

THE EFFECTS OF CERIUM PROMOTER ON THE PERFORMANCE OF COBALT-BASED CATALYSTS IN FISCHER TROPSCH SYNTHESIS FOR LIQUID FUEL PRODUCTION

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ABSTRACT: An intensive work of Fischer-Tropsch synthesis (FTS) on a cobalt-based catalyst supported with cerium as a promoter was presented. The influence of space velocity and inlet gas feed ratio on FTS reaction performance was studied for the synthesized catalysts. Incipient wetness impregnation method was utilized to synthesis both unpromoted (25%Co/ γ -Al₂O₃) and cerium promoted (1%Ce-25%Co/ γ -Al₂O₃) catalysts. The proposed catalysts were examined by N₂ adsorption and temperature-programed reduction (TPR). The performance of Ce-promoted and unpromoted cobalt-based catalysts in FTS was assessed in terms of activity and selectivity to desired products (C₅₊). The obtained results revealed that the addition of cerium by impregnation notably favours the reducibility of cobalt oxides by reducing the reduction temperature. In addition, the promoted catalysts exhibited higher activity and selectivity toward desired products at low space velocity and high inlet gas feed ratio as compared with the unpromoted catalysts. In conclusion, a cerium based cobalt catalyst considered as a suitable candidate to be used in gas to the liquid conversion process.

ABSTRAK: Kajian intensif sintesis Fischer-Tropsch (FTS) adalah tentang pemangkin berasas kobalt bersama penggalak cerium. Pengaruh tindak balas FTS pada halaju ruang dan nisbah suapan gas masuk dikaji menggunakan pemangkin yang disintesis. Kaedah impregnasi insipien basah telah digunakan bagi mensintesis pemangkin bukan penggalak (25%Co/ γ -Al₂O₃) dan penggalak cerium (1%Ce-25%Co/ γ -Al₂O₃). Pemangkin ini diuji dengan penjerapan N₂ dan pengurangan suhu terprogram (TPR). Hasil tindak balas penggalak-Ce dan bukan penggalak berasas kobalt dalam FTS diperiksa dari segi aktiviti dan pemilihan hasil (C₅₊). Tindak balas menunjukkan dengan penambahan cerium melalui kaedah impregnasi dengan ketara mengurangkan kobalt oksida bersama pengurangan suhu. Di samping itu, pemangkin penggalak menunjukkan aktiviti dan pemilihan ke arah hasil pada halaju ruang dan nisbah suapan gas masuk yang tinggi berbanding dengan pemangkin bukan penggalak. Kesimpulan, pemangkin kobalt berasas cerium dianggap sesuai sebagai pemangkin sintesis bagi digunakan dalam proses penukaran gas ke cecair.

KEYWORDS: catalyst, cerium promoter, Fischer-Tropsch synthesis, GTL, syngas;

1. INTRODUCTION

Over the past few decades, natural gas has been considered a plentiful and cleanest natural fuel that should be altered to liquid form to prevent safety hazards and to reduce transportation costs [1]. Natural gas, methane (CH₄) is commonly employed to produce synthesized gas (syngas) via different techniques, such as partial oxidation [2], steam reforming [3], and auto-thermal reforming [4].

Recently, the gas-to-liquid technique (GTL) has been considered one of the most efficient processes that is mainly used to convert natural gas into a syngas intermediate through a Fischer-Tropsch (FT) synthesis technology [5]. In general, the GTL process produces oil crudes that contain different fractions of useful hydrocarbons that can be amended and segregated to different types of necessary transportation sector fuels [6], in the presence of solid catalysts.

Because of their high C₅₊ selectivity, excellent activity, and ability to work at low operating temperatures (between 200 and 250 °C), Co-based catalysts are in the limelight recently as an effective catalyst for attaining heavy hydrocarbons in FT synthesis [7, 8]. Thus, it is of a great necessity to improve the efficiency of Co-based catalysts. Many researches have demonstrated that adding different promoters and loadings to the catalyst assists in improving the selectivity and activity of the catalyst towards C₅₊ contents. Guo et al. [9] reported that adding a small amounts of Lanthanum to the Co/ γ -Al₂O₃ catalyst could enhance the performance of the catalyst in terms of selectivity, activity, and Co reducibility to heavy hydrocarbons. Co reducibility was significantly increased by adding different loading of silver to the Co-based catalyst [10]. Furthermore, the addition of silver helps in decreasing the reduction temperatures by up to 100 °C and increasing the Co reduction, dispersion, and electronic properties.

