and TEM. The selected Ru loading was 0.15 wt.% while that of Co was 15.0 wt.% in all of the prepared samples by different order of impregnation. The catalyst prepared by co-impregnation method shifted both steps of cobalt oxide reduction temperatures to lower temperatures by about 100 °C. However, temperature shift was lower for the catalyst prepared by stepwise impregnation method. The highest CO conversion and C₅⁺ selectivity and the lowest methane selectivity were obtained for the catalyst synthesized by co-impregnation method. Two other catalysts with 0.3 and 0.6 wt.% of Ru loadings on 15.0 wt.% Co were synthesized by co-impregnation and its effect on the FTS was investigated. The prepared catalysts showed an increase in CO conversion with the increase of Ru from 0 to 0.30 wt.%. however, further increase in Ru led to lower CO conversion for a Ru loading of 0.6 wt.%. The effects of temperature and H₂/CO ratio for all catalysts were examined and their performance modeled by a Langmuir–Hinshelwood–Hougen–Watson (LHHW) rate expression.

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1. Introduction

In the Fischer–Tropsch synthesis (FTS), mixtures of hydrocarbons (HCs) are produced catalytically from synthesis gas (H₂ + CO). Regardless of the operating conditions, FT synthesis always produces a wide range of light gases and distillates, including olefins, paraffins and oxygenated products [1,2]. This synthetic fuel has high quality particularly in terms of cetane number and less pollution.

The most common catalysts for this process are cobalt- or iron-based catalysts. Co-based catalysts are typically more active than Fe-based ones though they require lower reaction temperature [3].

Some inorganic supports with high surface area such as silica and alumina have been used to increase dispersion of the cobalt. FT synthesis over cobalt on alumina catalysts allows the production of long chain alkenes even at atmospheric pressure [4,5]. Furthermore, Co/Al₂O₃ catalysts are well known to produce linear hydrocarbons, with high selectivity for heavy hydrocarbons, and have low activity for water gas shift reaction [4].

For alumina, the metal–support interaction is stronger than the other supports such as titania and silica [6]. However, the formation of irreversible cobalt–aluminates during pretreatment and under reaction conditions decreases the catalytic activity due to the loss of active cobalt metal for catalyzing the reaction [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]. Promoting effects, due to the presence of a second metal, on reducibility, activity and stability of the cobalt catalyst have been reported in numerous studies [12]. These promoters play a role of reducing the cobalt particles at lower temperature with an enhanced reducibility by the well-known mechanism of hydrogen spillover [3,13].
Vada et al. [14] reported that addition of Pt or Re to Co/Al₂O₃ significantly increased the FT activity, whereas the selectivity remained unchanged. They suggested that the higher activity was due to increased reducibility and increased number of surface cobalt atoms. Schanke et al. [15] have shown that addition of a small amount of Pt (0.4 wt.%) strongly improved the reducibility of Co/Al₂O₃ catalysts as did Li et al. [16] and Jacobs et al. [17]. Re [13,18] and Ru [7,9] were also reported to increase the reducibility and the catalytic activity of alumina supported cobalt catalysts. They proposed that hydrogen spillover from Re and Ru improved the reducibility of cobalt oxides. Addition of Ru also significantly increased the turnover rates on Co/SiO₂ and Co/TiO₂ catalysts, and it was proposed that Ru inhibited the deactivation of cobalt catalysts by catalyzing the hydrogenolysis of carbonaceous deposits [17].

Jacobs et al. [19] reported that addition of small amounts of group IB metals (Cu, Ag, Au) to Co/Al₂O₃ 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 these promoting effects include hydrogen spillover and formation of bimetallic particles. Among these promoters, ruthenium was reported [20] to act as a structural promoter for Co-based catalysts which also prevents the agglomeration of cobalt oxide particles during calcinations and results in high activity for Fischer–Tropsch reaction and better selectivity for C₅₊ products.

In this work ruthenium promoted Co/Al₂O₃ catalysts were prepared and tested during FT synthesis and the effects of preparation method along with the Ru loading on performance of the catalysts in a fixed bed reactor are investigated. Furthermore, UHWW rate parameters such as reaction rate constant and activation energy are reported.

