

Fischer-Tropsch synthesis on Co-Al₂O₃-(promoter)/ZSM5 hybrid catalysts for the production of gasoline range hydrocarbons

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Abstract—The Fischer-Tropsch synthesis (FTS) reaction was investigated for the direct production of gasoline range hydrocarbons (C₅-C₉) from syngas on Ru-, Pt- and La-promoted Co-Al₂O₃/ZSM-5 (Si/Al=25) hybrid catalysts prepared by co-precipitation method in a slurry. The hybrid catalysts were characterized by BET surface area, XRD, H₂-TPR and NH₃-TPD analyses. Their physicochemical properties were correlated with the activity and selectivity of the catalysts. The promoted Co-Al₂O₃-(promoter)/ZSM-5 hybrid catalysts were superior to the unpromoted Co-Al₂O₃/ZSM-5 catalyst in terms of better C₅-C₉ yield. In particular, the Co-Al₂O₃-Pt/ZSM-5 hybrid catalyst exhibited the highest catalytic activity with a low C₁ and olefin selectivity and a high C₅-C₉ selectivity. It could be due to not only a higher value for the reduction degree by H₂-TPR, but also assigned to weak acidic sites of a low temperature desorption peak by NH₃-TPD.

Keywords: Fischer-Tropsch Synthesis, Cobalt Hybrid Catalyst, Promoter, Gasoline, ZSM-5, Syngas

INTRODUCTION

The production of hydrocarbons by Fischer-Tropsch synthesis (FTS), using syngas derived from coal, natural gas or other carbon-containing materials, has recently received considerable attention for obtaining clean fuels and chemicals as a consequence of fast depletion of crude oil. Thus, FTS has emerged as one of the most promising routes to solve the energy crisis [1]. However, the polymerization mechanism, known as the Anderson-Schulz-Flory (ASF) distribution, of the FTS reaction inherently yields a wide-range of hydrocarbon distribution from methane to heavy waxy products as the distribution is governed by the chain growth probability. In general, the selectivity towards gasoline range products is known to be limited to a maximum of 48 mol% [2]. To obtain branched hydrocarbon selectively through FTS reaction directly without any upgrading, especially for high-octane gasoline production, many intensive efforts have been made by modifying cobalt-based catalysts with the addition of acidic components. Some researchers have investigated the hybrid or composite systems consisting of cobalt-based FTS catalysts and acidic zeolites as cracking catalysts by using the following preparation methods: i) cobalt-based FTS catalyst physically mixed with zeolite, ii) zeolite supported cobalt-based hybrid catalyst prepared by wet-impregnation method, and iii) zeolite membrane-coated Co-SiO₂ catalyst [3-8]. However, only marginal success has been achieved, leaving scope for further improvement. To facilitate the reduction of Co, which has strong interactions with Al₂O₃ researchers often add promoters such as Pd, Pt, Re and Ru

to the Co catalysts [9-20]. Lanthanum oxide shows interesting properties as promoter of highly dispersed metal catalysts and can modify the chemical behavior of some systems such as silica, ceria and alumina supports. It has been reported that the preparation procedure and composition strongly influences the microstructure of the promoter phase, the surface basicity and consequently the catalytic behavior [21-23].

We studied the FTS catalytic system for the direct production of gasoline range hydrocarbons from syngas by using Ru-, Pt- and La-promoted Co-Al₂O₃/ZSM-5 hybrid catalysts. The objective of the investigation is to examine the effect of the addition of the promoter on the performance of the hybrid catalyst during FTS reaction. The catalysts are characterized by surface area, pore size distribution, temperature-programmed reduction (TPR), X-ray diffraction (XRD), acidity temperature-programmed desorption (TPD) of ammonia measurements. An attempt was made to correlate the properties with the activity and selectivity of the catalysts.