Another study by Pedersen et al. [11] employed manganese (Mn) as a promoter for a Co-based catalyst supported by γ -Al₂O₃. They found that Mn enhanced the intrinsic Co catalyst activity, Co dispersion, and selectivity to C₅₊ species due to its stable effect on the adsorption of CO, C, H, O, CHX, thereby decreasing the CO dissociation barrier. Rare earth elements were also utilized to improve the performance of the Co-based catalyst supported by Al₂O₃, SiO₂, TiO₂, ZrO₂, and CNTs [12, 13].

Among all the discussed promoters, Co-based catalysts promoted with Cerium (Ce) attained excellent performance in FT synthesis technology due to its ability to facilitate the dissociation of CO, weaken the interaction between support and Co and improve the activity, C₅₊ selectivity and the olefin/paraffin ratio of the Co-based catalyst [13-15]. Although many studies have been conducted on Ce as a promoter for Co-based catalysts, there are great opportunities in further investigating the influence of reaction conditions on the cerium- promoted cobalt-based catalyst in FTS reactions.

Herein, we thoroughly study and evaluate the effects of reaction conditions (space velocity and H₂/CO ratio) on the cerium-promoted Co-based catalyst in terms of FTS activity and product selectivity. The developed catalyst shows excellent results as compared with those of the un-promoted cobalt-based catalyst.

2. MATERIALS AND METHODS

2.1 Catalysts Preparation

Incipient wetness impregnation method was employed to synthesize the Co-based catalysts supported by γ -Al₂O₃ (Axens) according to the method reported by Trépanier et

al. [16]. Initially, the support (γ - Al_2O_3) was calcined in airflow at 500 °C for 4 h. After cooling down the temperature to room temperature (25 °C), sequential impregnation with continuous stirring in aqueous solutions of Cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was performed at ambient temperature. Then, 25 % of Co by weight was laden to the mixture and left to dry for 12 h at 110 °C and then calcined at 400 °C for 6 h beneath airflow with a degree of temperature increase 2°C/min to attain 25 Co/ γ - Al_2O_3 reduced catalyst.

To obtain the Ce promoted catalyst, 1wt. % of Ce promoter was added to 25 Co/ γ - Al_2O_3 dried un-calcined catalyst by the co-impregnation in an aqueous solution of Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and dried overnight for 12 h at 110 °C. Later, the catalyst was calcined at 400 °C for 6 h with a heating rate of 2 °C/min under airflow. The developed catalysts were labelled as Co_0 and Co_1 representing unpromoted and Ce promoted Co-based catalysts, respectively.

2.2 Catalyst Characterization

The calcined prepared catalysts were characterized by temperature-programed reduction (TPR) and N_2 physisorption. The temperature-programed reductions were accomplished to decide the reducibility of metal oxides to metallic using a TP-5000 analyser fitted with a quartz tubular reactor and TCD. A 50 mg of each sample was exposed to a continuous argon gas flow at rate of 1.8 L/h containing 5 % of H_2 with heating temperature ranging from 25 °C to 900 °C with increments of 10 °C per min.

N_2 physisorption isotherm analysis was done using the Micromeritics ASAP-2020 system, to estimate the BET surface area, pore-volume, and the average pore radius for the γ - Al_2O_3 and catalysts.

2.3 Fischer-Tropsch Reaction (FTR)

As aforementioned, the FTR process was utilized to convert synthesized gas to liquid fuel (high molecules weight hydrocarbons). The activity and selectivity of the developed catalysts were investigated in a fixed-bed flow reactor made from a stainless steel metal with internal diameter of 10 mm. Two grams of the promoted and unpromoted Co-based was loaded in the centre of the reactor and fixed between two quartz beads, then heated under argon gas to reduction temperature, the reduction was conducted by (5% H_2 -95%Ar) gas mixture to convert the forms of metal from oxide to the metallic. After finishing the reduction, the reactant gases mixtures (H_2 and CO) were introduced to the reactor with a desired flow rate using a mass flow controller (Brooks 5850) fitted with a PID controller.

