Development of Composited Rare-Earth Promoted Cobalt-Based Fischer-Tropsch Synthesis Catalysts with High Activity and Selectivity

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Abstract

The objective of this research is to find an optimal ratio of rare earth elements (RE), lanthanum (La) and cerium (Ce), as promoters of Co-based Fischer-Tropsch synthesis (FTS) catalysts to achieve maximal diesel yield. These synthesized rare-earth promoted catalysts were characterized with Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) and hydrogen temperature programmed reduction (H₂-TPR). The effects of La/Ce molar ratio on the FTS performance of silica gel supported cobalt based catalysts were investigated in a fixed bed reactor at temperatures of 220 and 240 °C. The evaluation tests show that the catalysts promoted by composited rare-earth (CRE) with appropriate molar ratio La to Co have better FTS performance than unpromoted and individual rare-earth (IRE) promoted catalysts. The results show that the CRE promoted FTS catalysts are promising. The CO conversion is increased significantly and the selectivity for methane and C₂-C₄ is decreased while the selectivity for long chain hydrocarbons is greatly increased (C₅⁺ increased from 70.36% to 80.25% at 220 °C and from 69.94 % to 78.02 % at 240 °C, respectively). Among all CRE modified catalysts, based on the result of distribution of C₁₂-C₁₈ (weight % of hydrocarbons),

Co-1La2Ce/S.G (n RE: n Co = 0.1 and n La: n Ce = 1: 2) is proven as a highly efficient catalyst for production of diesel rich synthetic oil from coal-derived syngas.

Keywords: Fischer-Tropsch; Cobalt catalyst; Rare earth; Syngas; Diesel

1. Introduction

Fischer-Tropsch synthesis (FTS) converts syngas derived from natural gas, coal [1–3] and biomass to hydrocarbons (HCs) and oxygenates, which is an effective way to produce liquid fuels and other chemicals [4–8]. So far, two main types of catalysts, iron based catalysts and cobalt based catalysts, have been extensively used in the industry. Cobalt-based FTS catalysts have high activity, good stability and selectivity towards long chain hydrocarbons (synthetic oil and waxes). Recently, increasing attention has been paid to maximize the yields of C₁₀–C₂₀ and C₂₀⁺ products [9]. Various supports (e.g., SiO₂, γ -Al₂O₃, SBA-15 and MCM-41) and/or promoters (Re, Rh, ZrO₂, etc.) have been investigated to enhance the performance of cobalt catalysts. It was reported that the addition of small amounts of RE metal oxides could modify cobalt-based catalyst electronically or structurally, thus improving their performance to the desired products [10–14].

Lanthanum (La) has been reported as an excellent promoter for cobalt based catalysts on various supports. Compared to unpromoted catalysts, La promoted catalysts could enhance CO adsorption, therefore improving the selectivity and activity of γ -Al₂O₃ supported cobalt [15]. In addition, La doping could modify the chemical composition of the support, thus enhancing the selectivity and lifetime of the catalysts [16]. Function of lanthanum promoter could be greatly affected by preparation methods. Ledford et al. [17] studied two methods of preparing La modified Co/Al₂O₃ catalysts and found that promotion effects happened only when La was first

impregnated on Al_2O_3 . More importantly, La was also found to be a good promoter for Zr-Co catalysts on activated carbon (AC) [18]. Both CO conversion and C_5^+ selectivity increased, while methane selectivity decreased, when Zr-Co/AC catalysts were modified with 0.2 wt% La addition.

In addition to lanthanum, cerium is also a good promoter for cobalt-based catalysts. Mixed cobalt cerium oxide catalysts loaded on silica gel [19], TiO_2 [20] and $\gamma\text{-Al}_2\text{O}_3$ [21] have been investigated for FTS. Zeng et al. [21] reported that the addition of cerium to $\text{Co}/\gamma\text{-Al}_2\text{O}_3$ could significantly decrease the generation rate of carbon dioxide, methane and $\text{C}_2\text{-C}_4$ while increasing C_5^+ selectivity. Similar phenomena was found by Dai et al. [22], who established that addition of a small amount of ceria can increase the turnover rate and C_5^+ selectivity, and especially improve the selectivity for high hydrocarbons, due to the enhanced dispersion of cobalt and the accelerated dissociation of CO on the catalyst surface. Barrault et al. [23] found that CeO_2 could be partially reduced to CeO_{2-x} on the $\text{CeO}_2\text{-Co/C}$ catalyst to form new bi-nuclear catalytic sites together with Co, which would lead to increased selectivity for higher hydrocarbons and decreased selectivity for methane, however, at the same time, with a decreased adsorption ratio of H_2 and CO.

