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CoMn Catalysts Derived from Hydrotalcite-Like Precursors for Direct Conversion of Syngas to Fuel Range Hydrocarbons

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Abstract: Two different groups of CoMn catalysts derived from hydrotalcite-like precursors were prepared through the co-precipitation method, and their performance in the direct production of gasoline and jet fuel range hydrocarbons through Fischer–Tropsch (FT) synthesis was evaluated in a batch autoclave reactor at 240 °C and 7 MPa and H₂/CO of 2. The physicochemical properties of the prepared catalysts were investigated and characterized using different characterization techniques. Catalyst performance was significantly affected by the catalyst preparation method. The crystalline phase of the catalyst prepared using KOH contained Co₃O₄ and some Co₂MnO_{4.5} spinels, with a lower reducibility and catalytic activity than cobalt oxide. The available cobalt active sites are responsible for the chain growth, and the accessible acid sites are responsible for the cracking and isomerization. The catalysts prepared using KOH + K₂CO₃ mixture as a precipitant agent exhibited a high selectivity of 51–61% for gasoline (C₅–C₁₀) and 30–50% for jet fuel (C₈–C₁₆) range hydrocarbons compared with catalysts precipitated by KOH. The CoMn-HTC-III catalyst with the highest number of available acid sites showed the highest selectivity to C₅–C₁₀ hydrocarbons, which demonstrates that a high Brønsted acidity leads to the high degree of cracking of FT products. The CO conversion did not significantly change, and it was around 35–39% for all catalysts. Owing to the poor activity in the water-gas shift reaction, CO₂ formation was less than 2% in all the catalysts.

Keywords: Fischer-Tropsch; jet fuel; gasoline; CoMn; hydrotalcite-like precursors

1. Introduction

The impending depletion of fossil fuel sources and the growing demand for energy resources because of increasing population and economic development have led to new approaches to the production of renewable liquid fuels. X-to-liquid technologies for converting different carbon-containing sources, such as natural gas (GTL), coal (CTL), biomass (BTL), and waste/oil residues (WTL), to liquid fuels have received special attention [1]. Typical transformation processes for the conversion of non-petroleum carbon resources into liquid fuel are shown in Figure 1. Carbonaceous resources are transformed into syngas (H₂ + CO) through reforming, gasification, or partial oxidation and then converted to a wide range of hydrocarbons. These hydrocarbons are refined to produce final products, including liquefied petroleum gas, gasoline, jet fuel, distillate, diesel, and wax [2]. Fischer–Tropsch (FT) is a well-known process for the catalytic conversion of syngas into higher hydrocarbons and oxygenates, which are finally upgraded to sulfur and aromatic free transportation fuels and chemicals [3–7]. The FT process plays an essential role in the production of sustainable and clean liquid fuels through CO hydrogenation. The product distribution of the traditional FT process follows the Anderson-Schulz-Flory (ASF) law and can be determined using the value of chain growth probability.

However, controlling product selectivity for the production of specific hydrocarbons, such as gasoline (C_5 – C_{10}), diesel fuel (C_{11} – C_{22}), or jet fuel (C_8 – C_{16}), is extremely challenging [8,9]. Several researchers have reported efficient methods for directly synthesizing gasoline, diesel, and jet fuel [8,10–13]. The direct conversion of syngas to liquid fuels through the FT process reduces the demand for refining units, such as hydrocrackers, by increasing the product selectivity of desired liquid hydrocarbons. Different parameters, such as the active phase of the catalyst and its chemical state, physicochemical properties, support, and promoter, considerably influence the catalytic activity and product selectivity in the FT reaction. Therefore, developing selective catalysts for the direct production of targeted products through the FT process has attracted considerable attention from scientists.

Figure 1. Transformation of carbonaceous resources (natural gas, biomass, and coal) into liquid fuels.