EXPERIMENTAL

1. Preparation of Co-Al₂O₃-(promoter)/ZSM5 Hybrid Catalyst

The Co-Al₂O₃-promoter/ZSM5 hybrid catalysts were synthesized by co-precipitation method in aqueous solution containing Co nitrate (Co(NO₃)₂·6H₂O, Aldrich) and aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, Aldrich) metal precursor with the weight ratio of Co-Al₂O₃=20/100 and Na₂O₃ solution as a precipitating agent at 70 °C in a slurry of ZSM5 (Si/Al=25). ZSM5 (supplied by Zeolyst having Si/Al ratio of 25). The final solution pH was maintained at around 7 and the precipitate was further aged for 3 h at 70 °C followed by calcination at 500 °C for 5 h. The same procedure was followed for the addition of promoter using the nitrate precursor.

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sor. Finally, the ratios of cobalt and promoters (Ru, Pt and La) metal components using precursor $(\text{Ru}(\text{NO})(\text{NO}_3)_x(\text{OH})_y)$, 3.4 wt% $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ in dilute ammonium hydroxide solution and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) to that of ZSM5 in the hybrid catalysts were fixed at 20/30 and 0.3/30 by weight. The hybrid catalysts are noted as a $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM5.

2. Characterization

The BET surface area and BJH pore size distribution of the $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM5 hybrid catalysts were determined by N_2 -physisorption using Micromeritics ASAP 2400 apparatus at liquid- N_2 temperature at -196°C .

The TPR was carried out to determine the reducibility of the cobalt oxides. Prior to the TPR experiments, the samples were pre-treated in a He flow up to 400°C and kept for 2 h to remove the adsorbed water and other contaminants followed by cooling to 50°C . The reducing gas containing 5 vol% H_2/Ar mixture was passed over the sample at a flow rate of 30 ml/min, with a heating rate of $10^\circ\text{C}/\text{min}$ up to 800°C and then that temperature was maintained for 30 min.

The acidity of the catalysts was measured by the TPD of ammonia (NH_3 -TPD). Before the analysis, about 0.1 g of sample was pre-treated at 250°C in a flow of He for 2 h to remove the physisorbed water. After cooling to room temperature, ammonia was introduced into the reactor at 100°C for 1 h and the physisorbed ammonia was removed in a helium flow at 100°C for about 30 min. Subsequently, the sample was heated from 100 to 800°C , with a ramping rate of $10^\circ\text{C}/\text{min}$, and kept at the same temperature for 30 min in a flow of helium gas. The powder XRD patterns of the $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM5 hybrid catalysts were obtained with a Rigaku diffractometer using $\text{Cu-K}\alpha$ radiation to identify the crystalline phases of $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM5 hybrid catalysts. The particle on the fresh $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM5 hybrid catalysts was characterized by transmission electron microscope (TEM) analysis using a TECNAI G2 instrument operating at 200 kV. The elemental analysis of the cobalt content on the $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM5 hybrid catalysts was by using X-ray fluorescence (XRF; SEA5120).

3. Catalytic Activity Test

A catalytic activity test was performed a tubular fixed bed reactor (OD=12.7 mm) with 0.3 g of catalyst. Prior to the reaction, the catalyst was reduced at 450°C for 12 h in a flow of 8% H_2 balanced with N_2 . After reduction, the synthesis gas ($\text{H}_2/\text{CO}=2$) was fed into the reactor [15]. The FTS reaction was subsequently under the following reaction conditions: $T=240^\circ\text{C}$, $P=2.0\text{ MPa}$ and $\text{WHSV}=4,000\text{ ml/g}_{\text{cat}}\text{ h}$. The effluent gas from the reactor was analyzed by

an online gas chromatograph (YoungLin Acme 6000) employing a GS-GASPRO capillary column connected with an FID detector for the analysis of hydrocarbons and a Porapak Q/molecular sieve (5A) packed column connected with a TCD detector for the analysis of carbon mono-oxide, carbon-dioxide, hydrogen, methane and internal standard gas (Ar).