2. Experimental

2.1. Catalyst preparation

Cobalt supported catalysts were prepared by wet stepwise impregnation and co-impregnation of γ-Al₂O₃ (AkzoNobel, BET surface area of 200 m²/g and pore volume of 0.7 cm³/g) with well-mixed cobalt nitrate (Co(NO₃)₂·6H₂O from Merck) and ruthenium chloride (RuCl₃·xH₂O from Merck) precursor aqueous solutions. 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. In co-impregnation method, the precursors were dissolved in deionized water according to the specified weight ratio of Co–Ru (15%: 0–0.6%). The resultant solution and the support were mixed, subjected to evacuation at 70 °C for 4 h, dried at 120 °C for 12 h and calcined at 400 °C for 4 h under flow of dried air. In the stepwise impregnation method, the impregnated support with the first precursor is dried and calcined and the thus obtained catalyst is mixed with aqueous solution of the second precursor and then dried and calcined as mentioned previously. In the synthesis procedure, if first Co and then Ru precursors are impregnated on Al₂O₃ support consecutively, the sample is denoted as Co/Ru/Al₂O₃. If the order of impregnation is reversed the sample is denoted as Ru/Co/Al₂O₃ and finally if both precursors are impregnated simultaneously the catalyst is designated as CoRu/Al₂O₃. Prior to the activity test, the catalyst is reduced in situ under 60 scm (standard conditions cm³/min) of pure hydrogen in a fixed-bed reactor at 400 °C for 12 h. The weight ratio of cobalt metal to support was fixed at 15% for all the catalysts. The abbreviations for the pretreated catalyst samples used in this study are given in Table 1.

2.2. Catalyst characterization

The XRD patterns of the prepared catalysts were taken at room temperature using Phillips powder diffractometer with monochromatized Cu–Kα radiation. Cobalt phases were detected by comparing the diffraction patterns with those of the standard powder XRD file compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). Average Co₃O₄ crystallites sizes were calculated employing Scherrer’s equation, using the most intense Co₃O₄ peak at 2θ of 36.8.

The corresponding mean cobalt metal sizes in the reduced catalysts were first estimated by considering the relative molar volumes of Co⁰ and Co₃O₄ using Eq. (1) [21]:

\[
d(\text{Co}⁰) = 0.75 \times d(\text{Co₃O₄})
\]

(1)

To further study the changes of crystallite size and cobalt phase the following protocol was employed. The reduced catalysts were cooled to room temperature under hydrogen flow and passivated for 1 h in a flow of 20 sccm 1.0% O₂ in N₂. The passivated samples were then removed from the reactor and characterized by XRD. The average crystallites sizes of the passivated catalysts were also calculated by the characteristic peak of the metallic cobalt at 2θ of 44.4 using Scherrer’s equation.

The Co⁰ metal dispersions were calculated from the mean Co⁰ particle sizes assuming a spherical geometry of the metal particles with uniform size density of 14.6 atoms/nm² [21,22], using:

\[
D = \frac{96}{d}
\]

(2)

where D is the % dispersion and d is the mean particle size of Co⁰ in nm.

High-resolution transmission electron microscopy (HRTEM) analysis was performed using a JEOLJEM-2100 (200 kV) microscope equipped with an EDS analytical system. The powdered samples were ultrasonically dispersed in ethanol and the obtained suspensions were mounted on to a thin carbon film supported on a copper microgrid. For each catalyst, about 50 Co₃O₄ particles were measured in order to determine the average particle size and size distribution of the cobalt oxide particles.

Nitrogen adsorption–desorption isotherms for the support and promoted catalysts were measured at liquid nitrogen temperature, using a Quantachrome CHEMBET-3000 instrument. The samples (0.1 g, 60/100 mesh) were outgassed at 350 °C for 3 h, prior to the measurement. The surface area was calculated from the Brunauer–Emmett–Teller (BET) equation.

Catalysts were characterized by H₂-temperature programmed reduction (TPR) using a Quantachrome CHEMBET-3000 apparatus. For this purpose, 50.0 mg sample was placed in a U-tube quartz reactor as a shallow packed bed, heated in a pure He stream (30 standard conditions cm³/min) to 150 °C, and kept at this temperature for 4 h in order to degas the sample. The sample was then cooled down to room temperature in He and the gas was switched to 7.0%H₂/Ar. The sample temperature was then increased to 900 °C with 10 °C/min heating rate.

2.3. FTS setup

A schematic of the setup used for testing the catalysts under Fischer–Tropsch (FT) conditions is presented in Fig. 1. The mass flow controllers (MFC) were used to adjust the flow rates of CO and H₂ reactants, which passed through a 0.25 in OD stainless steel tube reactor packed with 0.5 g of sieved catalyst powder. The H₂ and CO were passed through two separate sets of moisture and oxygen traps, respectively. A bed of quartz chips, heated to 300 °C, was used downstream of the traps in CO stream to decompose possible metal carbonyls. The reactor was immersed in a molten-salt bath equipped with a PID-temperature controller and a stirrer to ensure effective heat transfer and uniform reactor temperature. The reactor effluent was passed through a 300 °C heated line, to prevent condensation of heavy products. Methane, C₂–C₄, and
Table 1
Catalysts abbreviations for the prepared catalyst in this study.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>First impregnation step</th>
<th>First calcination temperature (°C)</th>
<th>Second impregnation step</th>
<th>Second calcination temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/Al₂O₃</td>
<td>15% Co</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co/Ru/Al₂O₃</td>
<td>15% Co</td>
<td>400</td>
<td>15% Ru</td>
<td>400</td>
</tr>
<tr>
<td>Ru/Co/Al₂O₃</td>
<td>0.15% Ru</td>
<td>400</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Co.015Ru/Al₂O₃</td>
<td>0.15% Ru + 15% Co</td>
<td>400</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Co.030Ru/Al₂O₃</td>
<td>0.3% Ru + 15% Co</td>
<td>400</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Co.060Ru/Al₂O₃</td>
<td>0.6% Ru + 15% Co</td>
<td>400</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