The combination of rare earths promoters and cobalt-based catalysts was also studied. Zeng et al. [21] investigated the mixed rare earths on $\text{Co}/\gamma\text{-Al}_2\text{O}_3$, and found that promotion with appropriate mixed rare earths (MRE) was favorable for forming long-chain hydrocarbons. However, they only tested the MRE promoted catalysts with fixed RE molar ratio; the effects of the MRE with different ratios on the cobalt based catalysts haven't been studied thus far. In general, the addition of a single rare earth element mainly plays three different roles: suppressing both FT activity and selectivity, enhancing the selectivity (such as Ce) of some fractions, and

increasing the catalytic activity without changing the selectivity (La, Th) [15]. Therefore, to establish appropriate molar ratio of MRE promoted catalysts that have remarkable performance for both catalytic activity and valuable diesel fractions (C_{12} - C_{18}) selectivity is of great significance.

In the present study, individual rare-earth (IRE) and composited rare-earth (CRE) (La and Ce) modified cobalt-based catalysts (Co-LaCe/SiO₂) with various La/Ce ratios are prepared and evaluated in a fixed-bed reactor (FBR) at different temperatures. The comparison of catalytic activities and selectivities of each of the catalysts is discussed, and the CRE promoted catalysts with optimized molar ratios, that have both high activities and valuable diesel fractions selectivities, are also presented.

2. Materials and Methods

2.1 Materials

Cobalt (II) nitrate hexahydrate (Aldrich Chemicals, 99.999 % trace metals basis); silica gel (Sigma-Aldrich, St. Louis, MO, 40-75 μ m); nitric acid (Sigma-Aldrich, ACS reagent, 70%); cerium (III) nitrate hexahydrate (Aldrich Chemicals, 99 % trace metals basis); lanthanum (III) nitrate hexahydrate (Aldrich Chemicals, 99.99 % trace metals basis).

2.2 Preparation of catalysts

RE (individual or composited) and Co were impregnated onto SiO₂ support by the incipient wetness method. Incipient wetness occurred at about 1.2 mL (water)/g of silica. The reagents Co(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O and/or La(NO₃)₃·6H₂O were dissolved in water and the solution was added to the silica at the ratio of 1.2 mL /g of silica. The mixture was shaken

overnight on a shaking bed and then dried in a vacuum oven at 75 °C for 2 h and 100 °C for 4 h. The dried samples were heated at a ramping rate of 2 °C /min and calcined at 500 °C for 6 h. The catalysts were then activated in a hydrogen atmosphere with a space velocity of 1000 mL/g.cat/h by heating at a ramping rate of 1 °C/min and treating at 400 °C for 6 h. The catalysts contained 18 wt% Co and various amounts of composited rare-earth elements (n Re: n Co = 0.1, n La: n Ce = 1:0, 0:1, 1:1, 2:1, 1:2, 5:1 and 1:5). The catalysts were named as Co/S.G, Co-1La/S.G, Co-1Ce/S.G, Co-1La1Ce/S.G, Co-2La1Ce/S.G, Co-1La2Ce/S.G, Co-5La1Ce/S.G and Co-1La5Ce/S.G respectively.

2.3 Characterization of catalysts

BET surface area, pore volume, and average pore diameter of catalysts as prepared were measured by N₂ adsorption-desorption at 77 K using a Quantachrome Autosorb-iQ instrument. Prior to the tests, all the catalysts were degassed at 200 °C under high vacuum for 4 h with a ramping rate of 5 °C /min. The total pore volume (TPV) was calculated at a relative pressure of approximately 0.99. The particle size of Co aggregates was calculated by using Image J software.

The structure of catalysts was evaluated using a Rigaku Smartlab X-ray diffraction (XRD) system equipped with a 2 theta/theta scanning mode and a solid-state X-ray detector. The radiation source was a Cu K α 1 radiation (1.5406 Å) operating at 40 kV/40 mA, respectively. Runs were made with a scan range of 2 θ between 10 – 90 ° at a scan rate of 4 °/min with a chopper increment of 0.02 °. A thin layer of sample was mounted on a zero background quartz plate. The average size of Co₃O₄ particles was calculated according to Scherrer's equation [24]. Since it is difficult to determine the average size of the Co metal on the reduced catalysts directly, they are evaluated from the Co₃O₄ particle sizes after calcination and their sizes are calculated using $d(\text{Co}^0) = 0.75d(\text{Co}_3\text{O}_4)$ [25]. The reduced catalyst samples used for XRD tests were

prepared by reducing the fresh catalysts (0.1 g) in a self-assembled quartz reactor with pure H₂ (20 mL/min) at 400 °C, 0.10 Mpa for 6 h [26]. After the reduction, the catalysts were cooled to room temperature under the protection of nitrogen.