Cobalt-based catalysts with high selectivities to long-chain hydrocarbons, including diesel fuel and wax, are used more often than iron-based catalysts, which are suitable for gasoline production. Promoters can promote the reduction of cobalt oxide to its active metal phase and improve the catalyst's lifetime and mechanical stability by inhibiting carbon deposition on active Co^0 and decreasing Co sintering [14]. The 25% Co/Al_2O_3 catalysts promoted by Pt have been used as an active catalyst for the production of aviation fuel in a continuous stirred tank reactor (CSTR) at 1.8 MPa and 220 °C [15], and a CO conversion rate of approximately 30% and selectivity of 28%, 17%, and 40% to C_5 – C_{11} , C_{12} – C_{18} , and C_{19+} , respectively, was observed. In another study, a Co/ZrO_2 - SiO_2 catalyst prepared through the incipient wetness impregnation method and its catalytic performance in the direct synthesis of jet fuel from syngas in a slurry phase reactor was investigated by Li et al. [8]. A C_8 – C_{16} selectivity of 29% was obtained at 1 MPa and 240 °C. However, the addition of a co-fed additive of syngas containing 1-decene and 1-tetradecene (1:1) resulted in a significant increase in selectivity. The addition of Mn to Co/TiO_2 catalysts increases C_{5+} selectivity (from 30.9% to 43.5%) and decreases methane selectivity (from 32.7% to 22.3%) [16]. Co–Mn interactions in catalysts prepared through homogeneous deposition precipitation (HDP) decrease the Co reducibility. The decrease in reducibility did not affect catalyst activity; rather, it improved selectivity to higher hydrocarbons (C_{5+}). The addition of Mn to Co catalysts prepared through an impregnation method did not cause changes in reduction temperature, probably because of the absence of interactions between Mn and Co in these catalysts [16].

Hydrotalcite-like compounds (HTCs) comprise atomically dispersed mixed metals and are excellent precursors and/or catalyst supports [17–19]. HTCs are brucite-like layer materials with

a general formula of $(M_{1-x}^{2+}M_x^{3+}(OH)_2)^{x+}(A_{x/n}^{n-})^{x-}\cdot mH_2O$, where partial metal cation M^{2+}/M^{3+} replacement occurs and the excess of positive charge is counterbalanced by anions A^{n-} (such as CO_3^{2-} , SO_4^{2-} , NO_3^- , or other organic anions such as terephthalate) existing in interlayers, together with water molecules, and $x = M^{3+}/(M^{2+} + M^{3+})$, which generally ranges from 0.2 to 0.33, is the surface charge determined by the ratio of two metal cations; it can be changed for different applications [20,21]. HTC can be synthesized as catalyst precursors with divalent metal cations (M^{2+}) (e.g., Mg^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , or Zn^{2+}) and trivalent cations (M^{3+}) (e.g., Mn^{3+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Rh^{3+} , Ru^{3+} , Ga^{3+} or In^{3+}). The calcination of HTCs leads to their transformation into well-dispersed mixed metal oxides (MMOs) with high surface areas, numerous Lewis base sites, and good thermal stability against sintering. These features are highly suitable for catalysis applications. The formation of $O^{2-}-M^{n+}$ acid-base pairs is associated with the types of acidic-basic sites. The Lewis acidity is associated with the presence of low-coordination O^2 species that closely interact with M^{3+} cations, and Lewis basicity is due to M^{2+} cations [22,23]. The nature and strength of the acidic-basic sites of hydrotalcite-like compounds can be adjusted by adjusting the following parameters: (1) the nature of substituting cations in hydrotalcite structures; (2) characteristic M^{2+}/M^{3+} molar ratio; (3) nature of anions presented in interlayer regions; (4) thermal activation of layered materials; for example, a higher calcination temperature is favored for the creation of Lewis basic sites) [22,23].

The reduction of HTCs can be eminently suitable for the formation of highly dispersed and well-supported metallic particles [17–21,24–26]. Hydrotalcite-derived mixed oxides have been used as a catalyst in different catalytic reactions, such as steam reforming of ethanol [20,27,28], CO_2 hydrogenation to methanol [29,30], CO_2 reforming of methane for syngas production [31–33], formation of alcohols from syngas [19,34,35], and hydrocarbon production through FT reaction [36]. In the present study, CoMn catalysts derived from hydrotalcite-like precursors, with a Co/Mn molar ratio of 2, were synthesized using different preparation methods, and their catalytic activities in the FT reaction were evaluated. The physicochemical properties of the catalysts were characterized through thermogravimetric analysis (TG), inductively coupled plasma (ICP), scanning electron microscopy (SEM), hydrogen temperature-programmed reduction (H_2 -TPR), ammonia temperature-programmed desorption (NH_3 -TPD), and X-ray diffraction (XRD), and the effects of different preparation methods on the structures and catalytic performance of the catalysts were investigated.