RESULTS AND DISCUSSION

1. Textural Properties of $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM5 Hybrid Catalysts

The ZSM5 catalyst is used as a solid catalysts since the acid site density and acidic site strength are controllable, and it is also simple to exploit their contribution to catalytic activity due to the regular pore structure [24]. In the production of petrochemicals, as well as in the numerous reactions that they undergo-cracking, such as hydrocracking, hydration, dehydration, alkylation, isomerization, oxidative addition and dehydrocyclization [25]. In particular, ZSM5 is generally selected to elucidate the influences of these parameters on catalytic activity and product distribution for the FTS reaction [26]. Furthermore, we previously investigated FTS reaction with both Co-ZSM 5 and $(\text{Co-SiO}_2)/\text{ZSM5}$ catalysts [27].

The BET surface area and BJH pore size distribution results for $\text{Co-Al}_2\text{O}_3$ -(promoter using of Ru, Pt and La for the nitrate precursor-

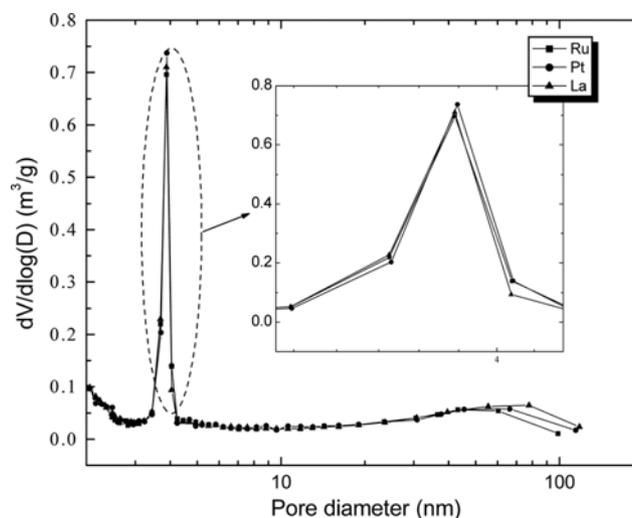


Fig. 1. Pore size distribution of the $\text{Co-Al}_2\text{O}_3$ -(promoter)/ZSM-5 catalysts.

Table 1. Physical properties and particle size of $\text{Co-Al}_2\text{O}_3$ -promoter/ZSM-5 catalysts

Notation	N_2 adsorption method			XRD ^a
	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	Particle size of Co_3O_4 (nm)
Co-Pt/ZSM-5	324.1	0.099	5.9	29.6
Co- Al_2O_3 /ZSM-5	241.5	0.555	11.0	5.9
Co- Al_2O_3 -Ru/ZSM-5	252.5	0.572	10.0	6.1
Co- Al_2O_3 -Pt/ZSM-5	262.9	0.659	11.7	9.7
Co- Al_2O_3 -La/ZSM-5	292.1	0.953	16.6	5.3

^aThe particle size of Co_3O_4 is calculated by using the X-ray line broadening method with the help of Scherrer's equation

sor)/ZSM5 hybrid catalysts are summarized in Fig. 1 and Table 1. As shown in Table 1, surface area and pore volume increased with the Co-Al₂O₃-La/ZSM5 > Co-Al₂O₃-Pt/ZSM5 > Co-Al₂O₃-Ru/ZSM5 > Co-Al₂O₃/ZSM5 catalysts, except for Co/ZSM5 without Al₂O₃ support and the particle size of Co₃O₄ was most high for the Co-Al₂O₃-Pt/ZSM5. As shown in Fig. 1, even though the mesopores in the region of 3-5 nm in pore size are not significantly altered with various promoter, the surface area of the promoted catalysts slightly increased compared to that of the Co-Al₂O₃/ZSM-5 catalyst. The large specific surface area and pore volume affects its reducibility and the catalytic performance during FTS reaction. The promoters such as Pt, Re and Ru have been used extensively to enhance the reducibility of Co oxide, which is otherwise limited by a strong interaction between the oxides and the supports like alumina or silica [28,29].

