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Preparation and Operating Conditions for Cobalt Cerium Oxide Catalysts Used in the Conversion of Synthesis Gas into Light Olefins

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Cobalt cerium oxides, prepared using a co-precipitation procedure, were studied as catalysts for the conversion of synthesis gas to light olefins (C₂-C₄). Specifically, we studied the effect of a range of preparation variables, including the molar ratio of the [Co]/[Ce] of the precipitation solution, ageing time and calcination temperature. In addition, the effects of supports and promoters on the catalysts' activity and selectivity and a range of reaction temperatures using synthesis gas with different H₂/CO molar feed ratios were investigated. The catalyst containing a molar ratio of 80% Co and 20% Ce, aged for 2 h, supported with 15 wt% SiO₂ without any promoter, at an operating temperature of 450 °C and an H₂/CO feed ratio of 2/1 (GHSV = 4500 h⁻¹), performed optimally for the conversion of synthesis gas to light olefins. The characterization of both the precursors and the calcined catalysts by powder X-ray diffraction, scanning electron microscopy, Brunauer-Emmett-Teller specific surface area measurements and thermal analysis methods, including TGA and DSC, show that all the preparation variables influenced the catalyst precursor structure.

Keywords: Co-precipitation, Ageing time, Fischer-Tropsch synthesis, Light olefins, Cobalt cerium catalyst, Characterization

INTRODUCTION

Fischer-Tropsch synthesis (FTS) has attracted increasing attention, since high quality diesel fuels without sulfur or aromatic compounds can be produced directly from synthesis gas derived from natural gas, coal, or biomass [1]. FTS also provides a means of converting coal and natural gas to petrochemicals and liquid transportation fuels. FTS involves a polymerization reaction beginning with a methylene intermediate to produce a wide distribution of hydrocarbons ranging from methane to wax (C₁-C₆₀) [2,3]. FTS hydrocarbon products are mostly n-paraffins or n-olefins. There is a considerable increase in the demand for light olefins such as ethylene, propylene and isobutylene because of the growing interest in their applications for the manufacture of highly desirable products such as polyethylene, polypropylene, methyl tertiary butyl ether (MTBE) and ethyl tertiary butyl ether (ETBE) [4].

Group VIII metals, such as Fe, Co, Ni and Ru are the most popular FTS catalysts [5,6]. Some researchers have argued that using bimetallic catalysts obtained from metal alloys may have some special advantages in CO hydrogenation [7-10]. Cobalt and iron are the two reasonable choices for catalysts for FTS, but the iron-based catalysts have a high water gas shift (WGS) activity, whereas cobalt-based catalysts are effective in FTS without significant WGS activity. Mixed oxide catalysts are commercially important in the conversion of synthesis gas [11-14].

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Numerous studies have been devoted to ascertaining the influence of oxide carriers (e.g., titania, silica, alumina, and zirconia) on the activity and stability of Co catalysts [15-20]. The effects of ceria seem rather controversial, because both solid-state interactions and enhanced reactivity toward the gas phase [21,22] affect the redox and electronic properties of the active phase, shaping a singular adsorption behavior reflected in the unusual catalytic features of active phases [22,23]. In particular, the enhanced reducibility and surface affinity of ceria for both H₂ and CO molecules [21,22] might well contribute to shaping the reactivity of the Co/CeO₂ system in FTS [22]. It has been also reported that the Co and Ce matrix plays a synergistic role in the chemisorption of reactant molecules, thereby controlling the reactivity of the title system in the FTS reaction [24]. Co-Ce catalysts have been investigated for their selectivity for lower molecular weight olefins [25-28]. Mixed cobalt-cerium oxide catalysts supported by SiO₂ [29,22] and TiO₂ [30] have also been used in FTS for the production of hydrocarbons. One study [22] on the effects of cerium oxide on the particle size of cobalt, reducibility of cobalt and catalytic performance of a Co/SiO₂ catalyst found that the degree of cobalt reduction decreased with the addition of cerium, even in low concentrations.