a M₁/M₂/M₃/O₃: stepwise impregnation of the first M₁ and then M₂.
b M₁/M₂/M₃/O₃: co-impregnation of M₁ and M₂.

Fig. 1. Simplified schematic of the experimental setup.

C₅⁺ hydrocarbons and unreacted CO in the effluent were analyzed on a multi-column and multi-valve Varian CP-3800 refinery gas analyzer (RGA) equipped with both thermal conductivity detector (TCD) and flame ionization detector (FID). A methaneizer at the end of the columns was used to convert separated CO and CO₂ to methane, which was then detected by the FID with much higher sensitivity. CO conversion and different product selectivity were obtained from the RGA analyses data and were calculated on carbon basis as follows:

\[
\text{CO conversion} \ (\%) = \frac{X_{CO}}{100} = \frac{\text{moles of inlet CO} - \text{moles of outlet CO}}{\text{moles of inlet CO}}
\]

\[
\text{CH}_4 \text{ selectivity} \ (\%) = S_{CH}_4 = \frac{\text{moles of CH}_4 \text{ produced}}{\text{moles of inlet CO} - \text{moles of outlet CO}} \times 100
\]

\[
\text{C}_x \text{ selectivity} \ (\%) = S_{C}_x = \frac{\text{moles of } C_x \text{ produced}}{\text{moles of inlet CO} - \text{moles of outlet CO}} \times 100
\]

\[
S_{C}_x = S_{C}_5 \text{ selectivity} \ (\%) = 100 - S_{CH}_4 - S_{C}_2 - S_{C}_3 - S_{C}_4
\]

Also, the Anderson–Schulz–Flory (ASF) chain growth probabilities (α value) for the C₁–C₄ hydrocarbon range from the slope of the curve Ln(Sₙ/n) versus n, where n is the carbon number and Sₙ is the selectivity to hydrocarbon with n-carbon atoms [23].

The prepared catalysts were tested under different operating conditions, such as temperature and H₂/CO ratio. CO conversion, product selectivity and the chain-growth probability (α value) for Fischer–Tropsch (FT) synthesis were calculated based on the results obtained. The catalysts were reduced at 400 °C for 12 h in 60 sccm (standard conditions cm³/min) hydrogen and then exposed to FTS at different operating conditions including temperatures and H₂/CO ratios as summarized in Table 2.

3. Result and discussion

3.1. XRD analysis

3.1.1. Effects of preparation method

Fig. 2 illustrates the XRD patterns of the prepared catalysts, i.e. oxide catalyst, and the passivated samples which exhibits clearly the presence of Co₃O₄ and cubic metallic Co. Fig. 2(a) shows that Co₃O₄ spinel phase (ICPDS file no. 9-0418) with 2θ values of 31.3, 38.8, 45.8, 59.4, and 65.3 is found in all the catalyst samples. The

Fig. 2. XRD patterns of the catalysts prepared by different order of impregnation: (a) before reduction and (b) after reduction.
Table 2
The sets of experiments performed on the catalysts.

<table>
<thead>
<tr>
<th>Test target</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Set no.</td>
</tr>
<tr>
<td>Temperature effect</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>H₂/O ratio effect</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>7</td>
</tr>
</tbody>
</table>

Table 3
Average Co₃O₄ crystallite size, Co⁰ crystallite size, dispersion, specific surface area of the samples prepared by different order of impregnation (15% Co with 0.15% Ru).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Specific surface area (m²/g)</th>
<th>Co₃O₄ crystallite size (nm)</th>
<th>Co⁰ crystallite size (nm)</th>
<th>Dispersion (%)</th>
<th>Hydrogen consumption in TPR (μmol H₂/g catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before reduction</td>
<td>After reduction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>190</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co/Al₂O₃</td>
<td>138</td>
<td>16.8</td>
<td>12.6</td>
<td>14.4</td>
<td>6.7</td>
</tr>
<tr>
<td>Ru/Co/Al₂O₃</td>
<td>168</td>
<td>14.8</td>
<td>11.1</td>
<td>12.5</td>
<td>7.7</td>
</tr>
<tr>
<td>Co/Ru/Al₂O₃</td>
<td>170</td>
<td>13.5</td>
<td>10.1</td>
<td>11.2</td>
<td>8.6</td>
</tr>
<tr>
<td>Co/Ru(Al₂O₃)</td>
<td>173</td>
<td>12</td>
<td>9</td>
<td>9.7</td>
<td>9.9</td>
</tr>
</tbody>
</table>

