

Acidity effects of K promoted Co-based catalyst with NH₄OH addition of the impregnation solution for Fischer-Tropsch synthesis

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Abstract. Fischer-Tropsch synthesis (FTS) with cobalt-based catalyst has been developed to produce wax as a feedstock for further catalytic cracking. During catalyst preparation, NH₄OH was added to the salt nitrate precursor to investigate the influence on catalyst acidity. Catalysts were prepared by the dry impregnation method and characterized by XRD, BET and NH₃-TPD analyses. These properties were correlated with activity and selectivity of the catalyst. Activity tests showed CO and H₂ conversion were in the range of 36.4% to 80.3% and 34.2% to 74.1% respectively. The cobalt particle size measurements exhibited 7.6-8.5 nm. The presence of weak acid sites on catalyst with large surface area and pore size is mainly responsible for obtaining high yields of C₅₊ hydrocarbon due to suppression of cracking properties. The product distribution showed a higher selectivity to C₅₊ in the range of 53.57% to 96.5%. In this study, FTS was evaluated by using fixed-bed reactor at 20 bar, 250 C, and WHSV of 1500 ml/g.cat/h-1.

1 Introduction

Production of synthetic fuel from natural gas, coal, or biomass by means Fischer-Tropsch synthesis (FTS) has regained interest as the worldwide reserves of crude oil are being depleted [1]. However, since FTS process found to yield a wide-range of hydrocarbon distribution, an intensive effort needs to be made in narrowing its distribution range. By using supported cobalt (Co) catalyst, the product selectivity may be directed towards long chain hydrocarbon (C₅₊) for further cracking [2]. Some of the problems encountered in this catalyst are related to the reducibility-activity and product selectivity enhancement problems.

The reducibility-activity problems can be overcome through the selection of suitable support with proper physicochemical properties [3]. Large pore size of the support often generates large Co particle size, which possess high reducibility, since it often exist as Co₃O₄ crystalline phase (fractions of cobalt which is easily reduced) [4]. Catita [5] reported that ease of reduction and good activity often observed in the Co particle size above 8 nm.

Alumina is known as one the most widely used catalyst support material and controlling the surface acid-base properties of γ -Al₂O₃ is a fundamental aspect for the active cobalt-based catalyst in FTS [6]. Iglesia et al., [7] reported that cobalt catalyst on non-acidic support enhances the formation of α -olefins and n-paraffins, led to the optimal formation of C₅₊ on large pore diameter. Many literatures [8-9] also have been reported on by using NH₄OH and NH₄NO₃ to pre-treat the γ -Al₂O₃ support, the pore size would expand, the acid amount

would decrease and the activity and selectivity for C₅₊ formation increased. This pretreatment method could be adopted and modify to alter the physicochemical properties of support as a template to generate desired cobalt particle size with desired level of surface acidity. In addition, the surface acidity of cobalt catalyst also depends upon the concentration of hydroxyl groups on the support surface, which will further affect on the cobalt dispersion [10]. Thus, changes in pH of the impregnation solution could become an effective way to change the surface acidity, influence the cobalt dispersion and attain the reducibility of cobalt oxide.

Promoter addition could be used to solve an activity and selectivity problems. Promotion with K enhances the olefin content as these promoters are used to promote the Fischer-Tropsch Fe-based catalyst [11]. Based on above studying literature, this study investigated the influence of the NH₄OH addition, as replacement of the impregnation solvent on the acidity of K promoted Co based catalyst for the catalytic performance and the synthesis of long chain hydrocarbon.

2 Materials and methods

2.1 Materials and reagents

Cobalt nitrate (Co(NO₃)₂·6H₂O, MerckTM) and Potassium nitrate (KNO₃, MerckTM) is used as precursors for the active phase and promoters. Commercially γ -Al₂O₃ (with an average pore size of 6.5 nm, surface area of 217.3 m²/gr, and pore volume of 0.46 cc/g) is used as the support. Aqueous ammonia (NH₄OH, MerckTM) is

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used as an impregnation solution. Syngas with the composition of N₂ 10,2%, CO 31,1%, and H₂ 58,7% from MESA Int. Tech is used as a feed for an activity test.