2. Measurement of the Particle Size of Cobalt Oxide by XRD

To understand the activity dependence of the Co-Al₂O₃-(promoter)/ZSM5 hybrid catalysts on their physicochemical properties, XRD study was also carried out and Fig. 2 displays the XRD patterns of the Co-Al₂O₃-(promoter)/ZSM5 hybrid catalysts. All the hybrid catalysts before the reaction show the characteristic reflection peak at $2\theta=36.8^\circ$ due to the presence of the Co₃O₄. The particle size of Co₃O₄ is calculated by using the X-ray line broadening method with the help of Scherrer's equation. The crystallite size of Co₃O₄ for the hybrid catalysts promoted by -Ru, -Pt and -La is 6.1, 9.7 and 5.3 nm, respectively. The cobalt particle size of the Co-Al₂O₃-Pt/ZSM5 hybrid catalysts is higher than that of the Co-Al₂O₃/ZSM-5 catalyst. The smaller particle size of the easily reducible cobalt species uniformly distributed inside the relatively larger pores is reported to be responsible for the higher activity of the promoted Co-ZSM-5 hybrid catalysts [27].

3. Temperature-programmed Analyses (H₂-TPR and NH₃-TPD)

TPR experiments were conducted to elucidate the reduction

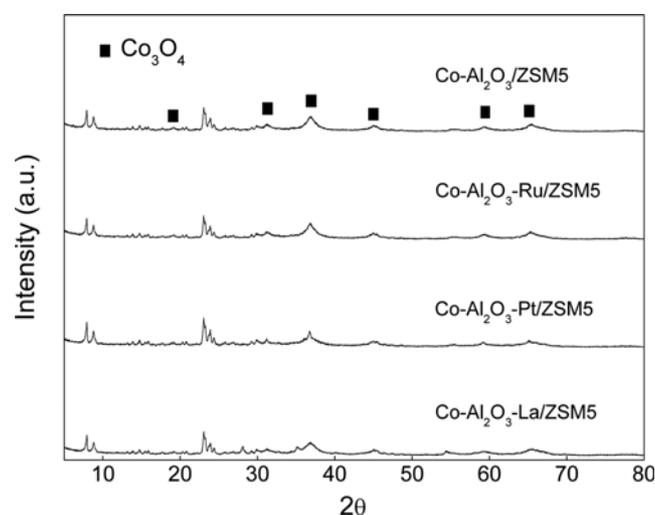


Fig. 2. XRD patterns of the Co-Al₂O₃/ZSM-5 and Co-Al₂O₃-promoter/ZSM-5 catalysts before the FTS reaction. The particle size of Co₃O₄ is approximately 5.9, 6.1, 9.7 and 5.3 nm on the Co-Al₂O₃/ZSM-5 and Co-Al₂O₃-(Ru, Pt and La)/ZSM-5 catalyst with a Si/Al ratio of 25, respectively.

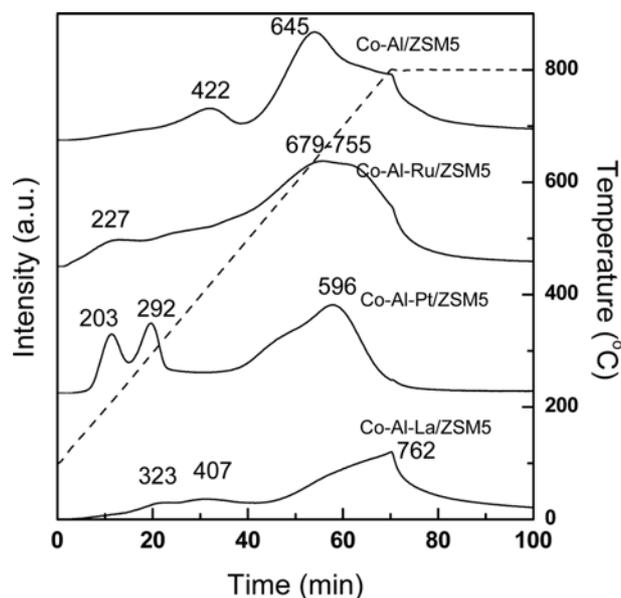


Fig. 3. H₂-TPR profiles of the fresh Co-Al₂O₃/ZSM-5 and Co-Al₂O₃-(Ru, Pt and La)/ZSM-5 catalysts.