*Co₃O₄ crystallite size of the calcined catalysts is determined using Scherrer’s equation at 2θ = 36.8, and listed in Table 3. The crystallite size of Co₃O₄ decreases when the ruthenium is present. However, no peak is observed for RuO₂ in the XRD patterns. This may indicate that ruthenium is present on the catalysts surface with crystallite sizes smaller than 5 nm [25,26].

For the passivated catalysts, some weak peaks of CoO were observed. This is due to the formation of a thin shell of oxide phase in the course of passivation treatment prior to the XRD measurement. No RuO₂ and Ru diffraction peaks are detected in Fig. 2(b) because of relatively low content and high dispersion of Ru. As is observed the average cobalt crystallite size decreases by addition of Ru in the samples regardless of the method used for the sample preparation. For each sample, the metallic Co size calculated by Eq. (1) is smaller compared to the one calculated by using the characteristic peak of the metallic cobalt in the Scherrer’s formula. The difference has been attributed mainly to the sintering of the surface cobalt species during the reduction followed by passivation [9]. Table 3 indicates that the cobalt dispersion increases with adding ruthenium by all of the preparation methods.

3.1.2. Effect of promoter loading

The XRD analysis for various amounts of Ru promoted on Co/Al₂O₃ catalyst by co-impregnation are provided in Fig. 3. It can be seen that for the unreduced catalysts, the intensity of Co₃O₄ XRD peak at 36.8 decreases in the presence of Ru. The extent of the intensity decreases with increase in the Ru loading. This trend is the same for the both unreduced and reduced samples.

Table 4 indicates that the cobalt dispersion increases with ruthenium content of the catalysts. It is suggested that ruthenium possibly aids in reducing small cobalt oxide clusters strongly interacting with the support to produce additional small particles or raft-like structures of the reduced cobalt metal [9]. The presence of these additional small metal particles would greatly decrease the average cobalt metal particle size [9,26]. Kogelbauer et al. [9] have also reported that addition of ruthenium decreases the particle size and increase the dispersion of cobalt. At higher cobalt...
dispersions, the number of ruthenium atoms in the vicinity of cobalt may increase and enhance the reducibility of cobalt oxide species.

3.2. BET result

The specific surface areas of the Ru-promoted cobalt catalysts, calcined at 400 °C for 4 h, are shown in Tables 3 and 4. Specific surface area of γ-Al2O3 support significantly decreases by addition of cobalt oxide, indicating the deposition of cobalt oxide inside the pores of alumina support. However, upon addition of ruthenium the surface area considerably increases. This may be due to a decrease in the particle size of cobalt oxide, in accordance with the XRD results [25,26].

3.3. TEM and EDX analysis

TEM micrographs and EDX analysis of Co/Al2O3 and CoRu/Al2O3 with 0.3 wt.% ruthenium are presented in Fig. 4. EDX analysis of CoRu/Al2O3 confirms the presence of ruthenium in the sample. The size distribution of cobalt oxide of the samples is also shown in Fig. 4 insets. Following addition of 0.3 wt.% Ru to Co/Al2O3, the average cobalt oxide nanoparticle size reduces from 17.2 to 11.1 nm and their distribution shifts to lower sizes with a narrower distribution. The average cobalt oxide nanoparticles sizes obtained from TEM micrographs are close to their average crystallites sizes estimated from XRD patterns (Tables 3 and 4).

Lattice fringes of unpromoted Co/Al2O3 catalyst and CoRu/Al2O3 sample promoted with 0.3 wt.% Ru are shown in Fig. 5. Lattice spacing of 0.24 nm of Co/Al2O3 sample corresponds to (3 1 1) planes and that of 0.28 nm to (2 2 0) plane of Co3O4 phase [27]. Two clear lattice fringes of 0.24 nm and 0.22 nm are observed in the TEM micrograph of CoRu/Al2O3 (Fig. 5(b)). The 0.24 nm lattice fringes correspond to the Co3O4 (3 1 1) inter-planar distance while the 0.22 nm lattice planes are ascribed to RuO2 (2 0 0) lattice fringes [27]. Therefore, RuO2 crystallite seems to be in intimate contact with the cobalt oxide nanoparticles for the sample prepared by co-impregnation method. Furthermore, selected area electron diffractions (SAEDs) of the ruthenium oxide and cobalt oxide in Fig. 5 insets suggest the intimate contact of the RuO2 and Co3O4 nanoparticles.
3.4. Catalyst reducibility