The morphology and the particle size as well as the dispersion of the catalysts were studied by a scanning electron microscope (SEM-EDS, FEI, Quanta FEG MK2; Oxford Instruments America, Model #51-XMX0005).

Static H₂ chemisorption was used to obtain an insight into the adsorption of the reactants on the reduced catalyst. H₂ temperature programmed reductions were carried out on a self-assembled reactor equipped with an online mass spectrometer (MS: Hiden, HPR-20 QIC). 0.1 g of catalyst was loaded in a quartz tube reactor and was treated with helium (He) at 20 mL/min and ramped from room temperature with a ramp rate at 10 °C/min to 200 °C. The temperature was held at 200 °C for 1 h to remove water and other volatiles. After the temperature cooled down to 50 °C, H₂/He (2 mL/20 mL) mixed gas was introduced to saturate the catalyst for 1 h. Then the catalyst was purged with He to remove physisorbed H₂.

2.4 Experimental set up and FTS performance test

Figure 1. The schematic diagram of fixed-bed reactor (FBR) system. (1) Hydrogen cylinder; (2) Carbon monoxide cylinder; (3)(3') Pressure regulators; (4)(6) Valves; (4')(6') By-pass valve; (5) Mass flow controller; (7) CM-400/scanner; (8) Automatic controller/scanner system; (9) Front pressure sensor; (10) Front pressure gauge; (11) Safety valve; (12) Thermocouple; (13) Furnace; (14) Sand; (15) Catalyst; (16) Fixed-bed reactor; (17) Hot trap; (18) Cold trap; (19) Chiller; (20) Back pressure gauge; (21) Back pressure sensor; (22) Back pressure regulator; (23) Wet gas flow meter; (24) Gas chromatography; (25) Carrier gas He; (26) Computer

FTS reactions were performed in a stainless fixed-bed reactor with an inner volume of 38 mL (Fig. 1). The catalyst (3.0 g) (label 15) was well dispersed with quartz sand (sand size: 30-40 mesh) and loaded in the center of reactor with a thermocouple inside. Two mass flow controllers (label 5 and 5') were used to automatically adjust flow rate of the inlet gases. A mixture of CO and H₂ was subsequently introduced into the reactor, which was placed inside a tubular furnace (label 13). Temperature was controlled by an automatic temperature controller (label 8) and monitored by a computer through a thermocouple (label 12) inserted into the catalytic bed. The catalyst was in situ reduced at atmospheric pressure under H₂ at 400 °C for 10 h before the reaction started. In each test, 3.0 g catalyst was loaded and all the data was collected after the time point of 48 h to ensure steady state operation was attained.

The FT reaction was carried out with a temperature of 220/240 °C and a total pressure of 2.0 Mpa, with the molar ratio of H₂ to CO of 2:1 and space velocity of 800 mL/g.cat/h. During the reaction, the synthetic wax was collected by a hot trap with temperature of 160 °C while the liquid oil was gathered by a cold trap (T = 0 °C). A pressure gauge located before the back pressure regulator (label 20) was used to monitor the desired pressure. The reaction parameters were controlled and recorded by LABVIEW FTS process program. After the cold trap, the tail gas was analyzed by on-line gas chromatography (GC-8610C, SRI instruments, Inc.) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID), through a molecular sieve 13x column and a 60m capillary column, respectively. The liquid products were analyzed via a different gas chromatograph (GC-7890A, Agilent, Inc.). The wax phase components were dissolved in CS₂ and analyzed by the Agilent GC. The reaction performance results, including CO and H₂ conversion, HCs selectivity, yield of products and rate of HCs production (C₁⁺(C₁-C₄) and C₅⁺) were subsequently calculated. The carbon monoxide conversion and hydrocarbon selectivity were calculated as follows:

$$CO \text{ conversion } (\%) = \frac{M_{CO,in} - M_{CO,out}}{M_{CO,in}} \times 100\% = \left(1 - \frac{M_{tg} \times P_{CO,tg}}{M_{fg} \times P_{CO,fg}}\right) \times 100\% \quad (E 1)$$

Where $M_{CO,in}$, $M_{CO,out}$, M_{tg} and M_{fg} are the moles of inlet CO, outlet CO, tail gas and feed gas, respectively; $P_{CO,tg}$ is the mole ratio of CO in tail gas and $P_{CO,fg}$ is the mole ratio of CO in feed gas.