The FT reactions were conducted at a temperature of 230 °C and pressure of 15 bar with different space velocity (SV) in the range of 2 - 8 L/h.g_{cat}. (with increments of 2) and different feed gas ratio (H_2/CO) of 1 to 2 (with increments of 0.5). The output stream from the reactor was lowered to atmospheric pressure by a control valve (BPR) and then went over two traps. The first one was at 100 °C and the other was 0 °C to condense the products. The compositions of products in a gas and liquid phase were analysed online and off-line using a gas chromatograph (GC-Shimadzu-2014) equipped with (TCD and FID) and Varian CP 3800 equipped with FID, respectively.

3. RESULTS AND DISCUSSION

3.1 Catalyst Characterization

The TPR profiles for the unpromoted (25%Co/ γ - Al_2O_3) and promoted (1%Ce-25%Co/ γ - Al_2O_3) calcined catalysts are illustrated in Fig. 1. Three reduction peaks are

clearly observed for the un-promoted Co-based catalyst. The reduction of Co_3O_4 to CoO ($\text{Co}^{3+} \rightarrow \text{Co}^{2+}$) and CoO to Co metal ($\text{Co}^{2+} \rightarrow \text{Co}^0$) can be allocated at 350 °C and 577 °C, respectively [17]. While, the weak peak noticed around 702 °C can be attributed to the reduction of cobalt aluminate compounds [18]. On the other hand, the catalyst promoting with 1% Ce has robustly influenced the TPR profile, as revealed in Fig. 1, where the first and second peaks obviously shifted to lower temperature, at 252 °C and 527 °C, respectively, due to the significant easy reduction of CoO to Co metal along with the low interaction between Co ions and the Al_2O_3 support [19, 20]. As a result, the third peak related to cobalt aluminate compounds observed in the un-promoted catalyst disappeared. In addition, the TPR outcomes confirmed that the selected reduction parameters (5% H_2 -95% Ar) mixture by rate of flow 1.8 L/h at 570 °C for 10 h) were appropriate for reducing the cobalt oxides into cobalt metal in- suite apparatus prior to the FT reaction.

Table 1 listed the results of single point pore volume, BET surface area (SA) and pore size for the calcined support ($\gamma\text{-Al}_2\text{O}_3$), Co_0 , and Co_1 catalysts. From the table, it can be noticed that the SA of $\gamma\text{-Al}_2\text{O}_3$, Co_0 , and Co_1 were found to be 145, 95.2 and 94.6 m^2/g , respectively.

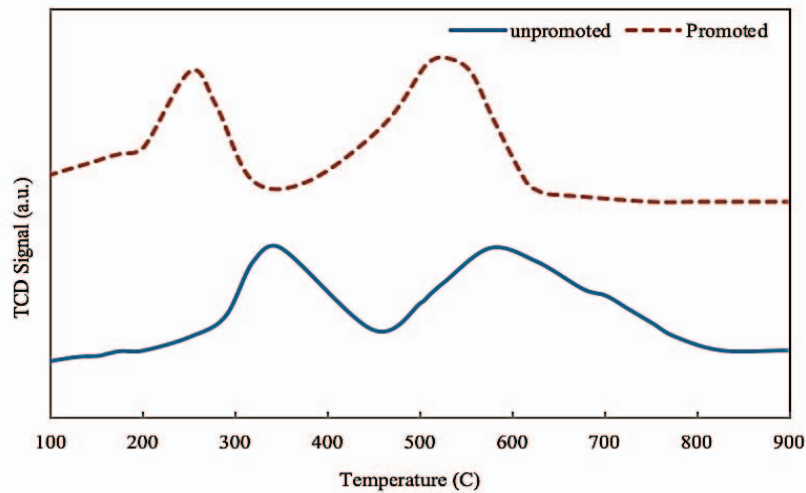


Fig. 1: TPR profiles for the un-promoted ($25\%\text{Co}/\gamma\text{-Al}_2\text{O}_3$) and promoted ($1\%\text{Ce-}25\%\text{Co}/\gamma\text{-Al}_2\text{O}_3$) calcined catalysts.