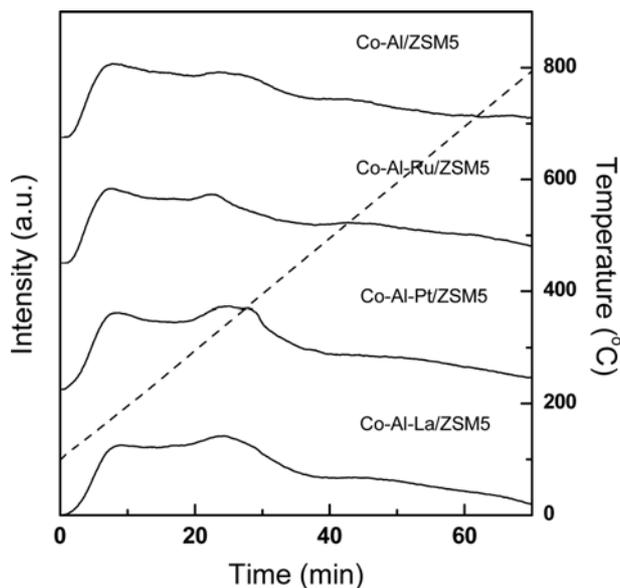
behavior of cobalt oxides, as the metallic cobalt surface sites are responsible for FTS activity. Fig. 3 shows the H₂-TPR profiles of the Co-Al₂O₃/ZSM-5 hybrid catalysts with different promoters. The TPR profiles of the Co-Al₂O₃-(promoter)/ZSM5 hybrid catalysts exhibit two or three distinct peaks. In the case of the promoted hybrid catalysts, the reduction process in H₂ occurs in two distinct stages: the first is attributed to the reduction of Co₃O₄ to CoO, and the second to the reduction of CoO to metallic cobalt.

In the case of the Co-Al₂O₃/ZSM-5 hybrid catalysts with promoted Pt, the TPR profiles clearly show a temperature peak at around 203 °C and 292 °C. However, the TPR profiles of the Co-Al₂O₃/Ru/ZSM-5 and Co-Al₂O₃/La/ZSM-5 hybrid catalysts show a distinctive shoulder peak at around 227 and 323 °C. The peak intensity at high temperature region (above 600 °C) suggests the facile reduction of cobalt oxide with little formation of inactive cobalt aluminates or silicates. The two reduction degrees were separately calculated based on the total hydrogen consumption and the theoretical value (Co₃O₄+4H₂=3Co+4H₂O; 3.68 mmol H₂/g_{cat}) by considering the actual Co content. Below 300 °C, the peak (%) was expressed as the ratio of the amount of hydrogen consumption to the theoretical hydrogen consumption on the fresh Co-Al₂O₃/ZSM-5 hybrid catalysts. The difference between these two reduction degrees suggests the possible formation of inactive cobalt species such as cobalt aluminate or silicate on Co-ZSM-5 catalysts [10]. As can be seen in Table 2, the total H₂ uptakes from the TPR experiments were estimated as 2.92, 2.00 and 1.37 mmol H₂/g_{cat} on the Co-ZSM-5 catalysts with Ru, Pt, and La promoters, respectively. Although the variation in the total reduction degree of the Co-Al₂O₃-Pt/ZSM-5 catalyst measured by TPR runs is not considerable, Co-Al₂O₃/ZSM-5 with Pt promoter shows a higher value for the reduction degree down to 300 °C.

The Co-Al₂O₃/ZSM-5 hybrid catalysts were examined by NH₃-TPD to determine the surface acidity. The effects of promoter addi-

Table 2. H₂ uptake of Co-Al₂O₃-promoter/ZSM-5 catalysts measured by H₂-TPR

Notation	H ₂ uptake, mmol H ₂ /g (degree of reduction, %)		
	Below 300 °C	Above 300 °C	Total
Co-Al ₂ O ₃ /ZSM-5	0.26 (11.1)	2.06 (88.9)	2.31
Co-Al ₂ O ₃ -Ru/ZSM-5	0.55 (18.7)	2.38 (81.3)	2.92
Co-Al ₂ O ₃ -Pt/ZSM-5	0.61 (30.8)	1.38 (69.2)	2.00
Co-Al ₂ O ₃ -La/ZSM-5	0.23 (16.8)	1.14 (83.2)	1.37