The aim of this work is to investigate the effect of a range of preparation variables on the structure of a precipitated cobalt-cerium catalyst for FTS. These preparation variables include the precipitate aging time, the [Co]/[Ce] ratio of the precipitation solution and the catalyst calcination temperature. We also report further results concerning the effects of different promoters and supports on the performance of the optimally-prepared catalyst, as well as the structural investigation by X-ray diffraction (XRD), scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) specific surface area measurements and thermal analysis methods, including thermal gravitational analysis (TGA) and differential scanning calorimetry (DSC). In addition, we also report the effect of two reaction conditions, testing various H₂/CO molar feed ratios (space velocity) and a range of reaction temperatures for the conversion of synthesis gas to light olefins.

EXPERIMENTAL

Preparation

All the catalysts tested in this study were prepared using the following co-precipitation procedure. Aqueous solutions of Co(NO₃)₂.6H₂O (0.5 M) and Ce(NO₃)₂.6H₂O (0.5 M) with different molar ratios were pre-mixed and the resulting solution heated to 70 °C in a round-bottomed flask fitted with a condenser. Aqueous Na₂CO₃ (0.5 M) was added dropwise to the mixed nitrate solution with stirring while the temperature was maintained at 70 °C until it reached pH 8.0. The resulting precipitate was then aged in this medium from 0 to 5 h. The aged suspension was then filtered, followed by several washes with warm distilled water until no further Na⁺ was observed in the washings, as tested by flame atomic absorption. The precipitate was then dried in an oven (110 °C, 16 h) to give a material, hereafter referred to as the catalyst precursor, which was subsequently calcined in static air in a furnace (600 °C, 6 h) to give the final catalyst. The optimum molar ratio of cobalt and cerium was determined by testing the catalysts' performance, including the activity and selectivity for the production of C₂-C₄ olefins, by the hydrogenation of CO using FTS.

To determine the best support material for this catalyst, the same amount (10 wt%) of each support (TiO₂, SiO₂, Al₂O₃, zeolite and magnesium silicate) was added separately to the mixed solution of cobalt and cerium nitrates with the optimal molar ratio of 80%Co:20%Ce. SiO₂ loading ratios of 10, 15, 20 and 25 wt%, based on the total catalyst weight, were used to determine the optimal amount of this support. The calcined supported catalyst was then promoted using Li, K, Rb and Mg by adding a small amount (1.5 wt%) of LiNO₃, KNO₃, RbCl and Mg(NO₃)₂.6H₂O separately to the suspension containing Co (80%) and Ce (20%) and SiO₂ (15 wt%).

Catalyst Characterization

X-Ray diffraction (XRD). Powder XRD measurements were performed using a D8 Advance diffractometer (Bruker AXS, Germany). Scans were taken with a 2 θ step size of 0.02 and a counting time of 1.0 s using a CuK_{α} radiation source generated at 40 kV and 30 mA. Specimens for XRD were prepared by compaction into a glass-backed aluminum sample holder. Data was collected over a 2 θ range from 4° to 70° and phases were identified by matching experimental patterns to

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Fig. 1. Schematic representation of the reactor used for the catalyst test. 1-Gas cylinders, 2-Pressure regulators, 3-Needle valves, 4-Mass flow controllers (MFC), 5-Monometers, 6-Non-return valves, 7- Ball valve, 8-Tubular furnace, 9-Reactor, 10-Catalyst bed, 11-Trap, 12-Condenser, 13-Silica gel column, 14-Gas chromatograph (GC).

entries in the Diffract^{plus} version 6.0 indexing software.

Thermal gravimetric analysis and differential scanning calorimetry. The weight changes in the catalyst precursors were measured using a TGA/DSC simultaneous thermal analyzer (model STA 1500+, Rheometric Scientific) under a flow of dry air. The temperature was raised from room temperature to 600 °C using a linear programmer at a heating rate of 10 °C per min. The sample weight was between 15 and 20 mg.

BET surface area measurements. BET surface area measurements were conducted using a surface area analyzer (model Nova 2000, Quantachrome Instruments, USA) using nitrogen (99.99% purity) as the adsorption gas. The catalyst samples were slowly heated to 300 °C for 3 h under nitrogen atmosphere. To obtain the BET specific surface area measurements, the different precursors and catalysts were evacuated at -196 °C for 66 minutes.