Table 1: BET surface area and pore volume for the developed catalysts

Catalyst	Symbol	BET (m^2/g)	SA pore volume (cm^3/g)	pore size (nm)
$\gamma\text{-Al}_2\text{O}_3$	-	145	0.542	6.8
$25\%\text{Co}/\gamma\text{-Al}_2\text{O}_3$	Co_0	95.2	0.276	4.9
$1\%\text{Ce-}25\%\text{Co}/\gamma\text{-Al}_2\text{O}_3$	Co_1	94.6	0.265	4.7

SA for the support was 145 m^2/g which plunged to 95.2 m^2/g for the un-promoted catalyst, the 25% of Co corresponds to 34% Co_3O_4 . According to the obtained cobalt oxide percentage, the theoretical value of the BET surface area catalyst was approximately 95.6 m^2/g for the un-promoted catalyst. The theoretical and experimental BET surface area values were more closed owing to the minimum pore plugged by cobalt species [21]. Adding the Ce promoter causes a small decrement in the surface area. In addition, the pore volume and pore size for the $\gamma\text{-Al}_2\text{O}_3$ were 0.542 cm^3/g and 6.8 nm, respectively, that

decreases to $0.276 \text{ cm}^3/\text{g}$ and 4.9 nm , accordingly, for Co_0 . Pore volume and pore size were slightly altered in Co_1 . These results are in good agreement with the results reported by Gnanamani et al. [22].

3.2 Fischer-Tropsch Synthesis

Production of liquid fuels by FT synthesis process is considered as one of the most important techniques used to tackle the problem of fuel shortage in the transport sector [23]. To investigate the influences of space velocity and inlet feed ratio (H_2/CO) on the activity of unprompted and Ce promoted catalysts and their selectivity toward liquid fuels production, number of experiments of Fischer-Tropsch reaction were conducted at a temperature of $230 \text{ }^\circ\text{C}$, pressure of 15 bar , and different space velocity and inlet feed ratios (H_2/CO). After steady-state condition of about 8 to 9 h, the percentage of carbon monoxide conversion ($\%X_{\text{CO}}$) and product selectivity (%) were examined.

3.2.1 Influence of Space Velocity on Catalyst Performance

Figure 2 shows that the CO conversion ($\%X_{\text{CO}}$) as a function of space velocities of the developed catalysts (Co_0 and Co_1) ranges from 2 to $8 \text{ L/h. g}_{\text{cat}}$ with different H_2/CO ratios between 1 and 2 for each SV at operating temperature and applied pressure of $230 \text{ }^\circ\text{C}$ and 15 bar , respectively. The obtained results demonstrated that the CO conversion sharply decreased when SV increased thereby, the residence time of reaction decreased. Thus, CO conversion and chain growth decrease, which assures the rapid increase in the formation of low molecular weight hydrocarbons (CH_4 and $\text{C}_2\text{-C}_4$) and the decrease in production of high molecular weight hydrocarbons (C_{5+}) [24].