2. Results and Discussion

2.1. Characterization of Catalysts

The inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis was performed to determine the chemical composition of the prepared catalysts, and the results are listed in Table 1. The Co/Mn molar ratios calculated from the ICP analysis are close to the theoretical value (Co/Mn = 2), indicating the complete precipitation of metal ions. The thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) curves for the CoMn catalysts derived from hydrotalcite-like precursors (CoMn-HTC catalysts) (Figure 2) exhibited several phases of weight loss because of the thermal decomposition of catalysts, and the same behavior was observed in the DTG curves. The peaks at 100–260 °C were attributed to the evaporation of physically adsorbed water and interpolated water molecules associated with the dried samples. This result is in good agreement with the mass spectroscopy results, showing that water was released at this temperature range, and weight loss mainly occurred at this range. The weak peak observed at higher temperatures was caused by the elimination of hydroxyl and carbonate anions from the interlayer space, along with interlayer water. Weight loss in the catalysts precipitated with KOH (group 2) was lower than that in the catalysts prepared using a mixture of KOH + K_2CO_3 as a precipitating agent. Compared with the other catalysts in each group, the catalysts prepared with the addition of H_2O_2 had a lower weight loss than the other catalysts. The peaks for released CO_2 were observed at around 280 °C and 240 °C for catalysts I and II, and no apparent peaks were observed for the other catalysts. The amount of released CO_2 is much

lower than that of released water. The low amount of released CO₂ may be due to the adsorption of CO₂ from air during the measurement.

Table 1. Inductively coupled plasma (ICP) analysis of the CoMn-HTC catalysts.

Samples	Concentration (wt.%)		Concentration (mol%)		Molar Ratio
	Co	Mn	Co	Mn	
CoMn-HTC-I.	41.3	14.7	0.70	0.27	2.62
CoMn-HTC-II.	41.0	15.2	0.70	0.28	2.51
CoMn-HTC-III.	42.3	19.5	0.72	0.35	2.02
CoMn-HTC-IV.	44.1	18.6	0.75	0.34	2.21
CoMn-HTC-V.	41.2	16.6	0.70	0.30	2.31
CoMn-HTC-VI.	43.3	18.6	0.73	0.34	2.17

Figure 2. Thermogravimetric analysis and mass spectrometry detector (TGA-MS) analysis of the CoMn-HTC catalysts.

The reducibility of CoMn-HTC catalysts was analyzed through hydrogen temperature-programmed reduction (H₂-TPR) analysis (Figure 3). The TPR profiles revealed two regions of low-temperature range at 180–450 °C and high-temperature range at 450–730 °C. The first weak peak in the range of 199–237 °C was ascribed to the partial reduction of easily reducible species of CoMn composite oxide:

Figure 3. Hydrogen temperature-programmed reduction (H_2 -TPR) profiles of the CoMn-HTC catalysts.

The second peak at 300–380 °C was attributed to the further reduction of Mn_3O_4 to MnO and Co_3O_4 to CoO:

The peaks at high temperature (>450 °C) were ascribed to the reduction of CoO to Co and Mn_3O_4 to MnO:

Compared with the TPR peaks of the catalysts prepared by KOH as the precipitating agent, the TPR peaks for the catalysts prepared by the mixture of KOH + K_2CO_3 as the precipitating agent shifted to lower temperatures. Precipitation in the presence of air did not cause a considerable change in catalyst II compared with catalyst I, while the peaks of catalysts V shifted to lower temperatures than those of catalyst IV. In CoMn-HTC III (from group 1) and CoMn-HTC VI (from group 2) catalysts (catalysts prepared with the addition of H_2O_2), all peaks shifted to lower temperatures compared with the catalysts of each group prepared without the addition of air or H_2O_2 . The different TPR profiles of CoMn-HTC catalysts could be due to the different Mn and Co species interactions, which are related to the preparation methods. The CoMn-HTC III catalyst had the lowest reduction temperatures. Thus, the preparation of catalysts precipitated by the mixture of KOH + K_2CO_3 in the presence of H_2O_2 enhanced the catalyst reducibility. Jung et al. [37] studied the effect of precipitants on nickel-based catalysts prepared through the co-precipitation method, and it was found that the catalysts prepared with K_2CO_3 as the precipitating agent had lower reduction temperatures and a higher hydrogen uptake than those precipitated with KOH. The catalyst prepared with K_2CO_3 also exhibited high pore volume and good catalytic activity for methane steam reforming [37].

The acidic properties of the prepared catalysts were determined through ammonia temperature-programmed desorption (NH_3 -TPD) analysis (Figure 4). The peaks at low temperatures, below 200 °C, were attributed to weak acid sites or physically adsorbed ammonia, and the peaks at higher temperatures in the range of 200–400 °C, were associated with the medium interaction between Brønsted acid sites and NH_3 . The peaks at temperatures above 400 °C belong to strong acid

sites [38–40]. Table 2 shows the concentration of both weak and medium acid sites ($\text{mmol NH}_3/\text{g}_{\text{cat}}$) of the catalysts. The acid sites (weak and medium acid sites) decreased, and the peaks shifted to higher temperatures in the catalysts prepared with KOH. Medium acid sites increased in both catalyst groups (precipitated by a mixture of $\text{KOH} + \text{K}_2\text{CO}_3$, and KOH) when they were precipitated by the addition of H_2O_2 to enhance the oxidation of metals.