Scanning electron microscopy. The morphology of the catalysts and their precursors was observed by means of a Cambridge S-360 scanning electron microscope.

Catalyst Testing

The catalysts were tested by using them in the FTS method, which was carried out in a fixed-bed micro-reactor (stainless steel) operating at atmospheric pressure (Fig. 1). All gas lines to the reactor bed were made from 1/8" stainless steel tubing. Three mass flow controllers (Brooks, model 5850E) equipped with a four-channel control panel (Brooks, model 0154) were used to automatically adjust the flow rate of the inlet gases (CO, H₂, and N₂ with purities of 99.999%). The mixed gases passed into the reactor tube, which was placed inside a tubular furnace (model ATU 150-15, Atbin Mfg. & Eng., Inc., Tehran, Iran), capable of producing temperatures up to 1300 °C and maintained by a digital programmable controller. The reactor tube was constructed of 1/4" stainless steel tubing, with an internal diameter of 3 mm, and a catalyst bed situated in the middle of the reactor. The reaction temperature was controlled by a thermocouple inserted into the catalyst bed. The meshed catalyst (1.0 g) was held in the middle of the reactor using a 70-cm length of quartz wool. The sample was pre-reduced in situ at atmospheric pressure in a

flowing H₂-N₂ stream (N₂/H₂ = 1, flow rate of each gas = 30 ml min⁻¹) at 300 °C for 8 h before synthesis gas exposure. The H₂/CO reaction was carried out at 300-500 °C (P = 1 atm, $H_2/CO = 1.00-4.00$, GHSV = 4050-5400 h⁻¹). The reactant and product streams were analyzed on-line using a gas chromatograph (Varian, model 3400) equipped with a 10-port sampling valve (VICI, Supelco, USA), a sample loop and thermal conductivity detector. The contents of the sample loop were injected automatically into a $30' \times 1/8''$ column, packed with HayeSep DB, 100/120 mesh (Altech Associates, Inc., USA). Helium was employed as a carrier gas for optimum sensitivity (flow rate = 30 ml min⁻¹). The calibration was carried out using various calibration mixtures and pure compounds obtained from Matheson Gas Products (USA). GC instrument control and collection of all chromatograms were performed via an IF-2000 single-channel data interface (TG Co., Tehran, Iran) using a Microsoft Windows[®] environment.

RESULTS AND DISCUSSION

Effect of Preparation Conditions

This study investigated the effect of a range of cobalt cerium oxide catalyst preparation variables at the precursor stage upon the morphology and structure of these materials, and the subsequent influence these morphological and structural effects have on the activity of the final calcined catalysts. The optimum preparation conditions were identified with respect to the catalytic activity for the conversion of synthesis gas to light olefins.

Effect of the solution [Co]/[Ce] ratio. Cobalt cerium oxide catalysts were prepared by co-precipitation (2 h ageing time) with a range of [Co]/[Ce] solution ratios varying from 100% Co to 100% Ce. After calcination of these materials (600 °C, 6 h) the performance of each catalyst for FTS under the same molar feed ratio of H₂/CO = 4/1 at 450 °C (GHSV = 4050 h⁻¹) was investigated. As shown in Fig. 2, the catalytic performance varied markedly with different Co/Ce molar ratios. However, the overall optimal catalyst for the conversion of synthesis gas to light olefins under these conditions had a molar ratio of 80%Co:20%Ce, with a high catalytic performance, the highest selectivity toward C₂-C₄ olefins and low selectivity for methane compared to the other catalysts with other [Co]/[Ce] molar ratios.

Characterization of the precursors was performed to establish the relationship of the structure of the catalyst precursor to that of the final catalyst and its consequent activity. Examination of the precursors and calcined catalysts prepared from different cobalt cerium molar ratios using powder XRD shows a great deal of variety in the resulting catalysts, including diverse phases (Figs. 3 and 4). The catalyst precursors with the highest amounts of cobalt (100% Co and 80% Co with 20% Ce) were found to be amorphous, rendering the other phases undetectable in the XRD patterns of these precursors, due to the cobalt hydroxide compound. For the 100% Ce precursor, CeCO₃OH (hexagonal) and $Ce_2(CO_3)_2(OH)_2 \cdot H_2O$ phases were identified. The other



Fig. 2. Effect of different [Co]/[Ce] molar ratios on the performance of cobalt-cerium oxide catalysts.