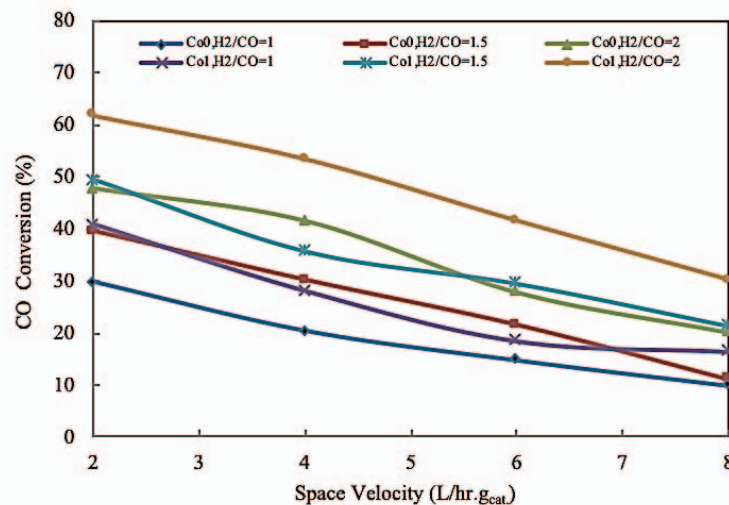


Fig. 2: Effect of space velocity on carbon monoxide conversion for the Ce-promoted and unprompted cobalt catalysts at $P = 15 \text{ bar}$, $T = 230 \text{ }^\circ\text{C}$, and $\text{H}_2/\text{CO} = 1, 1.5, \text{ and } 2$.

The selectivity of the developed catalysts (Co_0 and Co_1) toward CH_4 , $\text{C}_2\text{-C}_4$ hydrocarbons, C_{5+} , and CO_2 are demonstrated in Fig. 3(a-d). It is evident that the product selectivity of both catalysts against CH_4 , $\text{C}_2\text{-C}_4$ hydrocarbons, and CO_2 increased proportionally with SV while the desired product (C_{5+}) decreased. This is because an increase in SV leads to a significant decrease in the residence time of reaction, thereby decreasing the CO conversion, which is in agreement with the results reported in [24]. Figure 3a shows that the selectivity of Co_0 and Co_1 toward CO_2 were very small (< 3). This can be attributed to the little activity of water-gas shift mainly obtained by the Co

based catalyst [25, 26]. Furthermore, the promoted Co-based catalysts exhibited an excellent Co conversion and C₅₊ selectivity by decreasing the SV due to the presence of Ce promoter which aids in increasing the amount of chemisorbed hydrogen and weakening the strong bond of Co–H [27]. Table 2 summarized the obtained results.

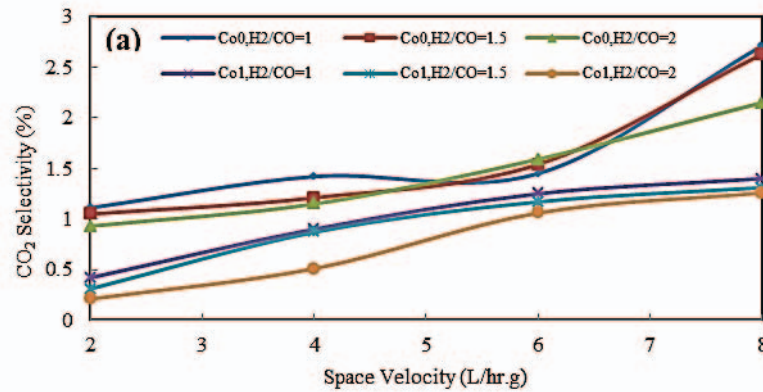


Fig. 3: (a) Effect of SV on CO₂ selectivity for the Ce-promoted and unpromoted cobalt catalysts at P = 15 bar, T= 230 °C and H₂/CO ranging from 1 to 2.

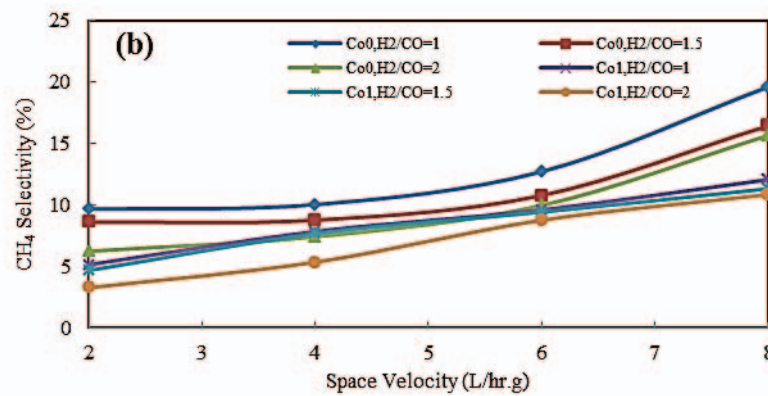


Fig. 3: (b) Effect of SV on CH₄ selectivity for the Ce-promoted and unpromoted cobalt catalysts at P = 15 bar, T= 230 °C and H₂/CO ranging from 1 to 2.