3.4.1. Effect of preparation method

TPR experiment was performed to investigate the reduction behavior of the catalyst samples. Fig. 6 shows the characteristic reduction behavior of the catalysts. As observed, the TPR profiles have at least two major reduction peaks. The first reduction peak is appeared at about 413 °C, while the second broad peak which starts at around 549 °C and terminated at about 660 °C. The two reduction peaks are believed to be based on the following reactions [28]:

\[
\text{Co}_2\text{O}_4 + \text{H}_2 \rightarrow 3\text{CoO} + \text{H}_2\text{O} \tag{7}
\]

The cobalt aluminates resulting from interaction of the cobalt species with the alumina support is usually very refractory and may not be reduced at temperatures below 800 °C [29,30]. The presence of Ru in all of the catalysts shifts both reduction peaks to lower temperatures, i.e. the first reduction temperature shifts from 413 to below 370 °C and the second reduction temperature shifts from 549 to below 500 °C. This may be attributed to a large spillover of hydrogen [31]. It worth noting that the extent of temperature shift for the Co/Co/Al\textsubscript{2}O\textsubscript{3} catalyst is larger, indicating very close contact between Co species and Ru. In the case of Co/Ru/Al\textsubscript{2}O\textsubscript{3} and Ru/Co/Al\textsubscript{2}O\textsubscript{3} catalyst samples, three peaks are observed. It has been proposed that the lowest temperature peak might be attributed either to the reduction of residual Co(NO\textsubscript{3})\textsubscript{2} remaining after calcinations [32] or reduction of ruthenium oxide [33]. Considering the fact that we calcined the catalysts at 400 °C for 4 h relating this peak to reduction of ruthenium oxide seems to be more plausible.

As was mentioned the cobalt species in Co/Ru/Al\textsubscript{2}O\textsubscript{3} catalyst which was prepared by co-impregnation method was reduced more easily as compared to the other catalysts, i.e. the catalysts prepared by stepwise impregnation.

3.4.2. Effect of promoter loading

The TPR profiles for various amounts of Ru promoted on Co/Al\textsubscript{2}O\textsubscript{3} catalyst by co-impregnation are provided in Fig. 7. It has been reported that cobalt can be present on the surface as individual oxides, CoO or Co\textsubscript{2}O\textsubscript{4}, or as surface compounds with the support, amount of which depends on the property of the support and the calcination temperature [29,34]. According to Fig. 6, as the Ru content increases from 0 to 0.3 wt% the TPR reduction peaks shifts more toward lower temperatures. Thus, the role of Ru could be regarded as decreasing the reduction temperature of Co species by forming Ru–Co or Ru–Co–Al complexes. This assumption can be related to the fact that Co\textsubscript{2}RuO\textsubscript{4} forms a spinel isostructural to Co\textsubscript{2}O\textsubscript{4} which can be reduced at lower temperatures than cobalt aluminates [30].

It is worthy to note that, since ruthenium oxide can be reduced at lower temperatures than cobalt oxide, metallic ruthenium could act as reduction nuclei via smooth spreading of hydrogen over the cobalt species [35]. As shown in Fig. 6 the reduction temperature peaks of Ru promoted catalyst, Co 0.15Ru/Al\textsubscript{2}O\textsubscript{3}, shifted from 413 °C to 301 °C and 549 °C to 447 °C as compared to Co/Al\textsubscript{2}O\textsubscript{3} catalyst due to the presence of Ru promoter which reduces the interaction of cobalt oxide with the support and enhances the reducibility of cobalt oxide. Also, the reduction temperature peaks

\[
3\text{CoO} + 3\text{H}_2 \rightarrow 3\text{Co}^0 + 3\text{H}_2\text{O} \tag{8}
\]
3.5. Catalyst activity and selectivity

3.5.1. Effect of impregnation method

CO conversion, product selectivities and chain growth probability (α) for Fischer-Tropsch (FT) synthesis on various catalysts at 220 °C and H2/CO = 2 and residence time of 2 s are summarized in Table 5. The highest CO conversion, i.e. 19.0%, is obtained for CoRu/Al2O3 catalyst, which is prepared by co-impregnation method, while that for Co/Al2O3 is 10.5%. Also among the catalysts which are synthesized by stepwise impregnation method, the catalyst with Ru promotion on Co supported alumina (Co/Ru/Al2O3) shows higher CO conversion, i.e. 15.3% as compared to Co impregnated Ru supported alumina (Ru/Co/Al2O3), i.e. 12.9% CO conversion.