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Fig. 3. XRD patterns for the catalyst precursors with different cobalt/cerium molar ratios.



Fig. 4. XRD patterns for the calcined catalysts with different cobalt/cerium molar ratios.

catalyst precursors have shown the same phases including $CoCO_3$ (rhombohedral), $Co(OH)_2$ (hexagonal), $CeCO_3OH$ (hexagonal) and $Ce_2(CO_3)_2(OH)_2$.H₂O. The calcined catalyst

prepared from the cobalt nitrate solution with no cerium component was composed of a cubic Co_3O_4 phase. Although this catalyst was active, it produced a high amount of methane

and showed a low selectivity with respect to C_2 - C_4 olefins (Fig. 2).

Co-precipitation in the presence of a cerium component resulted in a decrease in CO conversion and variation in the selectivity for C₂-C₄ olefins. In general, similar phases were identified for the catalysts with preparation ratios between 80% Co with 20% Ce and 20% Co with 80% Ce, the phases of which were Co_3O_4 (cubic) and CeO_2 (cubic); however, the relative diffracted intensities of these phases for the various catalysts were different (Fig. 4). The calcined catalyst synthesized from liquor, containing only cerium nitrate, was found to be less active than the other prepared catalysts. The material synthesized from this solution consisted of a CeO₂ (cubic) phase. The actual phases identified in the 80%Co:20%Ce catalyst under the specified preparation conditions were CeO₂ (cubic) and Co₃O₄ (cubic). In order to identify the changes in the 80%Co:20%Ce catalyst during the reaction and to detect the phases formed, this catalyst was characterized by XRD after the test. Its phases were found to be Ce (cubic), CeO₂ (cubic), Co (hexagonal), CoO (cubic), Co₂C (orthorhombic), Ce₂O₃ (cubic) and Co₃C (hexagonal).

Both precursor and calcined catalysts containing 80% Co with 20% Ce were characterized by SEM before and after the test (Fig. 5). The electron micrograph of the catalyst precursor depicts several larger agglomerations of particles (Fig. 5a) and shows that this material has a less dense and homogeneous morphology. After calcination at 600 °C (Fig. 5b), the catalyst has much smaller agglomerates compared to those of the precursor. Note that the calcined catalyst surface is covered with small crystallites of cobalt oxide, Co_3O_4 , which is in agreement with our XRD results. However, the size of these grains grew larger by agglomeration in the tested catalyst (Fig. 5c), which may be due to the sintering after the reactions.

Characterization of the 80%Co:20%Ce catalyst precursor was carried out to measure the weight loss as a result of the increase in sample temperature. The TGA and DSC curves of the amorphous precipitate for the 80%Co:20%Ce catalyst precursor are illustrated in Fig. 6. The weight losses found from TGA measurements agree fairly well with those expected for the decomposition of hydroxycarbonates, M₂CO₃(OH)₂, to different oxides of cobalt and cerium. For the amorphous precipitate of this catalyst precursor, the thermogravimetric curve seems to indicate a two-stage decomposition, including







Fig. 5. SEM images of the catalyst containing 80% Co and 20% Ce: (a) precursor, (b) catalyst before the test and (c) catalyst after the test.

the removal of physisorbed water (80-150 °C), followed by the decomposition of the hydroxyl or basic carbonate precursor (170-490 °C), for an overall weight loss of ca. 32%. The DSC measurement provides further evidence for the presence of the various species and evaluates their thermal behavior. As shown in Fig. 6, the endothermic peak at the lower temperature represents the removal of the physically adsorbed water from the material, while the endothermic peak at the higher temperature solely represents the decomposition of the amorphous hydroxycarbonates, M₂CO₃(OH)₂.