CO₂ selectivity (%):

$$S_{CO_2} = \frac{M_{tg} \times P_{CO_2,tg}}{M_{CO}} \times 100\% \quad (E 2)$$

CH₄ selectivity (%):

$$S_{CH_4} = \frac{M_{tg} \times P_{CH_4, tg}}{M_{CO}} \times 100\% \quad (E\ 3)$$

HCs selectivity (% , n = 2, 3, 4):

$$S_{HC_s} = \frac{M_{tg} \times P_{HC_s, tg}}{M_{CO}} \times 100\% \quad (E\ 4)$$

$$C_5^+ \text{ selectivity (\%): } 1 - S_{CH_4} - S_{C_2} - S_{C_3} - S_{C_4} \quad (E\ 5)$$

where n is the carbon number and S_{CO_2} , S_{CH_4} , S_{HC_s} , S_{C_2} , S_{C_3} and S_{C_4} are the selectivities of CO_2 , CH_4 , HCs, C_2 , C_3 and C_4 , respectively. $P_{CO_2, tg}$, $P_{CH_4, tg}$ and $P_{HC_s, tg}$ are the mole ratios of CO_2 , CH_4 and HCs in tail gas, and M_{CO} are the moles of converted CO.

3. Results and discussion

3.1 Characterization of catalysts

3.1.1 Physicochemical properties of catalysts

Table 1. Characterization of catalysts by XRD and other textural properties.

Catalyst	Co content (g : gSiO ₂)	RE content (nCo: nLa:nCe nSiO ₂)	Particle size (nm)*		BET (m ² /g)	Pore diameter (nm)	Pore volume (cm ³ /g)
			$d(Co_3O_4)$	$d(Co^o)$			
Co/S.G	18:82	1:0:0:4.47	12.54	9.41	377.596	6.904	0.650
Co-1La/S.G	18:81	1:0.1:0:4.20	12.73	9.55	280.296	4.920	0.360
Co-1Ce/S.G	18:81	1:0:0.1:4.18	14.21	10.66	300.867	5.134	0.463
Co-1La1Ce/S.G	18:81	1:0.05:0.05:4.19	12.63	9.48	272.451	5.130	0.438
Co-1La2Ce/S.G	18:81	1:0.033:0.066:4.19	14.70	11.03	297.259	5.131	0.474
Co-2La1Ce/S.G	18:81	1:0.066:0.033:4.19	13.64	10.23	295.084	5.123	0.490
Co-1La5Ce/S.G	18:81	1:0.017:0.083:4.19	13.64	10.23	304.912	5.841	0.531
Co-5La1Ce/S.G	18:81	1:0.083:0.017:4.18	13.54	10.15	320.950	5.852	0.588

* Particle sizes were calculated from the Scherrer's equation according to the diffraction peaks of Co_3O_4 .

BET surface area, pore volume, average pore diameter and particle sizes of Co_3O_4 and Co are presented in Table 1. As shown in Table 1, compared to the unpromoted Co-based catalyst

(Co/S.G), only slight changes of the diameters of Co_3O_4 and Co^0 crystal occurred with the addition of rare earth oxides. Co/S.G had a diameter of Co_3O_4 and Co^0 crystal around 12.54 and 9.41 nm, respectively. The addition of either IRE or CRE oxides may cause a slight increase in diameter of cobalt oxides, while La had less influence on Co^0 particle sizes. Table 1 also shows that both IRE and CRE modified catalysts presented lower BET surface areas, compared to Co/S.G, which indicate that cobalt oxides and rare earth oxides (CeO_2 and La_2O_3) partly entered and blocked the pore path of the supports and partly dispersed on the surface [27]. Another possible explanation might be that with the addition of RE, catalysts tended to be aggregated during the preparation process. Pore diameters also had slight decreases among RE modified catalysts, which further indicates that RE oxides blocked the pores on the support, resulting in the drop of pore diameters and pore volumes. In addition, except Co-1La1Ce/S.G, CRE modified catalysts had relatively higher pore volumes compared to IRE promoted catalysts [28].

Figure 2. XRD patterns of the catalysts at calcined state (A) and after reduction (B). a: Co/S.G; b: Co-1La/S.G; c: Co-1Ce/S.G; d: Co-1La1Ce/S.G; e: Co-1La2Ce/S.G; f: Co-2La1Ce/S.G; g: Co-1La5 Ce/S.G; h: Co-5La1Ce/S.G.