The catalytic activity in FTS primarily depends on two factors, the cobalt dispersion and cobalt degree of reduction [26]. The preparation method of the catalysts along with the low loading of ruthenium suggests that degree of reduction of cobalt (indicated as hydrogen consumption in Table 3) along with cobalt dispersion has contributions on performance of the catalyst. A close look at the TPR characterization section reveals that CoRu/Al2O3 catalyst have a lower reduction temperature as compared to the non-promoted catalyst or catalyst prepared by stepwise impregnation method. Also among the catalysts which are synthesized by stepwise impregnation method, the Co/Ru/Al2O3 catalyst has better reducibility pattern than the Ru/Co/Al2O3 catalyst. These similar trends between the reducibility patterns as depicted in Fig. 6 and the CO conversion as shown in Table 5 indicates that the activity of the catalysts could be proportional to the degree of reduction.

Selectivity of CH4 as one of the most undesirable product decreases in the order of Co/Al2O3 > Ru/Co/Al2O3 > Co/Ru/Al2O3 > CoRu/Al2O3. Thus, CoRu/Al2O3 shows the lowest CH4 selectivity, 25.9%, which is about 15.6% lower than its corresponding value for Co/Al2O3. However, the stepwise impregnation method does not significantly improve the Co/Al2O3 catalyst in lowering the CH4 selectivity due to the lower reducibility of cobalt oxide particles.

The C5+ selectivity in FT synthesis. The highest C5+ selectivity of 46.5% is obtained for CoRu/Al2O3 catalyst, for which the CH4 selectivity is the lowest and the chain growth is the highest at the expense of C3–C4 hydrocarbons. The stepwise impregnation method does not improve the C5+ selectivity either.

There are many reports about the increase in C5+ selectivity in the presence of Ru particles which is due to the easier dissociation of CO and chain propagation [8,39]. The bimetallic interaction between Co and Ru influences the dispersion and reducibility of supported metals which is reflected here in the results of TPR patterns only. The cleansing effect of Ru during CO hydrogenation due to its high hydrogenation ability prevents the formation of carbon deposits on the catalyst surface. This effect facilitate [40] the re-adsorption of olefins which in turn improves the chain growth probability. Thus, Ru-promoted samples enhanced the chain propagation by predominantly re-adsorbing lighter olefins and produce larger amount of C5+, hydrocarbons. This effect is more pronounced for the catalyst which is prepared by co-impregnation method. Because in this method, Ru and Co precursors are mixed well and thus in the calcinations and reduction steps remain in close contact with each other.

The effects of temperature and H2/CO ratio on CO conversion for catalysts with different impregnation methods are shown in Fig. 8. This figure demonstrates that, the presence of Ru enhances the CO conversion for all of the catalysts. However, this effect is more pronounced for the catalyst prepared by co-impregnation method, i.e. CoRu/Al2O3 catalyst. In conclusion the catalyst prepared with co-impregnation method improves significantly the desired performance compared to the unpromoted and promoted-Co/Al2O3 catalysts prepared by stepwise impregnation.

The effects of temperature and H2/CO ratio on CH4 and C5+, selectivity for different catalysts are presented in Fig. 9. As temperature and H2/CO ratio increases, for all of the catalysts, CH4 selectivity increases while the C5+ selectivity decreases. As is shown in these figures the catalyst prepared by co-impregnation method is the most sensitive catalyst to the temperature and H2/CO ratio.
Table 5
The performance of the Ru promoted Co supported catalysts with co- and stepwise-impregnation methods (15% Co with 0.15% Ru).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO conversion (%)</th>
<th>Selectivity</th>
<th>α</th>
<th>(O/P)%</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>C1</td>
<td>C1-C4</td>
<td>C5</td>
</tr>
<tr>
<td>Co/Al2O3</td>
<td>10.5</td>
<td>30.7</td>
<td>24.8</td>
<td>44.5</td>
</tr>
<tr>
<td>CoRu/Al2O3</td>
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<td>25.9</td>
<td>27.6</td>
<td>46.5</td>
</tr>
<tr>
<td>Co/RuO2/Al2O3</td>
<td>15.1</td>
<td>28.1</td>
<td>31.2</td>
<td>40.7</td>
</tr>
<tr>
<td>Ru/Co/Al2O3</td>
<td>12.9</td>
<td>29.4</td>
<td>27.5</td>
<td>43.1</td>
</tr>
</tbody>
</table>

Therefore, the proper operating condition could be adjusted in a more suitable way compared with the catalyst which is prepared by stepwise impregnation method.

The effects of temperature and H2/CO ratio on C2-C4 olefin/paraffin ratio and chain growth probability for samples by different order of impregnation are presented in Fig. 10.