Characterization of both precursors and calcined catalysts (before and after the reaction) was carried out using the BET surface area measurement shown in Table 1. In general, the BET results show that the catalyst precursors prepared with a range of [Co]/[Ce] solution ratios varying from 100% Co to 100% Ce, and the calcined catalysts (before and after the reaction) derived from these precursors, have different specific surface areas. However, as shown in Table 1, the catalyst precursors have higher specific surface areas than their calcined catalysts. Furthermore, the catalyst containing 80%Co:20%Ce has a higher specific surface area than the other catalysts (Table 1), which is one reason for the enhanced performance of this catalyst [31]. The BET data agree well with the SEM results, as the finer particles shown in Fig. 5b for the calcined catalyst containing 80%Co:20%Ce would be expected to have a higher surface area than those with coarser agglomerate in Figs. 5a and c.

Effect of ageing time. The ageing time, defined as the time between the formation of precipitate and the removal of solvent, is one of the most important factors for catalytic performance. In our previous studies [32-40] we demonstrated



Fig. 6. TGA/DSC curves of the 80%Co:20%Ce catalyst aged for 2 h.

the importance of ageing time with respect to catalyst activity for the oxidation of CO by mixed copper manganese oxides and mixed copper zinc oxides. We have also studied the effect of ageing time on the performance of mixed iron cobalt oxide [41,42] and mixed cobalt manganese oxide [43] catalysts for FTS. The results of all of these investigations have shown that the ageing of the precipitates obtained by co-precipitation leads to phase changes toward forms that are more thermodynamically stable.

The activity with respect to ageing time for these catalysts has shown two features that require comment. First, there is considerable variation in the catalytic activity with different ageing times. Second, all the catalysts require a stabilization period for the steady-state activity to be achieved, and the

Co/Ce	Specific surface area			
molar ratio	(m^2/gr)			
	Catalyst	Calcined catalyst before	Calcined catalyst	
	precursor	test	after test	
100%Co/0%Ce	93	49	51	
80%Co/20%Ce	114	90	92	
60%Co/40%Ce	112	46	49	
50%Co/50%Ce	76	40	43	
40%Co/60%Ce	69	43	44	
20%Co/80%Ce	55	48	53	
0%Co/100%Ce	59	30	33	

Table 1. BET Results for the Catalysts with Different Cobalt Cerium Molar Ratios





Fig. 7. Effect of different ageing times on the catalytic performance.



Fig. 8. XRD patterns for the aged catalyst precursors containing 80%Co/20%Ce.

catalysts with the poorest steady-state performance require the longest stabilization period. The variation in catalytic activity is, however, apparent for the ageing time results.

In this study, to examine the effect of ageing on the performance of cobalt cerium oxide catalysts for the hydrogenation of CO, a series of mixed cobalt cerium oxide ([Co]/[Ce] = 4/1) catalysts were prepared with a range of ageing times between 0 h (unaged) to 5 h for the precipitate. The catalysts were calcined at 600 °C for 6 h, and were then tested for hydrogenation of CO. The effect of ageing time on

catalytic performance is shown in Fig. 7. These results show that there is considerable variation in the catalytic performance with respect to ageing time, with the sample aged for 2 h giving the optimal catalytic performance for FTS. Thus, ageing time is a parameter of crucial importance in the preparation of active mixed cobalt cerium catalysts for the hydrogenation of CO. The 80%Co:20%Ce catalyst precursors prepared at different ageing times and their calcined catalysts were identified by XRD and their patterns are presented in Figs. 8 and 9, respectively. The precursors aged between 0 h Preparation and Operating Conditions for Cobalt Cerium Oxide Catalysts



Fig. 9. XRD patterns for the aged calcined catalysts containing 80%Co/20%Ce.

		Specific surface area (m ² /gr)	
Age(h)	Catalyst	Calcined catalyst before	Calcined catalyst after test
	precursor	test	
0	117	88	90
1	141	78	79
2	114	90	92
3	133	76	80
4	120	59	69
5	109	75	76

Table 2. BET Results for the Catalysts with Different Ageing Times

to 3 h were found to be amorphous by XRD (Fig. 8), and the presence of the amorphous phases in the XRD patterns of these precursors makes the other phases undetectable. For the catalyst precursors aged for 4 h and 5 h, phases including $Co(OH)_2$ (hexagonal), $Ce_2O(CO_3)_2.H_2O$, $CeCO_3OH$ (orthorhombic) and $Ce_2(CO_3)_2(OH) \cdot H_2O$ were identified. The XRD patterns for their calcined samples were similar to each other, although the relative diffracted intensities from the

phases were slightly different (Fig. 9). The actual phases identified in these catalysts under the specified preparation conditions were CeO_2 (cubic) and Co_3O_4 (cubic).