Fig. 2 shows the XRD patterns of all catalysts before and after reduction. The particle sizes of Co_3O_4 and Co^0 in Table 1 were calculated from Scherrer's equation according to the diffraction peaks in this figure. The diffraction peaks of Co_3O_4 , especially the cubic spinel phase of Co_3O_4 at 36.52° (Fig. 2A), appeared in all of the spectra of the catalysts, indicating that cobalt oxides were well dispersed on the silica gel supports. The diffraction peak of well-defined structure Co_2SiO_4 spinel could not be found in the spectra, suggesting that the content of the difficult reductive cobalt species was very low in the catalysts and the formation of cobalt on the silica gel support was mainly in the form of Co_3O_4 . Compared to the Co, the content of REs was relatively low in catalysts. Therefore, the intensities of Co_3O_4 peaks in each spectrum were quite similar. The spectra peaks (28.32° , 32.9° and 47.4°) of cerium oxide (CeO_2) were found in all Ce modified catalysts and the peak intensity of CeO_2 (28.32°) was proportional to the molar ratio of Ce. When the molar ratio of CeO_2 dropped to 0.017 (Catalyst h, Co-5La1Ce/S.G), peaks 32.9° and 47.4° almost disappeared. In both Fig. 2A and 2B, no apparent peaks attributed to La_2O_3 could be found. It was reported that La_2O_3 could be formed from $\text{La}(\text{NO}_3)_3$ at 450°C by air calcination while La_2O_3 was hard to reduce to lower valence lanthanum oxide at 400°C by hydrogen [29]. Therefore, the most probable explanation is that crystals of La_2O_3 are quite finely dispersed on the surface of silica gel, and thus can hardly be detected by XRD.

Fig. 2B shows the XRD patterns of reduced Co-based catalysts, demonstrating that the active phase of cobalt catalyst is metal cobalt, rather than cobalt oxides. In this figure, except for the peak at 36.52° , almost all the diffraction peaks of Co_3O_4 disappeared after reduction, while the diffraction peaks of cubic Co (44.42° and 76.18°) appeared, which indicated that cobalt oxides were almost completely reduced and cubic metal Co was well dispersed on the support after the

reduction. The catalysts with higher La content, Co-1La/S.G and Co-5La1Ce/S.G, had weaker Co_3O_4 peaks, indicating that La could improve the reduction of cobalt oxide to fcc metallic cobalt, which was the main crystalline phase detected by XRD. However, La promoted catalysts had lower Co peaks intensities, which might be because the crystallinity of Co crystals was poor. Ce modified catalysts showed significant enhancement of diffractive intensities of cubic Co compared to the unpromoted catalyst, which might contribute to the improvement in reduction of the difficult reductive cobalt species [21]. The diffraction peaks of CoO were also detected at 36.5° and 42.5° , indicating that Co_3O_4 particles partially reduced to CoO crystals [30]. However, the intensity of CoO peaks is very low. Similarly, after the reduction, diffraction peaks of CeO_2 were still observed in all Ce modified catalysts, which indicated that CeO_2 was hardly reduced at 400°C and atmospheric pressure [31].

Figure 3. SEM images of eight catalysts before reduction. (HV: 20.00KV; Detector: BSED; Magnification: 60K X)

SEM was further used to characterize the morphology and metal distributions of the catalysts (Fig. 3). Fig. 3 shows the SEM results of all the catalysts before reduction. From the SEM images, Co_3O_4 (large white particles) was well dispersed on the surface of the silica, with an average particle size of around $1.75\ \mu\text{m}$. Since the average diameter of Co_3O_4 particles calculated from XRD (using Scherrer's equation) was around 13 nm, the large Co_3O_4 particles detected by SEM were clusters composed of small crystals. The diameter of Co_3O_4 particles increased slightly when the catalysts were modified with REs, and it approached $4.31\ \mu\text{m}$ when the molar ratio of La and Ce equaled 2 to 1. When cobalt catalysts were modified by cerium, CeO_2 could be detected as small white dots (red arrows) with an average diameter of 200-500 nm, which were distributed homogeneously on the surface of silica. Similar to the XRD results, particles of La_2O_3 were not identified by high magnification SEM, further proving that La_2O_3 was dispersed quite finely on silica gel.

Figure 4. H₂-TPR profiles of RE promoted and unpromoted cobalt-based catalysts. (a: Co/S.G; b: Co-1La/S.G; c: Co-1Ce/S.G; d: Co-1La1Ce/S.G; e: Co-1La2Ce/S.G; f: Co-2La1Ce/S.G; g: Co-1La5Ce/S.G; h: Co-5La1Ce/S.G)

3.1.2 H₂-Temperature programmed reduction

The reduction behaviors of all catalysts were investigated by H₂-TPR (Fig. 4). Pure Co₃O₄ had two identical peaks at 347 °C and 438 °C, which was due to its two step reduction to CoO, and then CoO to Co, respectively [32]. Once the Co₃O₄ was loaded on the silica gel support, both of these two peaks were shifted to the lower temperature. The first peak moved from 347 to 330 °C and the second one moved from 438 to 430 °C. Compared to the curve of unpromoted catalyst a, catalysts b, e, f and h all had an obvious broad peak at around 190 °C, which was attributed to the reduction of the surface adsorbed species [21]. Compared to Co/S.G, the location of two Co₃O₄ reductive peaks did not change too much in the catalysts modified with a different molar ratio of La and Ce. The reason might be related to the low mole ratio of the RE compared to cobalt (n RE: n Co = 0.1). There was a small peak (339 °C) between two Co₃O₄ reductive peaks, and the number slightly increased (348-355 °C) when La and Ce were used. This small peak can also be assigned to the reduction of cobalt oxide [33] and it was significantly influenced by the metal-support interaction. When the temperature increases to 650 °C, a flat and wide peak appears and ends at about 870 °C. This high temperature species is attributed to the hardly reducible Co silicate [34]. The interesting thing is when Co-based catalyst was modified with the composited rare-earth elements, this peak shifted slightly to the lower temperature (770 to 750 °C), indicating that the CRE could promote the reduction of partially reducible Co silicate.