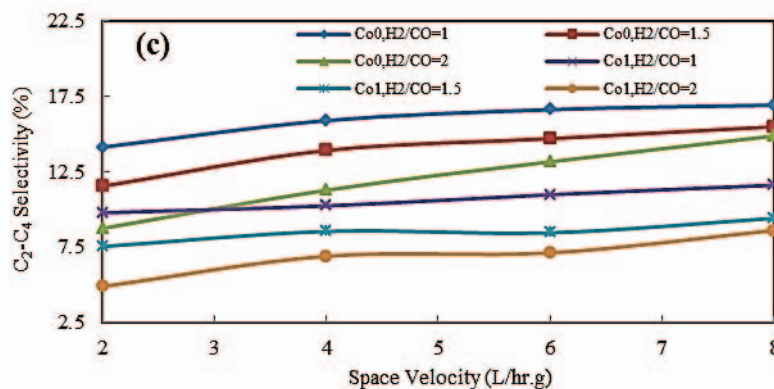


Fig. 3: (c) Effect of SV on C₂-C₄ selectivity for the Ce-promoted and unpromoted cobalt catalysts at P = 15 bar, T= 230 °C and H₂/CO ranging from 1 to 2.

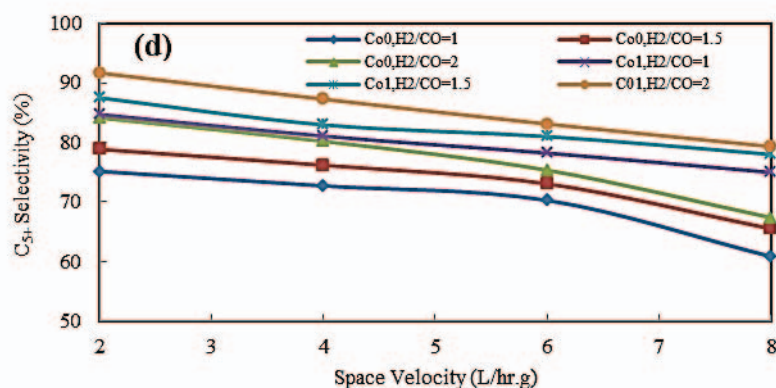


Fig. 3: (d) Effect of SV on C₅+ selectivity for the Ce-promoted and unpromoted cobalt catalysts at P = 15 bar, T= 230 °C and H₂/CO ranging from 1 to 2.

3.2.2 Influence of Inlet Feed Ratio (H₂/CO) on Catalyst Performance

The effect of inlet feed ratio (H₂/CO) on the developed catalysts (Co₀ and Co₁) has been thoroughly investigated in terms of %XCO and selectivity at operating temperature of 230 °C and under a pressure of 15 bar with different SV, as shown in Fig. 4 and Fig. 5 and listed in Table 2.

Table 2: Catalytic performance of Co-based catalysts during CO hydrogenation

Catalyst	SV (L/hr. gcatt.)	H ₂ /CO ratio	%X _{CO}	%Selectivity			
				CH ₄	C ₂ -C ₄	C ₅ +	CO ₂
25%Co/γ-Al ₂ O ₃ (Co ₀)	2	1	29.8	9.65	14.12	75.12	1.11
		1.5	39.5	8.6	11.53	78.82	1.05
		2	47.8	6.23	8.74	84.1	0.93
	4	1	20.4	10.02	15.88	72.68	1.42
		1.5	30.2	8.75	13.9	76.14	1.21
		2	41.5	7.41	11.27	80.17	1.15
	6	1	14.7	12.7	15.6	70.25	1.45
		1.5	21.6	10.76	14.68	73.02	1.54
		2	27.8	9.95	13.15	75.31	1.59
	8	1	9.8	19.58	16.9	60.81	2.71
		1.5	11.2	16.42	15.47	65.48	2.63
		2	20.1	15.64	14.86	67.35	2.15
1%Ce-25%Co/γ-Al ₂ O ₃ (Co ₁)	2	1	40.8	5.13	9.77	84.68	0.42
		1.5	49.4	4.67	7.54	87.48	0.31
		2	61.9	3.26	4.89	91.64	0.21
	4	1	28.1	7.84	10.23	81.03	0.9
		1.5	35.7	7.66	8.54	82.93	0.87
		2	53.5	5.34	6.9	87.25	0.51
	6	1	18.5	9.59	10.97	78.19	1.25
		1.5	29.5	9.41	8.45	80.97	1.17
		2	41.6	8.75	7.12	83.07	1.06
	8	1	16.5	12.05	11.6	74.95	1.4
		1.5	21.4	11.31	9.41	77.97	1.31
		2	30.2	10.84	8.61	79.29	1.26