Characterization of both precursors and calcined catalysts (before and after the reaction) was carried out using BET surface area measurement and the results are presented in Table 2. Note that the catalyst precursors have higher specific surface areas than their calcined catalysts (before and after the

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Fig. 10. Effect of different calcination conditions on the catalytic performance.



Fig. 11. XRD patterns for the precursor and calcined catalysts containing 80%Co/20%Ce with different calcination conditions.

test). Furthermore, the calcined catalyst aged for 2 h has a higher specific surface area than the other catalysts; again, one reason for the better catalytic performance of this catalyst [31].

Effect of calcination temperature. In this investigation, the calcination temperature was found to have a marked effect on catalyst performance. Two samples were prepared ([Co]/[Ce] = 4/1, ageing time = 2 hr), the first of which was calcined at 700 °C (high temperature) for 5 h and the second

sample at 500 °C (low temperature) for 7 h. These samples were then tested under the same reaction conditions (H₂/CO = 4/1, P = 1 atm, at 450 °C) for the hydrogenation of CO. These results were compared with the previous results of the sample ([Co]/[Ce] = 4/1) that had been calcined at 600 °C (medium temperature) for 6 h and tested for the hydrogenation of CO under the same reaction conditions (H₂/CO = 4/1, P = 1 atm, at 450 °C). The results presented in Fig. 10 show that the

optimum calcination temperature is 600 °C, and at this temperature the selectivity with respect to C_2 - C_4 was higher than that of the other two catalysts calcined at lower and higher temperatures, which showed a high selectivity with respect to methane, an unwanted product in this study.

These samples were characterized by XRD (Fig. 11). The actual phases identified in these catalysts were CeO_2 (cubic) and Co_3O_4 , (cubic) and their precursors were found to be amorphous. Although the phases identified in the calcined catalysts at different temperatures were similar, the relative diffracted intensities of the lines and the presence of sharp reflections in the various patterns of these materials differed to a large degree, indicating the presence of varying amounts of the crystalline phases.

In order to ascertain the origin of the higher catalytic performance at 600 °C, we also characterized these three samples that had been calcined at different temperatures using SEM. The SEM images displayed in Fig. 12 indicate that the catalyst morphology is closely related to the calcination conditions. As shown, the catalyst that was calcined at 600 °C for 6 h (Fig. 12b), has a homogeneous agglomeration with smaller particles, which is associated with the better catalytic performance. The catalysts calcined at low and high temperatures (Figs. 12a and 12c, respectively) have rough and disproportionate agglomerate.

Effect of supports and support loadings. In order to study the effect of different supports, including TiO₂, SiO₂, Al₂O₃, zeolite and magnesium silicate, in the mixed cobalt cerium oxide catalyst, 10 wt% of each support was added separately to a solution containing cobalt and cerium (Co)/[Ce] = 4/1). All of the different supported catalysts were tested for the selectivity of hydrogenation of CO toward C₂-C₄ light olefins under the same reaction conditions ($H_2/CO = 4/1$, P = 1 atm, at 450 °C). The catalytic activity and selectivity of the catalysts containing different supports are shown in Fig. 13. The catalyst supported by SiO_2 is more active than the other supported catalysts, but with a higher selectivity for ethylene than the other olefins, as with all the other supported catalysts. The XRD characterizations of the SiO₂-supported catalyst for both the precursor and the calcined catalyst (before and after the test) are shown in Fig. 14. Its precursor was found to be amorphous and, as previously noted, the presence of an amorphous phase in the XRD pattern of the precursor





Fig. 12. SEM image of the catalyst containing 80%Co/20%Ce with different calcination conditions (a) low calcination conditions, (b) medium calcination conditions and (c) high calcination conditions.





Fig. 13. Effect of different supports on the catalytic performance.