3.2 F-T synthesis performances

Table 2. The performance of different catalysts on Fischer-Tropsch synthesis ($H_2/CO = 2.0$, $P = 2.0$ Mpa, $T = 220$ °C and 240 °C, $SV = 800$ mL/g.cat/h.)

	CO conversion (%)		CO ₂ selectivity (mol %)		HCs selectivity (mol%)						Catalyst Productivity (g HC/g-cat/h)				α in ASF equation	
					CH ₄		C ₂ C ₄		C ₃₊		C ₁₊		C ₃₊			
	220 °C	240 °C	220 °C	240 °C	220 °C	240 °C	220 °C	240 °C	220 °C	240 °C	220 °C	240 °C	220 °C	240 °C	220 °C	240 °C
Co/S.G	65.08	86.00	3.95	4.69	19.82	22.58	14.97	17.88	61.260	54.840	0.060	0.110	0.054	0.059	0.818	0.854
Co-1La/S.G	66.56	88.06	2.37	3.46	11.56	13.37	10.59	10.43	75.490	72.740	0.050	0.070	0.061	0.090	0.884	0.917
Co-1Ce/S.G	59.54	87.45	2.21	2.38	11.44	12.98	6.93	5.46	79.410	79.180	0.034	0.045	0.084	0.088	0.913	0.910
Co-1La1Ce/S.G	81.51	97.00	2.04	2.12	13.57	14.01	4.43	5.85	80.250	78.020	0.038	0.050	0.090	0.108	0.922	0.914
Co-1La2Ce/S.G	76.50	95.35	2.59	2.13	11.31	15.58	6.42	5.60	80.180	76.690	0.041	0.050	0.085	0.146	0.929	0.909
Co-2La1Ce/S.G	78.16	99.36	4.40	3.40	11.51	13.97	5.11	6.35	78.980	76.280	0.039	0.060	0.104	0.120	0.912	0.909
Co-1La5Ce/S.G	74.49	95.12	2.42	2.43	13.37	14.26	5.41	7.35	78.800	75.970	0.040	0.056	0.078	0.084	0.892	0.878
Co-5La1Ce/S.G	91.85	94.67	4.45	4.56	17.95	20.45	7.24	5.06	70.36	69.94	0.07	0.06	0.08	0.08	0.890	0.886

F-T synthesis performance of the catalysts pretreated in hydrogen atmosphere was carried out under conditions of 220/240 °C, 2.0 Mpa and $H_2/CO = 2.0$. After 48 hours and the attainment of steady state, products were collected, data were taken, and results calculated. The catalytic activities and selectivities of all catalysts are listed in Table 2. The results show that the catalytic activities and selectivities of catalysts as well as CO conversion are sensitive to the molar ratio of the La and Ce. CO conversion decreased in the single Ce modified catalyst (Co-1Ce/S.G), however, the CO conversion of all the other catalysts modified with La or CRE increased at both temperatures. At the reaction temperature of 220 °C, the CO conversion of single Ce modified catalyst dropped from 65.08% to 59.54 % compared to the unpromoted catalyst Co/S.G, while the CO conversion of single La modified catalyst increased slightly, which indicates that cerium has little facilitation on the activity of Co catalysts [21]. The CO conversion of catalysts modified with CRE significantly increased, especially when the molar ratio of La was higher. The CO conversion of Co-5La1Ce/S.G was as high as 91.85% while the CO conversion of Co-

1La5Ce/S.G was only 74.49%. These results were consistent with the XRD results in Fig. 3. Co-5La1Ce/S.G had almost no Co_3O_4 peaks left after reduction, while Co-1La5Ce/S.G still had some Co_3O_4 peaks remaining.

When temperature was increased to 240 °C, CO conversion of all catalysts increased around 25 - 30 %. When the molar ratio of La and Ce was 2: 1, the highest CO conversion (99.36%) was achieved, while the CO conversion of Co-5La1Ce/S.G only slightly increased to 94.67%, indicating that temperature plays an even more important role on the catalyst activity than promoters. All the CO conversion results in Table 2 clearly showed that CRE modified Co-based catalysts had a synergistic effect and achieved higher catalytic activity compared to the unpromoted and IRE promoted catalysts.