**Fig. 4.** NH₃-TPD profiles of the Co-Al₂O₃/ZSM-5 and Co-Al₂O₃-(Ru, Pt and La)/ZSM-5 catalysts.**Table 3.** Surface acidity of Co-Al₂O₃-promoter/ZSM-5 catalysts by NH₃-TPD

Notation	Acidic site (mmol NH ₃ /g)		
	First	Second & third	Total
Co-Al ₂ O ₃ /ZSM-5	0.018	0.035	0.053
Co-Al ₂ O ₃ -Ru/ZSM-5	0.027	0.028	0.055
Co-Al ₂ O ₃ -Pt/ZSM-5	0.022	0.034	0.056
Co-Al ₂ O ₃ -La/ZSM-5	0.013	0.042	0.055

Table 4. CO hydrogenation^a over Co-Al₂O₃-promoter/ZSM-5 catalysts

Notation	ZSM5/(Co-SiO ₂)	CO conv.	To CO ₂ conv.	Selectivity in hydrocarbons				O/(O+P) ^b	%Yield in C ₅ -C ₉
	Temp. (°C)			C ₁	C ₂ -C ₄	C ₅ -C ₉	C ₁₀₊		
Co-Pt/ZSM-5	240	42.1	0.2	8.91	9.48	13.9	67.7	14.1	5.8
Co-Al ₂ O ₃ /ZSM-5	240	32.8	1.6	21.9	26.1	16.9	35.1	33.7	11.0
Co-Al ₂ O ₃ -Ru/ZSM-5	240	30.9	0.9	10.4	12.9	21.4	55.3	21.5	16.6
Co-Al ₂ O ₃ -Pt/ZSM-5	240	41.3	0.7	10.2	10.3	17.8	61.7	17.9	25.1
Co-Al ₂ O ₃ -La/ZSM-5	240	20.7	1.5	15.6	24.1	14.1	46.2	17.4	8.9

^aCO hydrogenation was carried out at H₂/CO=2, WHSV=4,000 ml/g·h and P=2.0 MPa

^bOlefin selectivity (denoted as O(olefin)/(O(olefin)+P(paraffin))) in the range of C₂-C₄ hydrocarbons

tion on the surface acidity are possibly responsible for the variance in catalyst performance, especially the product distribution. The desorption patterns of NH₃ are shown in Fig. 4 and the quantitative values of acidic sites (mmol NH₃/g) are presented in Table 3. The desorption peaks can be separated into three peaks, although the resolution of the peaks is not significant. The low temperature desorption peak (below 200 °C) is assigned to weak acidic sites and the high temperature desorption peak to strong acidic sites. The high temperature desorption peak is not responsible for the FTS reaction and product distribution; it mainly contributes to water evolution by dehydration of hydroxyl groups on the surfaces [30]. Therefore, consideration of only the first peak (weak acid sites) reveals that the number of weak acid sites is higher on the Co-Al₂O₃-Pt/ZSM5 and Co-Al₂O₃-Ru/ZSM5 hybrid catalysts. The variation of acidity can be further related to the hydrocarbon selectivity of the Co-Al₂O₃/ZSM5 hybrid catalysts.

4. The Activity and Selectivity of the Co-Al₂O₃-(promoter)/ZSM5 Hybrid Catalysts

The catalytic performance of the Co-Al₂O₃-(promoter)/ZSM5 hybrid catalysts was measured at 240 °C, 2.0 MPa, WHSV=4,000 ml/g_{cat}·h and H₂/CO=2. The activity of the catalysts was tested for over 40 h. The CO conversion and product distribution data obtained on the hybrid catalysts are presented in Table 4 as steady state average values obtained after 30 h. As is well known, a catalyst with a large surface area and a large pore diameter is beneficial for obtaining a small cobalt crystallite size and for the facile transport of heavy hydrocarbons formed during the FTS reaction. In addition, the large pores on the FTS catalysts have been suggested to be linked to less coke or wax deposition [31]. In Table 4, the difference in CO conversion can be possibly attributed to the difference in reducibility (low reduction temperature from H₂-TPR) because of the presence of nano-cobalt particles of size above 5 nm on all the hybrid catalysts. The Co-Pt/ZSM-5 hybrid catalyst possessing a smaller cobalt particle size (high metallic surface area) and facile reducibility shows higher catalytic activity, as confirmed by the XRD data [32].

