Effect of Lanthanum as a Promoter on Fe-Co/SiO₂ Catalyst for Fischer-Tropsch Synthesis

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Abstract

Iron-Cobalt catalyst is well known from both operational and economical aspects for Fischer-Tropsch synthesis. Effort to increase the efficiency of this kind of catalyst is an important research topic. In this work, the effect of lanthanum on characteristic behavior, conversion and selectivity of a Fe-Co/SiO₂ Fischer-Tropsch catalyst was studied. The Fe-Co-La/SiO₂ catalysts were prepared using an incipient wetness impregnation method. These catalysts were then characterized by XRF-EDAX, BET and TPR techniques, and their performances were evaluated in a lab-scale reactor at 250 ºC, H₂/CO = 1.8 of molar ratio, 16 barg pressure and GHSV = 600 h⁻¹. TPR analysis showed that the addition of La lowered the reduction temperature of Fe-Co catalyst, and due to a lower temperature, the sintering of the catalyst could be mitigated. Furthermore, from these tests (about 4 days), it was found that lanthanum promoted catalyst had higher selectivity toward hydrocarbons, and lower selectivity toward CO₂.

Keywords: Fischer-Tropsch synthesis; Catalysis; Fe-Co catalyst; Lanthanum

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1. Introduction

Fischer-Tropsch (FT) process converts syngas (mixture of H₂ and CO) into liquid hydrocarbons. Because of increasing in transportation fuels demand, it is an attractive and economical method which has high potential to produce such fuels. In the FT process, the choice of the catalyst to synthesis hydrocarbons is very important. Cobalt and iron catalysts are the most widely used in FT process [1]. Among other FT catalysts such as nickel and ruthenium, only cobalt and iron appear to be economically feasible at an industrial scale [2]. Iron-based catalysts are more selective toward olefin and gasoline range hydrocarbons, and produce CO₂ whereas cobalt-based catalysts produce wide range of hydrocarbons and water as a major product [3]. It has been shown that using a Fe-Co catalyst would allow to control the hydrocarbon product spectrum [4] by varying structure, electronic properties and metal particle size of the catalysts [5]. During the last two decades, Fe-Co catalysts have been used by many authors to investigate their property. Some reports showed
that the use of Fe-Co catalysts lead to increase
in selectivity, especially for small olefins and alco-
hol s [6-9].

It is reported that the activity and hydrocar-
bon distribution of FT catalysts are also strongly
depended on the addition of other metals as pro-
mitters. Some researchers have studied the ef-
effect of lanthanum and ruthenium as promoters on the activity of the FT catalysts [10-12]. In
their studies, they have found that lanthanum
and ruthenium could increase the activity and
stability of the Co catalyst. In other studies, the
effect of ruthenium and niobium as promoters on
the activity of iron catalysts was studied [13-
17], and it was found that these promoters
could increase the C5+ product. Ma et al. [18]
studied the effect of adding potassium and zir-
conium on the activity of Fe-Co catalyst, and
found that these promoters could enhance the
activity of the catalyst and increase the CO con-
version.

Up to now, few studies have been done on
the effect of lanthanum on the Fe-Co catalysts
for FT process. The aim of the present research
was to investigate the effects of lanthanum on
Fe-Co catalysts yield for these purposes.

2. Materials and Methods

2.1. Material used

SiO2 used as catalyst support was pur-
b chased from Fluka (Art No. 60744). Analytical
grade Fe(NO3)3·9H2O, Co(NO3)2·6H2O, and
La(NO3)3·6H2O were purchased from Merck
(Art No. 103883), Fluka (Art No. 60883) and
Merck Company (Art No. 105326), respectively.

2.2. Catalyst preparation and characteri-
ization

2.2.1. Fe-Co/SiO2 catalyst

The Fe-Co/SiO2 catalyst was prepared by
wet-impregnation method. Amount of 5 g of
SiO2 particles with the mesh size between 30
and 40 were calcined at 500 °C for 6 h, then put
in a rotary vacuum evaporator, and kept at 80
°C. Meanwhile, 2.12 g of Fe(NO3)3·9H2O and
2.9 g of Co(NO3)2·6H2O were dissolved in 4.63 g
of deionized water at 80 °C. The solution was
then added to silica particles in the rotary vac-
uum evaporator, and kept at 80 °C at a speci-
fied time. The prepared catalyst was dried at
120 ºC for 2 h, and kept at room temperature
for 24 h. Temperature was then increased to 80
°C under vacuum condition, and the catalyst
was calcined at 400 °C for 6 h.