Fig. 14. XRD patterns for the catalyst containing 80%Co/20%Ce/10% SiO₂ at different states (precursor, calcined catalyst before and after the test).

makes the other phases undetectable. However, the calcined catalyst before the test did show the different phases, which were CeO_2 (cubic), Co_3O_4 (cubic), $CoSi_2$ (cubic), SiO_2 (monoclinic), and Co_2SiO_4 (cubic).

In order to identify the changes in calcined catalyst that occurred during the reaction and to detect the phases formed, this catalyst was characterized by XRD after the test, at which point its phases were found to be Co_2SiO_4 (cubic), $CoSi_2$ (cubic), Si (cubic), CeO₂ (cubic), CoO (cubic), Co₂C (orthorombic), Co₃C (orthorombic), Si-O, Ce (cubic), C (hexagonal), Co (hexagonal) and Ce₂C₃ (cubic).

Characterization of this catalyst was also carried out using

BET specific surface area measurement, the data of which are compared with the results of the unsupported catalyst in Table 3. As shown, the supported catalyst has a higher specific surface area than the unsupported catalyst, which may be a reason for the better catalytic performance of the supported catalyst. The results in Table 3 also show that the catalyst precursors have higher specific surface areas than their calcined catalysts (before and after the test) and the tested catalysts have a higher specific surface area than the catalysts before the test.

To understand the influence of SiO₂, as the optimal support material, on the catalytic performance of mixed cobalt cerium

Table 3. BET	Γ Results for	the Supported	Catalyst and	Unsupported	Catalyst

	Specific surface area (m ² /gr)				
Catalyst	Catalyst	Calcined catalyst before	Calcined catalyst after		
	precursor	test	test		
Supported by SiO ₂	132	118	120		
Unsupported	114	90	92		



Fig. 15. Effect of SiO₂ loading on the catalytic performance.

oxide catalysts, a series of 80%Co:20%Ce catalysts were prepared with SiO₂ loadings of 10, 15, 20 and 25 wt% based on the total catalyst weight. The changes in catalytic performance become more apparent when considering catalysts prepared with different amounts of SiO₂ as supports, as shown in Fig. 15. The catalyst loaded with 15 wt% SiO₂ showed the optimal catalytic performance.

A detailed SEM study of the precursor, calcined and tested catalysts containing 15 wt% SiO₂ was also carried out (Fig. 16), which shows major differences in their morphology. Note that the addition of SiO₂ as a catalyst support slightly increases the particle size and the supported catalyst is structurally different, probably due to the presence of SiO₂. This catalyst is comprised of large grains embedded in a mixture of small grains (Fig. 16b). A previous report states that the catalyst surface is covered with white crystallites of cobalt oxide, Co_3O_4 [44]; however, after the test, the size of these grains are

larger due to agglomeration (Fig. 16c), which may be due to the sintering after the reaction. This observation is in agreement with Galarrage *et al.* [44], who indicate that high temperature could cause agglomeration of these small grains, which correlates with catalyst deactivation under high temperature. The agglomeration is also caused by the lack of homogeneous distribution of the metal precursor (Fig. 16a).

Effect of promoters. To determine the utility of promoters on the catalytic performance of mixed cobalt cerium oxide catalysts, a small amount (1.5 wt%) of the alkali metal promoters, LiNO₃, KNO₃, RbCl and Mg(NO₃)₂'6H₂O, were separately introduced to the resulting suspension containing 80% Co, 20%Ce and 15 wt% SiO₂. Then, all of these different promoted catalysts were tested under the same reaction conditions (H₂/CO = 4/1, P = 1 atm, at 450 °C) for activity and selectivity toward the production of light olefins (Fig. 17). A comparison of Figs. 15 and 17 leads to the conclusion that the

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Fig. 16 . SEM images of the catalyst containing optimum amount of SiO_2 support in (a) precursor, (b) catalyst before the test and (c) catalyst after the test.

unpromoted catalyst (80%Co:20%Ce, 15 wt% SiO₂) is more active than the promoted catalysts and the selectivity with respect to C₂-C₄ light olefins actually decreases in presence of promoters. Thus, taking these results into consideration, the catalyst containing 80% Co, 20% Ce and 15wt% SiO₂ without any promoter and aged for 2 h, appears to be the optimum modified catalyst for the conversion of synthesis gas to C₂-C₄ light olefins.

