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Research Article

Effect of Lanthanum as a Promoter on Fe-Co/SiO_2 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/SiO_2 Fischer-Tropsch catalyst was studied. The Fe-Co-La/SiO_2 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 °C, H_2/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 CO_2.

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

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1. Introduction

Fischer-Tropsch (FT) process converts syngas (mixture of H_2 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 CO_2 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

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that the use of Fe-Co catalysts lead to increase in selectivity, especially for small olefins and alcohols [6-9].

It is reported that the activity and hydrocarbon distribution of FT catalysts are also strongly depended on the addition of other metals as promoters. Some researchers have studied the 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 C^{5+} product. Ma et al. [18] studied the effect of adding potassium and zirconium on the activity of Fe-Co catalyst, and found that these promoters could enhance the activity of the catalyst and increase the CO conversion.

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 this purposes.

2. Materials and Methods

2.1. Material used

SiO_2 used as catalyst support was purchased from Fluka (Art No. 60744). Analytical grade $Fe(NO_3)_2.9H_2O$, $Co(NO_3)_2.6H_2O$, and $La(NO_3)_3.6H_2O$ were purchased from Merck (Art No. 103883), Fluka (Art No. 60883) and Merck Company (Art No. 105326), respectively.

2.2. Catalyst preparation and characterization

2.2.1. Fe-Co/SiO₂ catalyst

The Fe-Co/SiO_2 catalyst was prepared by wet-impregnation method. Amount of 5 g of SiO_2 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 $Fe(NO_3)_2.9H_2O$ and 2.9 g of $Co(NO_3)_2.6H_2O$ 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.

2.2.2. La-Fe-Co/SiO₂ catalyst

To study the effect of lanthanum on Fe-Co catalyst characteristic, La-Fe-Co/SiO_2 was prepared by wet-impregnation method. 5 g of SiO_2 particles with the mesh size between 30 and 40 was calcined at 500 °C for 6 h, then put in a rotary vacuum evaporator, and kept at 80 °C. 2.12 g of $Fe(NO_3)_2.9H_2O$, 2.9 g of $Co(NO_3)_2.6H_2O$ and 0.193 g of $La(NO_3)_3.6H_2O$ 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 catalysts was determined by nitrogen adsorption-desorption isotherms employing a Quantasorb surface area analyzer (Quantachrome Corporation) using a 3:7 ratio of a N_2/He mixture. Typically, 0.1 – 0.3 g of sample was used for the measurement, and it was out-gassed at 300 ºC for 2 h prior to N_2 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 reduction (TPR) experiment which was carried out using a Micromeritics TPD/TPR 2900 Analyzer. About 0.15 g freshly prepared catalyst was loaded into the quartz reactor and treated with a mixture of 6 % H_2/Ar. The temperature was increased from 27 to 827 °C at a rate of 5 °C/min. H_2O formed during TPR were removed by the cold trap, and the effluent gas was monitored 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 cm^3 of milled quartz particles, was loaded in the reactor. The catalyst bed was heated to 420 °C with the temperature 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 H_2/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/SiO_2 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 Co_3O_4 to CoO and also partial reduction of Fe_2O_3 to Fe_3O_4, at 410 °C complete reduction of Fe_2O_3 to Fe_3O_4, at about 500 °C reduction of CoO to Co, at 680 °C reduction of Fe_2O_3 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/SiO_2

Table 1. Chemical composition of the prepared catalysts

Type of Catalyst	Co (wt%)	Fe (wt%)	La (wt%)
Fe-Co/SiO_2	7.62	4.05	-
Fe-Co-La/SiO_2	6.79	3.4	0.63

Table 2. BET surface area of the prepared catalysts

Catalyst	BET surface area (m^2/g)
Fe-Co/SiO_2	337
Fe-Co-La/SiO_2	323

Table 3. Test conditions and product compositions for the Fe-Co/SiO_2 catalyst

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
H_2/CO		mol/mol	1.8	1.8	1. 8	1.8
CO Conversion		mol%	94.0	98.5	98.2	98.0
CO_2 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	CH_4	mol%	28.86	37.91	39.25	39.32
	C_2-C_4	mol%	3.60	4.86	4.10	3.80
	C_5^+	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/SiO_2 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). CO_2 selectivity considerably was decreased leading to a lower CO conversion which affected the waste products; (2). The C_2-C_4 and C_{5+} 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/SiO_2 catalyst was much higher than Fe-Co/SiO_2 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.

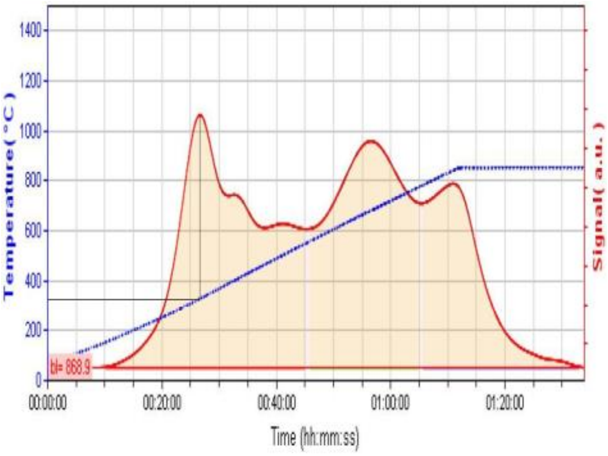

Figure 1. TPR profile of Fe-Co/SiO_2 catalyst

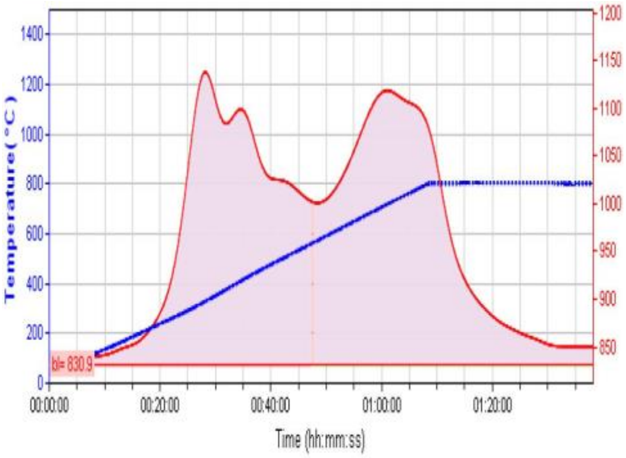

Figure 2. TPR profile of Fe-Co-La/SiO_2 catalyst

Table 4. Test conditions and product compositions for the La-Fe-Co/SiO_2 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
H_2/CO		mol/mol	1.8	1.8	1.8	1.8
CO Conversion		mol%	82.8	82.7	77.8	76.4
CO_2 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	CH_4	mol%	35.24	36.83	28.837	27.94
	C_2-C_4	mol%	5.41	4.83	6.128	4.31
	C_5^+	mol%	0.30	0.25	0.811	0.23

4. Conclusions

The presence of lanthanum as a promoter on the behavior of Fe-Co/SiO_2 for Fischer-Tropsch synthesis i.e. selectivity and conversion were studied. Two types of catalysts, i.e. Fe-Co/SiO_2 and Fe-Co-La/SiO_2 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 C_1-C_4 and C_5^+ formations in the gas product, increasing the liquid productivity, decreasing the CO_2 selectivity and decreasing the operating temperature of the process. The latter could be important in decreasing catalyst deactivation rate.

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