Effects of reaction temperature and molar ratio of promoters on catalytic performances, such as selectivities and productivities, are also shown in Table 2. CO_2 selectivity of all catalysts had no obvious differences, which were all in the range of 2.0 - 4.6 %, with values increasing slightly when the temperature increased. It was reported that La could decrease methane selectivity due to the relative lower content of unreduced cobalt oxides [35]. It was also reported that CeO_2 could form new bi-nuclear active sites together with Co^0 and lead to a decrease in the amount of CH_4 due to the decreased adsorption ratio of H_2 and CO [23]. In Table 2, CH_4 selectivity increased when reaction temperature increased from 220 to 240 °C, however, it decreased dramatically when IRE or CRE were used as promoters, which was consistent with results in the literature. In addition, Zhang et al. [36] reported that the selectivity of methane is influenced with particle size of cobalt species; larger cobalt particle size contributes to lower methane selectivity. Based on the results in Table 1, the rare earth promoted catalysts had larger sizes of

cobalt oxides and cobalt metal than unpromoted catalyst. Therefore, the lower CH₄ selectivity of promoted catalysts might also be due to the larger size of cobalt particles on the surface.

Similar phenomena were found in the light gaseous hydrocarbons (C₂-C₄) selectivities. At 220 °C, the C₂-C₄ selectivity decreased from 14.97% to as low as 4.43% when either IRE or CRE were added, further, CRE promoted catalysts had even lower C₂-C₄ selectivity compared to IRE promoted catalysts. The selectivity of C₂-C₄ had a slight increase when temperature increased to 240 °C, which might be due higher CO conversions at this temperature [37]. Table 2 also shows the results of hydrocarbons selectivity for all the catalysts. It was noticeable that both La and Ce had significant positive effects on C₅⁺ selectivity enhancement and the C₅⁺ selectivity increased when CRE were used as promoters. Co-1La2Ce/S.G and Co-1La1Ce/S.G had C₅⁺ selectivity higher than 80%. The reason may be related to the enhancement of dispersion degree of cobalt metals caused by cerium and/or improved reducibility of catalysts resulting from lanthanum addition [38]. All the results indicate that REs modified cobalt catalyst facilitate chain growth reactions and CRE promoted catalysts with appropriate ratios have even better C₅⁺ selectivity as well as CO conversion.

With the same H₂/CO ratio and reaction pressure, when the temperature increased from 220 °C to 240 °C, the catalyst productivity of C₁⁺ also increased. When either IRE or CRE was used as promoters, the catalyst productivity of C₁⁺ decreased while the catalyst productivity of C₅⁺ increased. However, at 220 °C, when the molar ratio of Ce increased in the CRE promoted catalysts, the catalyst productivity of C₅⁺ decreased. Therefore, at 220 °C, the addition of Ce could obviously reduce the production of C₁-C₄ while La/Ce modified cobalt catalysts with higher molar ratio of Ce could decrease the formation of C₅⁺ products. The possible reason might be that CeO₂ was partially reduced to CeO_{2-x} and the dissociation of CO increased through

forming new active sites during FTS. With increasing reaction temperature, the productivity of C_5^+ also increased with all the catalysts except the Co-5La1Ce/S.G, which was due to its higher selectivity of methane. However, the C_5^+ productivity of Co-5La1Ce/S.G was still higher than unpromoted catalyst. Among all catalysts, Co-2La1Ce/S.G showed the highest productivity of C_5^+ at 220 °C (0.104 g HC/g-cat/h) while Co-1La2Ce/S.G presented the highest C_5^+ productivity at 240 °C (0.146 g HC/g-cat/h). Under the same reaction conditions, these two catalysts also had higher CO conversion compared with the IRE modified catalyst, which strongly suggests that with appropriate molar ratio of REs, high CO conversion and high productivity of C_5^+ can be achieved at the same time.

Anderson Schulz-Flory (ASF) plot is a reference model for describing FT product distribution over carbon numbers. For carbon number n , in a single chain growth probability α , the mole fraction of product Mn is given by [39]:

$$Mn = (1 - \alpha) \times \alpha^{n-1} \quad (E\ 6)$$

Which can be further presented as:

$$\log \frac{Wn}{n} = n \log \alpha + \log \frac{(1-\alpha)^2}{\alpha} \quad (E\ 7)$$

where ' n ' is carbon number, ' Wn ' is the mass percentage of the component with carbon number n , ' α ' is chain growth probability. The probability α of all catalysts at two temperatures was calculated and listed in Table 2. It shows that after addition of La and Ce, the chain growth factor increased from 0.818 to 0.929, and 0.854 to 0.917 at 220 and 240 °C, respectively, corresponding to the changeable trend with C_5^+ selectivity.