Effect of FTS Reaction Conditions

Another category of factors with a marked effect on catalytic performance is the operating conditions, among which the effect of H_2/CO feed molar ratios and reaction temperatures were examined in this study.

Effect of H₂/CO molar feed ratio. The influence of the reaction H₂/CO molar feed ratio on the steady state catalytic performance of the cobalt cerium oxide catalyst containing 80% Co, 20% Ce and 15 wt% SiO $_2$ for the Fischer-Tropsch reaction at 450 °C under atmospheric pressure was investigated and the results are presented in Fig. 18. H₂/CO feed ratios from 1/1 through 4/1 gave different selectivities of light olefins; however, at a H₂/CO ratio of 2/1, the total yield of light olefins products was higher than that at the other H₂/CO feed ratios at the same temperature and pressure. It is also apparent that, using the 2/1 H₂/CO molar feed ratio, the catalyst has the highest selectivity toward ethylene. Therefore, 2/1 was chosen as the optimum feed ratio for converting synthesis gas to C₂-C₄ light olefins using the cobalt cerium catalyst. The actual phases identified in the catalyst at the 2/1 feed ratio after the test were CoSi₂ (cubic), Si (cubic), CeO₂ (cubic), CoO (cubic), C (hexagonal), Co₃C (orthorhombic), SiO, Ce (cubic), Co (hexagonal) and Ce₂C₃ (cubic). As shown, the tested catalyst has oxidic and cobalt carbide phases, both of which are active phases in the catalyst. Oxidic phases are highly selective for the preparation of olefins, and carbide phases are active in the hydrogenation of CO [45,46]. It should be mentioned here that all the tested catalysts are mixed with coke, which accounts for the noise in all the XRD patterns.

Effect of reaction temperature. The effect of reaction temperature, ranging from 300-500 °C, on the performance of the catalyst (80%Co:20%Ce, 15 wt% SiO₂) was studied (Fig. 19; P = 1 atm, H₂/CO = 2/1 and GHSV = 4500 h⁻¹). According to the obtained results, the optimum reaction temperature was



Fig. 17. Effect of different promoters on the catalytic performance.



Fig. 18. Effect of different H₂/CO feed ratios on the catalytic performance.

450 °C, at which temperature the total yield of light olefins was higher than those at the other reaction temperatures under the same operating conditions. In general, an increase in the reaction temperature leads to an increase in the catalytic performance; however, it was also shown that the reactor temperature should not be too low. At low reaction temperatures, the conversion percentage of CO is low, giving a high level of methane production. On the other hand, we found that an increase in the reaction temperature leads to the formation of large amounts of coke, an unwanted by-product. The actual phases identified in the catalyst, after testing at the optimum operating temperature of 450 °C, were $CoSi_2$ (cubic), Si (cubic), CeO₂ (cubic), CoO (cubic), C (hexagonal), Co₃C (orthorhombic), SiO, Ce (cubic) and Co (hexagonal), Ce₂C₃ (cubic).

CONCLUSIONS

Many variables in the preparation of the catalyst during the co-precipitation procedure and the subsequent calcination step

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Fig. 19. Effect of different reaction temperatures on the catalytic performance.

are important in controlling the performance of cobalt cerium mixed oxide catalysts for conversion of synthesis gas to light olefins. In this study, we varied the ageing time, temperature of calcination and [Co]/[Ce] ratio in the precipitation liquor. The optimum catalyst has a molar [Co]:[Ce] ratio of 80%Co:20%Ce and is supported by 15 wt% SiO₂ based on the total catalyst weight, aged for 2 h and calcined at 600 °C for 6 h. The optimum operating conditions were found to be 450 °C with molar feed ratio of $H_2/CO = 2/1$ (GHSV = 4500 h⁻¹) under atmospheric pressure. The characterization of both precursors and calcined catalysts by powder XRD, SEM, BET specific surface area and thermal analysis (TGA/DSC) methods, showed that the catalyst precursors are sensitive to preparation conditions. Ageing time, calcination the temperature and cobalt cerium molar ratios of the precipitate were shown to be important factors influencing the structure of the precursors and calcined catalysts. These parameters should be incorporated into the design of experimental programs involving precipitation as the method of catalyst preparation.

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