2.2 Catalyst synthesis

A series of modified-potassium promoted-15% w/w cobalt-based catalyst was prepared by conventional incipient-wetness co-impregnation method by changing the impregnation solution of deionized water with the aqueous ammonia solution of required composition. To obtain the desired cobalt loading, a two step impregnation method was used with drying at 110 °C and calcining at 350 °C, following each impregnation. For each catalyst, the impregnation was carried out by adding dissolved nitrate salt precursor in aqueous ammonia solution to the alumina support and stirring the slurry continuously for 30 minutes at room temperature. After impregnation, the sample was dried for 2 h and calcined for 6 h. The prepared catalyst composition were listed in **Table 1**.

2.3 Catalyst testing

The catalyst pellets (about 1 g) was crushed and sieved (40/60 mesh) then charged into a stainless steel tubular fixed-bed reactor (O.D. = 20 mm). A Thermocouple was placed at the top of the catalyst bed to assure precise temperature control. Before catalytic testing, the catalyst was reduced by H₂ at a flow rate of 90 NTP ml/min at 400 °C and 5 Bar for 6 h, then cooled down to reaction temperature of 250 °C in flowing H₂. During testing, the pressure of reacting system was set to 20 Bar and the syngas feed (molar ratio of H₂/CO = 2 : 1) with a flow rate of 25 ml/min was passed over the catalyst. About 10 %N₂ was added to the syngas as an internal standard to allow an accurate mass-balance. The duration of each test was lasted for a period of 12 h or so to ensure the reaction was stable. All the catalyst samples were tested at the same level operating condition. Conversion of CO was calculated by gas chromatography (GC) analysis of gaseous feed and effluent taken every 1 h from the inlet and outlet reactor. Gas chromatography for gas analysis are equipped with a molsieve packed column and Thermal Conductivity Detector (TCD) detector. The liquid and wax product was collected in the trap, taken at the end of the reaction, and analyzed using a GC equipped with an Rtx-1 packed column and Flame Ionization Detector (FID) detector.

2.4 Catalyst characterization

The physical properties of samples (BET surface area, average pore diameter, and pore volume) were determined by N₂ physisorption at 77 K using NOVA 3200e instrument. Crystalline phase of the oxidized catalysts active phase was measured by X-ray diffraction (XRD) in a Bruker 8D Advance diffractometer using

monochromatic Cu-K α radiation, the 2 θ range from 20 to 90° was examined. According to the Scherrer equation the average size of the Co₃O₄ crystallites of the samples was determined by the line width of the most intense reflection at 2 θ = 36.9°, referring to its [311] crystal face. The obtained particle size of Co₃O₄ could be used to calculate that of metallic cobalt particle size by using Schancke equation. The catalyst surface acidity was examined by Temperature Programmed Desorption (NH₃-TPD) using Micrometrics Auto Chem II 2920 apparatus, which incorporates a TCD that measured the amount chemisorbed ammonia. Relative acidity (L_{Cat}/L_{Co-0}) was measured by comparing the area percent of catalyst sample and divide it by the area percent of catalyst reference (Co).

3 Results and discussion

3.1 Physical properties of modified catalyst

The physical properties of modified catalyst are summarized in **Table 1**. The support γ -Al₂O₃ shows an average pore diameter about 8.4 nm with BET surface area of 227.3 m²/g. After impregnation of the cobalt species on the support (Co/Al₂O₃ or Co catalyst), all of the physical parameters (the BET surface area, pore diameter, and pore volume) were decreased, suggests that pore filling mechanism has occurred. Further modification, either by increase the NH₄OH concentration at fixed K loading or by increase the loading of K promoter at a fixed NH₄OH concentration shows an increased in the surface area, and pore diameter as compared with those of Co catalyst. The most probable interpretation of this phenomenon is related to the external pore formation. As more K loading or NH₄OH concentration increased, only the surface area that changes. It therefore appears that the effects of K promoter combined with the effects of NH₄OH as replacement of impregnation solvent bring about the change on the classic behavior expected for an impregnation mechanism.