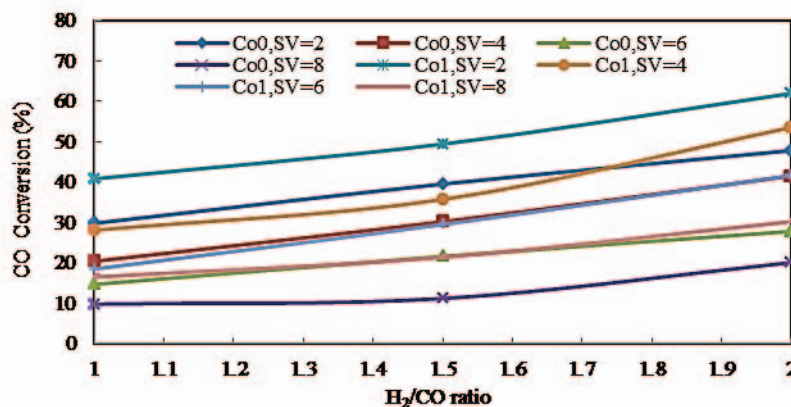


Fig. 4: Effect of H₂/CO ratio on CO conversion for the Ce-promoted and unpromoted cobalt catalysts at P = 15 bar, T= 230 °C and SV= 2, 4, 6 and 8 L/h. g_{cat.}.

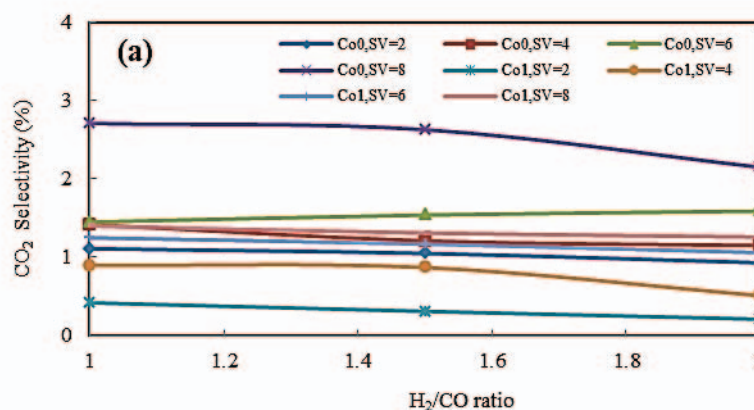


Fig. 5: (a) Effect of H₂/CO ratio on CO₂ selectivity for the Ce-promoted and unpromoted cobalt catalysts at P = 15 bar, T= 230 °C and SV= 2, 4, 6 and 8 L/h. g_{cat.}.