2.2.2. La-Fe-Co/SiO2 catalyst

To study the effect of lanthanum on Fe-Co
catalyst characteristic, La-Fe-Co/SiO2 was pre-
bared by wet-impregnation method. 5 g of SiO2
particles with the mesh size between 30 and 40
was calcined at 500 °C for 6 h, then put in a ro-
I tary vacuum evaporator, and kept at 80 °C. 2.12 g of Fe(NO3)3·9H2O, 2.9 g of
Co(NO3)2·6H2O and 0.193 g of La(NO3)3·6H2O
were dissolved in 4.63 g of deionized water
at 80 °C. The solution was then added to silica
particles in the rotary vacuum evaporator, and
kept at 80 °C at a specified time. The prepared
catalyst was dried at 120 °C for 2 h, and kept
at room temperature for 24 h. Temperature was
then increased to 80 °C under vacuum condition,
and the catalyst was calcined at 400 °C for 6 h.

2.2.3. Characterization

The BET specific surface area of the cata-
lysts was determined by nitrogen adsorption-
desorption isotherms employing a Quantasorb
surface area analyzer (Quantachrome Corpora-
tion) using a 3:7 ratio of a N2/He mixture. Typi-
cally, 0.1 – 0.3 g of sample was used for the
measurement, and it was out-gassed at 300 °C
for 2 h prior to N2 adsorption at -196 °C; then,
specific surface area values were calculated by
the BET equation. The chemical compositions
of catalysts were measured by Perkin-Elmer
2380 atomic absorption spectrophotometer.
Moreover, the reducibility of the metal oxides
was determined by temperature program redu-
duction (TPR) experiment which was carried out
using a Micromeritics TPD/TPR 2900 Ana-
lyzer. About 0.15 g freshly prepared catalyst
was loaded into the quartz reactor and treated
with a mixture of 6 % H2/Ar. The temperature
was increased from 27 to 827 °C at a rate of 5
°C/min. H2O formed during TPR were removed
by the cold trap, and the effluent gas was moni-
tored by a thermal conductivity detector (TCD).
Finally, a Varian gas chromatograph device
(model CP-3800), equipped with a TCD was
used to analyze the feed and products during
catalyst activity test.

2.3. Activity test

The study of catalyst activity was carried out
in a laboratory scale reactor with 1.25 cm
internal diameter and 60 cm height. 2.5 g of
catalyst with average particle size of 0.4-0.6
mm (mesh 30-40), diluted with 10 cm3 of milled
quartz particles, was loaded in the reactor. The
catalyst bed was heated to 420 °C with the tem-
perature ramp of 2 °C/min under hydrogen flow with GHSV = 1000 h⁻¹ and pressure of 5 bars, and kept at 420 °C for 16 h. The temperature was then decreased to 100 °C and hydrogen flow was stopped. A mixture of H₂/CO with the molar ratio of 1.8 and GHSV = 600 h⁻¹ was introduced to the reactor at 16 bar. The temperature was slowly increased to 250 °C, and kept at this temperature to study catalyst activity. During the activity test, the product was analyzed by GC. The test was carried out for 4 days.

3. Results and Discussion

The chemical compositions of the prepared catalysts are shown in Table 1. In this table, actual loadings of FT catalysts, following the described methods in Section 2.2.1 and Section 2.2.2, are reported.

BET surface areas of the prepared catalysts are shown in Table 2. These results show that the surface area of the Fe-Co catalyst is slightly higher than the catalyst promoted with lanthanum.

Temperature programmed reduction (TPR) profiles of prepared catalysts are shown in Figures 1 and 2. In Figure 1, the TPR profile of Fe-Co/SiO₂ shows that this catalyst has a multi-step reduction temperature in which each peak corresponds to the reduction temperature of a different compound. At 330 °C reduction of Co₃O₄ to CoO and also partial reduction of Fe₂O₃ to Fe₃O₄, at 410 °C complete reduction of Fe₂O₃ to Fe₃O₄, at about 500 °C reduction of Fe₂O₃ to Fe, and finally at about 840 °C the cobalt and iron phases which are hard to reduce.

In Figure 2, it can be seen that lanthanum loading slightly decreases the reduction temperatures of the catalyst. The decrease in reduction temperature lowers the partial oxidation, and therefore catalyst sintering.