3.2 Cobalt Particle Size of Modified Catalyst by XRD

From XRD patterns of catalysts shown in Fig. 1, only peak assigned to Co₃O₄ and Al₂O₃ were observed, no diffraction peak of CoO, Cobalt aluminate or other Co species were found. Other species such as K₂O, originate from the addition of promoters was also not detected. All XRD patterns look similar, the only difference is in the intensity of the peak. The strongest diffraction peak of Co₃O₄ was at 2 θ = 36.9°, which was corresponding to the [311] crystal phase of Co₃O₄ crystalline phase [12]. This diffraction peak is used to calculate the particle size of Co₃O₄ with the help of Debye-Scherrer equation, while the particle size of Co, is estimated using Schancke equation with consideration of changes in molar volume occurring during Co₃O₄

Table 1. The nomenclature and physical properties of the prepared catalyst composition

Catalysts	Loading			pH	BET surface area (m ² /g)	Pore diameter (cm ³ /g)	Pore volume (cm ³ /g)	XRD cobalt particle size (nm)
	Co (%w/w)	K (%w/w)	NH ₄ OH (%v/v)					
γ-Al ₂ O ₃	-	-	-	-	227.3	8.4	0.46	-
Co	15	-	-	4.02	153.0	6.1	0.38	10.2
Co-0.5K/0.035IB	15	0.5	0.035	-	171.8	8.1	0.35	10.2
Co-1K/0.035IB	15	1	0.035	4.66	176.5	8.2	0.36	8.5
Co-1.5K/0.035IB	15	1.5	0.035	-	165.5	8	0.33	8.3
Co-1K/1IB	15	1	1	5.03	-	-	-	8.2
Co-1K/2.5IB	15	1	2.5	5.38	169.4	8	0.34	7.6

transition to Co⁰. The results of the cobalt particle size calculation are given in **Table 1**. It shows that the average cobalt particle size obtained is in the range of 7.6-10 nm, there is only one catalyst sample (Co-1K/2.5IB) which has a cobalt particle size around 7.6 nm. According to [5], the range around 8-10 nm is within the range that is indicated will bring the positive synergy on catalytic activity.

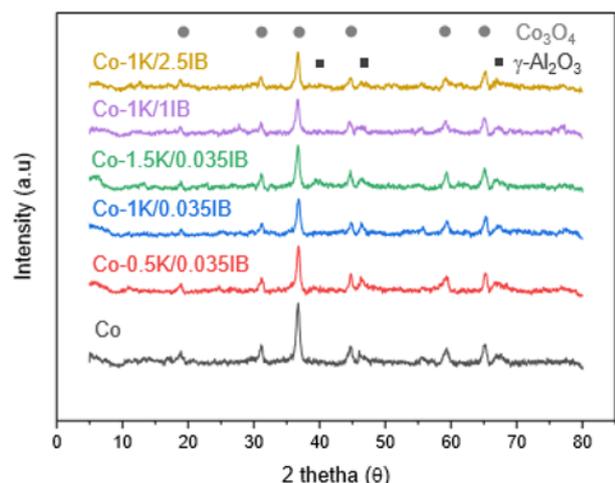


Figure 1. X-ray diffraction pattern of the modified catalyst.

3.3 Surface acidity of modified catalyst

The surface acidity of catalyst was examined by NH₃-TPD, the results were shown in **Fig. 2**. There are two desorption peak observed, the low temperature is assigned to weak acidic sites (below 300 °C) and the high temperature (above 400 °C) to strong acidic sites. The catalytic performance of the catalyst, especially the product distribution is possibly influenced by surface acidity properties as a result of suppression of cracking properties. It was observed that almost all of the surface acidity of prepared catalysts are expected to have a beneficial effects on activity since there are an increase in the peak area and also shifts in both desorption peak to the lower temperature. According to [13] the weak acidic sites are responsible for FTS reaction and product distribution while the strong acidic sites, even are still on debate, is mainly contributed to dehydration of hydroxyl groups on surfaces. From **Fig. 3**, it was shown that, compared with those of Co catalyst, further modification by increase the NH₄OH concentration at fixed K loading, shows an increase the relative acidity. Meanwhile, modification by increase the loading of K