As reported in our previous work, a different product distribution was obtained on the promoted Co-ZSM-5 hybrid catalysts. The Co-Pt/ZSM-5 and Co-La/ZSM-5 hybrid catalysts showed higher CO conversion than that of the Co-ZSM-5 catalyst, which was taken as the reference in the FTS reaction at 260 °C. This can be explained by the presence of acidic sites of varying strength on the catalyst leading to hydrocracking of olefins. The high content of weak acidic

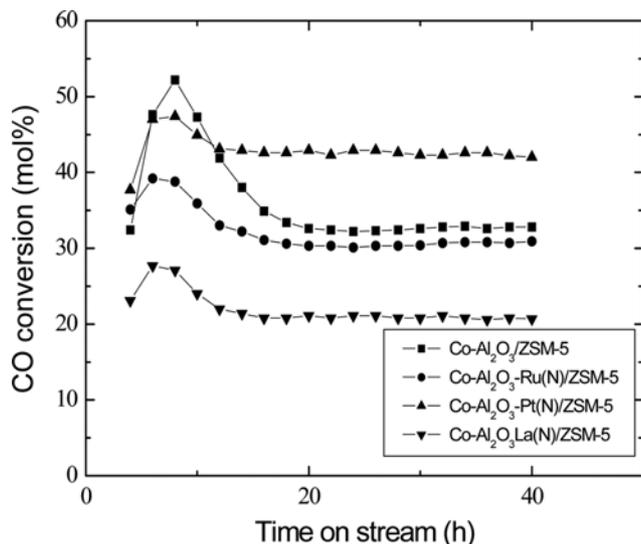


Fig. 5. The CO conversion on the Co-Al₂O₃/ZSM-5 and Co-Al₂O₃-(Ru, Pt and La)/ZSM-5 catalysts with time on stream.

sites is also responsible for high yields of C₅-C₉ hydrocarbons, due to the possible catalytic cracking of higher molecular-weight olefins on acidic sites of zeolites [3,10].

Catalytic performance as a function on time (h) is shown in Fig. 5, and the averaged CO conversion, CH₄ and C₅+ selectivity, C₂-C₄ selectivity and olefin selectivity (O/(O+P) molar ratio) are presented at steady state FTS reaction in Table 4.

The Co-Al₂O₃-Pt/ZSM5 hybrid catalyst shows the highest CO conversion of 41.3% for a long time and also highest C₅-C₉ yield (25.1%) at 240 °C. The catalyst's olefin selectivity is also low at 17.9%. This reduced selectivity towards lower hydrocarbons could be correlated with the suppressed olefin cracking properties of heavy olefin products due to the presence of fewer acidic sites [13]. In addition, the presence of a greater number of weak acidic sites (assigned to the first peak in the NH₃-TPD experiments) on the Co-Al₂O₃-Pt/ZSM5 hybrid catalyst may be responsible for the high yield of C₅-C₉ hydrocarbons.

CONCLUSIONS

The activity and C₅-C₉ selectivity during the FTS reaction of the hybrid catalysts varied according to the promoters. The Co-Al₂O₃-Pt/ZSM5 hybrid catalyst offered higher CO conversion and C₅-C₉ yield. The reducibility and concentration of weak acid sites were higher, thereby increasing the CO conversion and C₅-C₉ yield. The superior catalytic performance was attributed to the presence of weak acid sites on the Co-Al₂O₃-Pt/ZSM-5 hybrid catalyst with large pore size and pore volume, and to the nano-cobalt particle size due to the high reducibility.

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