Figure 5. ASF plot of hydrocarbons products of selected catalysts at 240 °C.

The hydrocarbon distribution, $\log(\frac{W_n}{n})$ versus carbon number at 240 °C, is shown in Fig. 5. The figure shows that unpromoted catalyst Co/S.G had a lower products proportion in the whole distribution range while the catalysts modified with IRE or CRE presented higher proportion of the products with the carbon number > 12. In addition, Co-1La2Ce/S.G presented an obvious higher proportion of products (C₁₂-C₂₂) and lower proportion of long chain hydrocarbons (C₂₆⁺) compared with IRE promoted catalysts. It was reported that main active carbon species over the Co/SiO₂ catalyst was CH₂ species and the chain growth unit -CH₂- can be easily formed. Addition of CeO₂ increased the concentration of surface-active carbon species CH_x, especially the chain growth unit -CH₂-, thus increased the catalytic activity and favored the chain growth

and the selectivity for long chain hydrocarbons [22]. Also, certain amount of La_2O_3 as promoter will increase CO conversion and C_5^+ selectivity, while decrease methane selectivity [16]. Therefore, when the molar ratio of La to Ce is 1:2, CREs achieved the best synergistic effect. It was also noticeable that, for catalyst Co-1La2Ce/S.G, C_2 came below the ASF curve, the possible explanation might be that the rate of liberation of the free C_2 hydrocarbons from the catalysts' surface was slower than the rate of C_2 polymerization, which was surface-attached related [40]. The other two points, C_4 and C_5 , also did not fit well with the curve, which might be because of vaporization of light hydrocarbon products from the liquid gasoline phase during sample collection from the high-pressure cold trap [41].

In order to present the details of product distributions, the selectivities (weight percentage) of $\text{C}_5\text{-C}_{19}^+$ were listed in the Fig. 6. In Fig. 6A, CRE promoted catalysts showed higher proportion of $\text{C}_{12}\text{-C}_{18}$ while a similar proportion of $\text{C}_5\text{-C}_{11}$ (35 - 42%) remained, compared to IRE promoted and unpromoted catalyst. The heavy hydrocarbon with $n > 19$ in the products was in proportion to the cerium concentration. The highest proportion of C_{19}^+ (17.35%) was achieved with IRE promoted catalyst (Co-1Ce/S.G) while this value became to 13.72% with the CRE (catalyst Co-1La2Ce/S.G) promoted catalysts at 220 °C.

When temperature increased to 240 °C (Fig. 6B), the selectivity of C_5^+ components decreased at different levels, while the productivity of C_5^+ increased inversely (Table 2) due to enhanced CO conversion. The selectivity of $\text{C}_5\text{-C}_{11}$ increased with the increasing ratio of Ce in the CRE promoted catalysts except when the ratio of Ce to La was 2: 1. When the molar ratio of Ce to La

Figure 6. Selectivities of (C₅-C₁₉⁺) of different catalysts at temperature 220 °C (A) and 240 °C (B).

equaled 5:1, the highest C₅-C₁₁ was achieved (44%), however, the diesel fraction rapidly dropped down to 12.28 % compared to 17.24 % at 220 °C. The highest diesel fraction (C₁₂-C₁₈) was obtained (26.77 %) when the ratio of Ce to La was 2: 1. All of the results in Fig. 6 further indicate that the modification of CRE facilitates the formation of diesel and gasoline fraction,

which may be related to the synergistic effect of La and Ce. Overall, catalysts modified with IRE have higher selectivity of C_5^+ compared with unpromoted ones at both temperatures, and the catalysts promoted with CRE have even better performances. At the appropriate molar ratios of La to Ce, such as 2:1, 1:1 and 1:2, the proportion of diesel fraction is maintained at a high level at both temperatures.

4. Conclusions

Silica gel supported cobalt based FTS catalysts promoted with IRE or CRE were synthesized for producing high-value chemicals and fuels, especially diesel, through coal-derived syngas. The effects of different molar ratios of RE on the catalytic performance were studied. A synergistic effect of La_2O_3 and CeO_2 to cobalt based catalysts was found, and both catalytic activity and valuable diesel fractions ($C_{12} - C_{18}$) selectivity were achieved with the optimized molar ratio of the RE. Meanwhile, high selectivity of C_5^+ and low productivity of methane were also achieved. Different characterization techniques, such as, BET, XRD, SEM and H_2 -TPR, were combined to characterize the textural properties and phase composition of the modified catalysts. N_2 adsorption-desorption results showed clearly that catalysts modified with CRE presented lower surface area, lower pore diameter and pore volume compared to unpromoted catalyst, thus resulting in the excellent catalytic performance. The CRE promoted catalysts with optimized La and Ce molar ratio may have a potential industrial application via FTS to produce diesel rich synthetic oil.

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