3.5.2. Effect of Ru loading

Three catalysts with 0.15%, 0.3% and 0.6% Ru loading on 15% cobalt supported alumina were synthesized with co-impregnation method and their catalytic performance were measured under operating conditions of 220 °C and H2/CO = 2 and 2 s residence time. The results are summarized in Table 6.

The catalysts show a considerable increase in activity, from 10.5% to 21.1%, with the increase of Ru content from 0 to 0.3 wt.%. However, after passing a maximum, the CO conversion decreases and reaches a value of 10.2% at a Ru loading of 0.6 wt.%.

It has been reported that ruthenium in contact with cobalt oxide can form a spinel type of structure, i.e. Co3RuO4 [20]. This structure saturates at Ru content of 0.3 wt.%. Ru loading beyond 0.3 wt.% might have resulted in the segregation of RuO2 from the surface of Co3O4 particles [33]. Ru particles chemisorb hydrogen molecules dissociatively. In order to be effective in reduction of cobalt oxide they must be in close contact with the cobalt oxide particles. Thus, the segregated Ru particles, beyond 0.3 wt.%, are not effective anymore. After reaching the maximum of Co2RuO4 formation, the excess Ru might migrate to the Al2O3 support. Ru helps in activating the hydrogen molecule to its atoms and in turn leads to reduction of Co3O4. Because of segregation of Ru this activity is brought down. This might have reduced the CO hydrogenation activity in the case of 0.6 wt.% Ru catalyst. Lower reducibility has been reported to be one of the factors causing lower activity of cobalt catalysts for CO hydrogenation.

These results show that the increase in Ru content from 0 to 0.60 wt.% does not change considerably the C5+ selectivity. Thus the
Co 0.30Ru/Al2O3 catalyst showed the best performance compared to the other catalysts.

The effects of temperature and H2/CO ratio on CO conversion for catalysts with different Ru loading are shown in Fig. 11. It is evident that the catalyst with 0.30% Ru is most active in FT synthesis as temperature and H2/CO ratio rises.

The CO conversion decreases in the order of Co 0.30Ru/Al2O3 > Co 0.15Ru/Al2O3 > Co 0.60Ru/Al2O3 > Co/Al2O3 as the temperature rises. Also this catalyst is more sensitive to temperature than to H2/CO ratio.

CH4 and C5s selectivity for the catalysts with different ruthenium loadings are shown in Fig. 12. As temperature and H2/CO ratio increases, for all the catalysts, CH4 selectivity increases while the C5s selectivity decreases. As is evident from these figures, for all of the catalysts, at moderate temperature and H2/CO ratio the C5s Selectivity does not change significantly. This means that for the catalyst with high CO conversion the yield of C5s is the highest.

Therefore, regarding the C5s yield the catalyst with 0.3% Ru loading has better performance.

The effects of temperature and H2/CO ratio on C2–C4 olefin/paraffin ratio and chain growth probability for the catalysts with different ruthenium loadings are shown in Fig. 13.

3.6. Impregnation and Ru promotion effects on kinetics

The overall stoichiometry of the Fischer–Tropsch reaction for the synthesis of high molecular weight hydrocarbons is given by:

$$n(\text{CO} + 2\text{H}_2\text{O}) \rightarrow -(\text{CH}_2)_n + n\text{H}_2\text{O}$$

(9)

This reaction describes the stepwise incorporation of \(\text{CH}_2\) species into a growing chain and the removal of oxygen atoms as water. This chemical equation represents a sequence of elementary steps leading to the formation of hydrocarbons from CO and \(\text{H}_2\).

Table 6
Catalytic activity on Co/\(\gamma\)-Al2O3 with different Ru content.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO conversion (%)</th>
<th>Selectivity</th>
<th>(\alpha)</th>
<th>(O/P)%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C1 - C5s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co/Al2O3</td>
<td>10.5</td>
<td>30.7</td>
<td>42.5</td>
<td>0.60</td>
</tr>
<tr>
<td>Co 0.15Ru/Al2O3</td>
<td>19</td>
<td>29.9</td>
<td>46.5</td>
<td>0.72</td>
</tr>
<tr>
<td>Co 0.30Ru/Al2O3</td>
<td>21.1</td>
<td>26.2</td>
<td>44.5</td>
<td>0.70</td>
</tr>
<tr>
<td>Co 0.60Ru/Al2O3</td>
<td>10.2</td>
<td>28.1</td>
<td>45.7</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Fig. 11. The effects of (a) temperature and (b) H₂/CO ratio on CO conversion for catalysts with different Ru content.