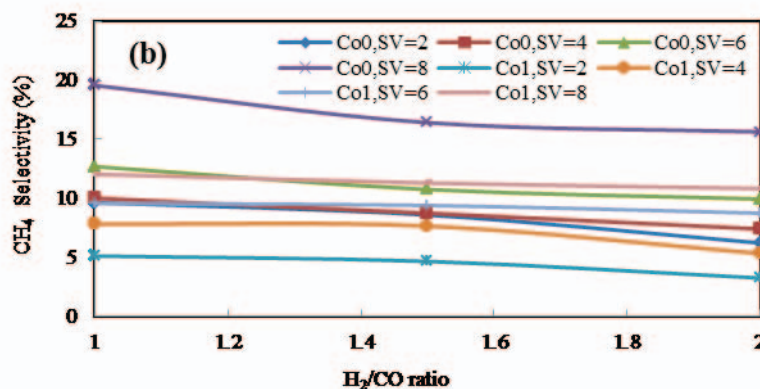


Fig. 5: (b) Effect of H₂/CO ratio on CH₄ selectivity for the Ce-promoted and unpromoted cobalt catalysts at P = 15 bar, T= 230 °C and SV= 2, 4, 6 and 8 L/h. g_{cat.}.

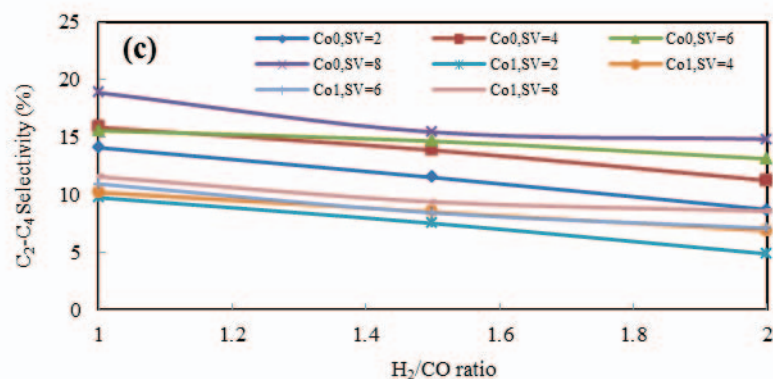


Fig. 5: (c) Effect of H_2/CO ratio on C_2-C_4 selectivity for the Ce-promoted and unpromoted cobalt catalysts at $P = 15$ bar, $T = 230$ °C and $SV = 2, 4, 6$ and 8 L/h. g_{cat} .

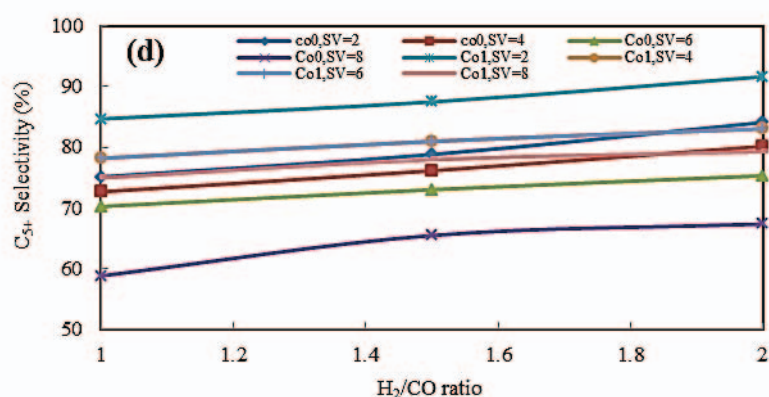


Fig. 5: (d) Effect of H_2/CO ratio on C_{5+} selectivity for the Ce-promoted and unpromoted cobalt catalysts at $P = 15$ bar, $T = 230$ °C and $SV = 2, 4, 6$ and 8 L/h. g_{cat} .

4. CONCLUSION

In conclusion, the performance of FT synthesis reaction for unpromoted and Ce-promoted cobalt-based catalysts was investigated based on space velocity and inlet gas feed ratio reaction conditions. The relevant results demonstrated that the addition of Ce promoter remarkably enhances the reducibility of cobalt oxides by decreasing the reduction temperature. In addition, Ce promoted Co-based catalysts show a significant C_{5+} selectivity and CO conversion ascribed to the high reducibility of Co that provides huge number of active sites for the reactant species. For both Co catalysts, the results exhibited that the reaction properties have strongly affected the catalysts' activity and products' selectivity, consequently, improved C_{5+} selectivity with low water-gas shift reaction activity were observed at high H_2/CO ratio and low space velocity. Thus, Ce based Co catalyst is considered to be a suitable candidate for use in the gas to liquid conversion process.

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