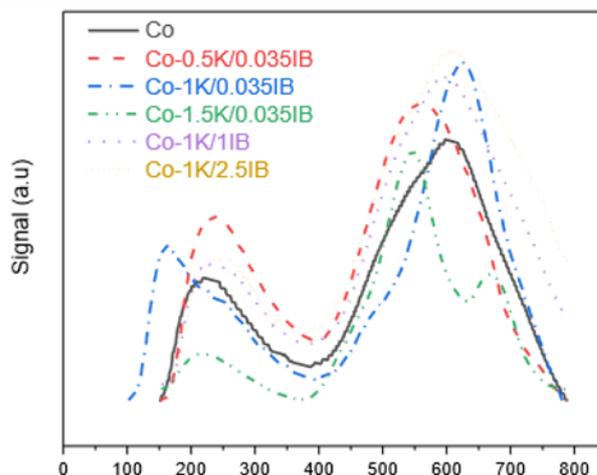


Figure 2. NH₃-TPD profile of the modified catalyst.

promoter at a fixed NH₄OH concentration shows a decrease in relative acidity. The adjustment of surface acidity to the lower extent resulted in lowering the interaction between cobalt species and the supports, improved the reducibility, thus improved the activity and the selectivity for heavy hydrocarbon [9].

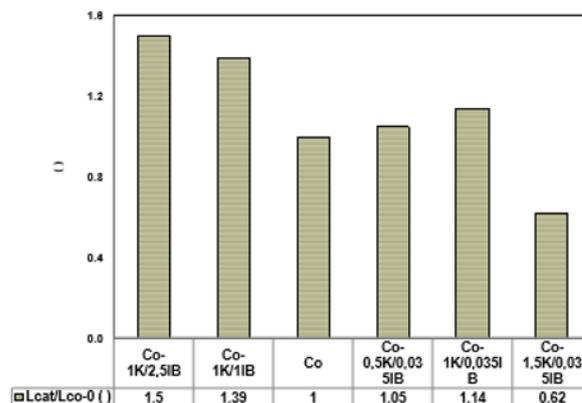


Figure 3. Relative acidity of the modified catalyst

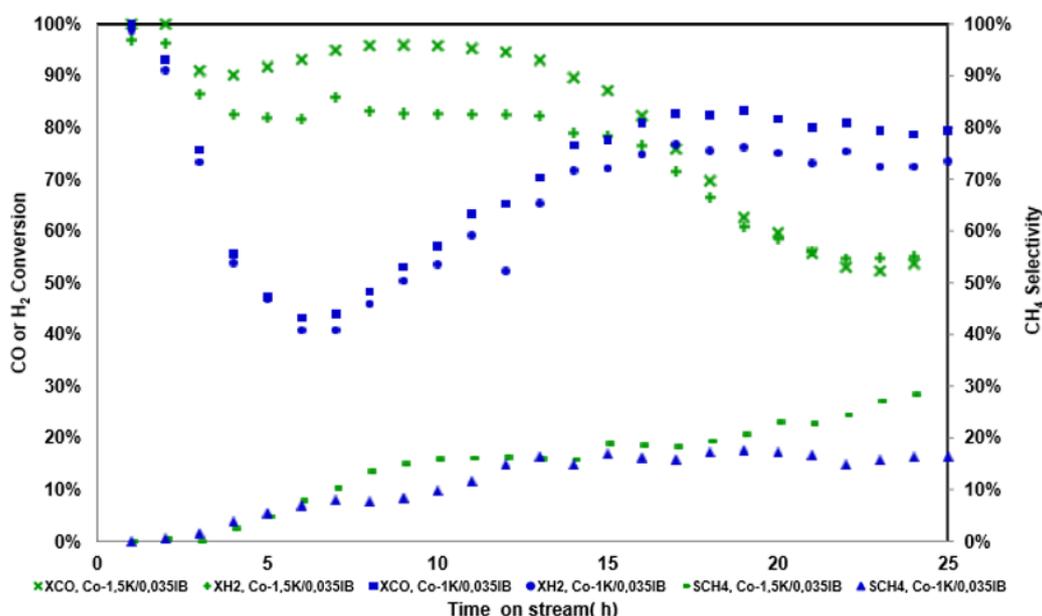


Figure 4. Catalytic test of Co-1K/0,035IB and Co-1,5K/0,035IB at, 20 bars, 250 C, WHSV of 1500 ml/g.cat/h⁻¹ and H₂/CO 2:1