Test conditions and product specifications for the performance evaluation of Fe-Co/SiO₂

| Property             | 1st day | 2nd day | 3rd day | 4th day |
|----------------------|---------|---------|---------|---------|
| Temperature          | °C      | 250     | 250     | 250     | 250     |
| Pressure             | bar     | 16      | 16      | 16      | 16      |
| GHSV                 | h⁻¹     | 600     | 600     | 600     | 600     |
| H₂/CO                | mol/mol | 1.8     | 1.8     | 1.8     | 1.8     |
| CO Conversion        | mol%    | 94.0    | 98.5    | 98.2    | 98.0    |
| CO₂ Selectivity      | mol%    | 23.1    | 27.8    | 29.4    | 30.7    |
| Organic Liq. Percentage | wt%  | 25.32   | 21.24   | 19.19   | 24.78   |
| Total Liq. Product   | g       | 11.5    | 8.9     | 8.0     | 8.5     |
| Gas phase composition |        | CH₄ mol% | 28.86   | 37.91   | 39.25   | 39.32   |
|                      |         | C₂-C₄ mol% | 3.60    | 4.86    | 4.10    | 3.80    |
|                      |         | C₅⁺ mol% | 0.02    | 0.16    | 0.10    | 0.06    |
catalyst are shown in Table 3. The product selectivity and CO conversion for this catalyst was evaluated at interval time of 1 day for a period of 4 days. With the same reaction conditions as shown in Table 3, Fe-Co-La/SiO₂ catalyst was tested, and no liquid product was in the reactor effluent (i.e. the indication of FT synthesis catalyst performance). Therefore, reaction conditions such as temperature and GHSV were changed until the liquid products were obtained (see Table 4).

Comparison the results shown in Table 3 and Table 4 showed that the presence of La in the catalyst results in: (1). CO₂ selectivity considerably was decreased leading to a lower CO conversion which affected the waste products; (2). The C₂-C₄ and C₅⁺ selectivity of the gas product was increased; (3). While GHSV increased by 300 %, the percentage of the organic components in the liquid product was not changed. This showed that the productivity of Fe-Co-La/SiO₂ catalyst was much higher than Fe-Co/SiO₂ catalyst; (4). Lower operating temperature results in lower coke deposition on the catalyst, which was an important operation factor.

From the above results, it is seen that the presence of lanthanum promoter in the catalyst can improve the productivity of the Fe-Co catalyst, and probably increases the catalyst life.

Table 4. Test conditions and product compositions for the La-Fe-Co/SiO₂ catalyst

| Property             | 1st day | 2nd day | 3rd day | 4th day |
|----------------------|---------|---------|---------|---------|
| Temperature  °C      | 235     | 235     | 235     | 235     |
| Pressure bar         | 16      | 16      | 16      | 16      |
| GHSV h⁻¹             | 1821    | 1821    | 1821    | 1821    |
| H₂/CO mol/mol        | 1.8     | 1.8     | 1.8     | 1.8     |
| CO Conversion mol%   | 82.8    | 82.7    | 77.8    | 76.4    |
| CO₂ Selectivity mol% | 12.4    | 12.7    | 9.8     | 9.3     |
| Organic Liq. Percentage wt% | 20.90 | 20.49 | 19.40 | 22.27 |
| Total Liq. Product g | 33.3    | 32.6    | 32.4    | 34.2    |
| Gas phase composition CH₄ mol% | 35.24 | 36.83 | 28.837 | 27.94 |
|                      | C₂-C₄ mol% | 5.41 | 4.83 | 6.128 | 4.31 |
|                      | C₅⁺ mol%  | 0.30   | 0.25   | 0.811  | 0.23 |

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4. Conclusions

The presence of lanthanum as a promoter on the behavior of Fe-Co/SiO₂ for Fischer-Tropsch synthesis i.e. selectivity and conversion were studied. Two types of catalysts, i.e. Fe-Co/SiO₂ and Fe-Co-La/SiO₂ were prepared, and their characteristics were studied by BET and TPR techniques. Their performances were evaluated in a fixed-bed micro-reactor, and results showed that the lanthanum had a slight effect on the catalyst surface area, but had more effect on catalyst reduction temperatures.

The results showed that addition of lanthanum resulted in catalyst to have better performance in terms of increasing C₁-C₄ and C₅⁺ formations in the gas product, increasing the liquid productivity, decreasing the CO₂ selectivity and decreasing the operating temperature of the process. The latter could be important in decreasing catalyst deactivation rate.

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