Fig. 12. The effects of temperature and H₂/CO ratio on CH₄ selectivity (a and b) and C₅⁺ selectivity (c and d) for catalysts with different Ru content.
The hydrogenation of CO and the formation of each individual Cn hydrocarbon, obey Langmuir Hinselwood kinetic expressions as summarized by Wenping et al. [41]. The LHHW kinetic reported by Iglesia et al. [42] as given in Eq. (10) is selected here to describe the effects of impregnation method and Ru promotion on kinetic rate and activation energy of the overall reaction.

\[
r_{CO} = \frac{kPCO^{a}H_{2}^{b}}{1+mP_{CO}}
\]

(10)

where \( k = k_0 \exp(-E/RT) \) is the apparent kinetic rate constant, \( a \) and \( b \) are apparent reaction orders for CO and \( H_2 \), respectively, and \( m \) is defined to be a carbon monoxide effect parameter. The value of these parameters has been reported for Co and Ru catalysts to be as follows: \( a = 0.65, b = 0.6 \) and \( m = 3.3 \). These values are valid over a wide range of pressure (100–2100 kPa) and \( H_2/CO \) ratios (1–10) [42]. Pressure orders were independent of metal dispersion or metal oxide support.

3.6.1. The effects of impregnation method on kinetics

Coalt supported \( \gamma \)-Al2O3 catalysts which are prepared by stepwise impregnation and co-impregnation methods were tested in different operating conditions in Fischer–Tropsch synthesis as was discussed in previous sections. The experimental results obtained were correlated to the empirical rate as expressed by Eq. (10). The kinetic rate constant, pre-exponential factor and activation energy at three different temperatures, are given in Table 7.

It is apparent that addition of Ru promoter enhances the reaction rate constant for these catalysts. However, the extent of enhancement is the largest for the catalyst prepared by co-impregnation and the activation energy of the reaction becomes more than two times higher than its corresponding value obtained for the un-promoted catalyst. These results are in agreement with TPR characterization test which was discussed in the previous section. Addition of Ru by co-impregnation method shifted both steps of cobalt oxide reduction temperature to lower temperatures by about 100 °C. The extent of shift in reduction temperature is lower for the catalysts prepared by stepwise impregnation method. It appears that the Ru promoter enhances the reducibility of the small metal particles and the small metal particles adsorb CO more strongly [41]. Thus, the activation energy for the catalyst with better reducibility becomes higher. Furthermore, these results are in agreement with those presented in Fig. 8 indicating that the catalyst prepared by co-impregnation method, is the most active for FTS as temperature rises.

3.6.2. Effects of Ru loading on kinetics

The reaction rate constant and activation energy for the catalysts promoted by 0.15, 0.3 and 0.6 wt.% of Ru prepared by co-impregnation method are presented in Table 8. As is shown the catalysts exhibit a considerable increase in reaction rate constant and activation energy with the increase in Ru content from 0.0 to 0.30 wt.%. However, after showing a maximum, the reaction rate constant and its corresponding activation energy decrease at the loading of 0.6 wt.%.
Incorporation of Ru enhances Co dispersion in alumina-supported catalysts, compared to their un-promoted catalysts; however, change in Ru content does not affect the dispersion significantly. Segregation of Ru on the surface of alumina support seems to be responsible for a decrease in the rate constant. The segregated Ru on the surface has a great tendency for hydrogen adsorption which in turn reduces the hydrogen concentration on the Co sites which according to Eq. (10) are responsible for hydrogenation of carbon monoxide. This effect has been also reported by Iglesia et al. [4].

4. Conclusion

In the present investigation the effects of catalyst preparation method on the performance of Fischer–Tropsch (FT) synthesis was studied. The Ru-promoted cobalt catalysts were prepared by stepwise impregnation and co-impregnation of γ-Al2O3 with well-mixed aqueous solution of cobalt and ruthenium precursors. The TPR results indicate that the presence of Ru in all of the catalysts shifts both Co reduction peaks to lower temperatures, i.e. the first reduction temperature shifts from 413 to below 370 °C and the second reduction temperature shifts from 549 to below 500 °C. This effect is more pronounced for the catalyst which was prepared by co-impregnation method due to very close contact between the cobalt and ruthenium species. The catalytic performance of the catalysts was examined under specified operating conditions, and CO conversion, product selectivity and chain growth probability (α) were obtained. The highest CO conversion, C5+ selectivity and chain growth probability (α) and the lowest methane selectivity were obtained for the catalyst synthesized by co-impregnation method. This catalyst shows up to 100% higher conversion, 4.5% improvement in C5+ selectivity and 15.5% suppression in methane selectivity.

The effect of Ru loading on the performance of the catalysts was also investigated. Ru was found to have a remarkable promoting effect on performance of the Co/Al₂O₃ catalyst. The prepared catalysts show a considerable increase in CO conversion, i.e., from 10.5 to 21.1%, with the increase of Ru content from 0 to 0.30 wt.% due to better reducibility of cobalt and the synergistic effect between ruthenium and cobalt. However, further increase in Ru content led to a significant drop in CO conversion.

References