Table 2. Summary of reaction results on the modified catalyst

Catalyst	Conversion (%)		Alpha (α)	Selectivity (%)			Yield (%)			
	XCO	XH ₂		SC ₁	SC ₂₋₄	SC ₅₊	YC ₁	YC ₂₋₄	YC ₅₊	Y _{Gas}
Co	36.4	34.2	0.84	8.8	37.7	53.5	3.22	13.74	19.47	16.96
Co-0,5K/0,035IB	54.5	53.3	0.85	2.2	14.1	83.7	1.21	7.67	45.66	8.88
Co-1K/0,035IB	80.3	74.1	0.94	0.4	3.1	96.5	0.33	2.50	77.47	2.83
Co-1,5K/0,035IB	56.4	54.0	0.90	0.9	6.7	92.4	0.53	3.78	52.09	4.31
Co-1K/1IB	63.2	62.2	0.88	1.7	11.4	86.9	1.07	7.21	54.92	8.28
Co-1K/2,5IB	49.2	49.7	0.87	1.7	11.5	86.8	0.84	5.66	42.71	6.50

3.4 Surface acidity of modified catalyst

The results of catalytic test can be seen from the data presented in **Table 2.**, while conversion and selectivity profile of CO, H₂ and CH₄ respectively, with time on stream for catalyst Co-1K/0,035IB and Co-1.5K/0,035IB were shown in **Fig. 4.** Compared with those of Co catalyst, all modifications increases the CO conversion and the selectivity of C₅₊. Further modification by increasing the NH₄OH concentration at fixed K loading, decrease the activity and C₅₊ selectivity. This decrease in catalytic activity could be explained by the more NH₄OH added, the more Co(OH)₂ precipitate is formed. The amount of cobalt used in the formation of a precipitate, will compete with cobalt required for the loading of the active phase. Thus, it will affect on the size of the particle of cobalt (The cobalt particle size of Co-1K/2.5IB catalyst around 7.6 nm) which led to the decrease of reducibility, and eventually led to the decrease in catalytic activity.

Meanwhile, for catalyst with modification of K promoter at fixed NH₄OH concentrations as shown in **Fig. 4.**, increase the K loading (Co-1.5K/0.035IB) show higher initial activity than on Co-1K/0.035IB, but the decrease in catalytic activity is also faster as can be seen from the conversion profile. At first, catalyst Co-1.5K/0.035IB is thought to be very fast in achieving the

steady-state condition with high CO and H₂ conversion. However, after the 14th h, suddenly a significant decrease in conversion accompanied by an increase in CH₄ selectivity was observed. This decrease in catalytic activity could be explained by the presence of high molecular mass waxes formed and clogged on the catalyst pores. When wax deposition occurs, the catalyst pore will be filled with wax. As a result, access to the active site will be blocked, so the conversion will decrease. CO gas has a much larger size and molecular mass when compared to H₂ gas. This will affect the diffusivity of the two gases to the active site. The diffusivity of H₂ gas will be much better when compared to CO gas. As a result, the H₂ conversion will much higher compared that of CO. If there is more H₂ on the catalyst surface than CO, then over-hydrogenation will occur and that CH₄ selectivity rises.

4 Conclusion

The NH₄OH addition, as an impregnation solution replacement influences the physicochemical and catalytic properties of cobalt catalyst during the FTS reaction, especially the acidity of the catalyst surface. The size of cobalt particle and their distribution also plays an important role to enhance the CO conversion and product distribution. Relative acidity was obtained to

the different results according to the extent of the modification. The modification with slightly low NH₄OH concentration offers higher CO conversion with slightly higher in relative acidity. While the modification with K promoter offers higher C₅+ selectivity with lower relative acidity. The presence of temperature shifts at

peaks of acidic sites to the lower temperatures on the catalyst with cobalt particle size above 8 nm is mainly responsible for showing a high catalytic performance due to the high reducibility of cobalt particles.

This research was financially supported by P3MI ITB.

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