Figure 4. Ammonia temperature-programmed desorption (NH_3 -TPD) profiles of the CoMn-HTC catalysts.

Table 2. Surface acidity of CoMn catalysts measured by ammonia temperature-programmed desorption (NH_3 -TPD).

Catalyst	Acidic Site ($\text{mmol NH}_3/\text{g}$)		
	First Peak	Second Peak	Total
CoMn-HTC-I	0.172	0.276	0.448
CoMn-HTC-II	0.147	0.201	0.348
CoMn-HTC-III	0.184	0.353	0.537
Co-Mn-HTC-IV	0.212	0.104	0.316
CoMn-HTC-V	0.208	0.196	0.404
CoMn-HTC-VI	0.073	0.151	0.224

The higher number of acid sites could be attributed to the porous structure of the catalyst. The surface acidity of porous $\text{Mn}_2\text{Co}_1\text{O}_x$ catalysts prepared by the combustion (CB) and co-precipitation (CP) methods was studied by Qiao et al. [41]. They found that the ammonia desorption peaks shifted to a lower temperature region for the catalyst prepared by the co-precipitation method. The desorption of NH_4^+ ions bonded to Brønsted acid sites are easier at lower temperatures. For the catalyst prepared by the combustion method, with larger specific surface area and porous structures than those prepared by the co-precipitation method, the peaks shifted to slightly higher temperatures, indicating the presence of abundant Lewis acid sites; the stronger acid strength could be due to the stronger interaction between the cobalt oxide and manganese oxide species [41]. Since the acid sites enhance the cracking and isomerization of heavier hydrocarbons [12], the catalysts with higher acid sites are expected to have better performance for the production of lighter hydrocarbons. Liu et al. [42] reported that the

H₂O₂-modified catalysts have a larger number of surface acid sites, especially Brønsted acid sites. They reported that the NH₃-TPD peaks at low temperatures (<250 °C) are due to the desorption of physisorbed ammonia and partial ionic NH₄⁺ bound to weak Brønsted acid sites, and the peaks at higher temperatures (>250 °C) belong to the Lewis acid sites and ionic NH₄⁺ bound to Brønsted acid sites. Brønsted acid sites are ascribed to surface protons, whereas Lewis acid sites, which are stronger than Brønsted sites, are attributed to the Co-O-Mn species located within a CoO structure and containing Mn³⁺ cations mainly in octahedral sites.

The X-ray diffraction (XRD) patterns of the prepared catalysts are shown in Figure 5. The XRD patterns of dried catalysts (Figure 5a) showed that the CoMn-HTC catalysts had crystallized hydrotalcite structure forms, with characteristic peaks at 11.9°, 23.5°, 34.3°, 39°, 47.5°, 60.8°, and 62.9°, which correspond to the (0 0 3), (0 0 6), (0 0 9), (0 1 5), (0 1 8), (1 1 0), and (1 1 3) planes (JCPDS #70–2151) [43–45].

Figure 5. X-ray diffraction (XRD) patterns of the (a) dried and (b) calcined CoMn-HTC catalysts.

The CoMn-HTC-IV, CoMn-HTC-V, and CoMn-HTC-VI catalysts had no clear layered structure and did not show apparent peaks belonging to the hydrotalcite structure. Most peaks were attributed to CoMn composite carbonate ($\text{Co}_x\text{Mn}_{1-x}\text{CO}_3$) in the catalysts prepared with KOH. The peaks of the hydrotalcite structure in the CoMn-HTC-III catalyst shifted to the right (mainly on the characteristic basal plane 0 0 3), and this can be attributed to the presence of anions in the interlayer regions. The difference in anions (carbonate or hydroxyl) occurred during the catalyst synthesis process, and H_2O_2 addition or air bubbling during the precipitation process affected the competition among anions occupying the interlayer region. The small peaks at 60.8° and 62.9° were attributed to the interlayers of carbonate and nitrate anions [46]. The presence of the peaks belonging to $\text{Co}(\text{OH})_2$ and $\text{Mn}(\text{OH})_2$ could be due to incomplete moisture removal during the drying process. After calcination at 300°C in air, no peaks associated with the hydrotalcite phase were observed in the XRD patterns (Figure 5b), indicating the destruction of the layered structure and the transformation of the hydrotalcite phase into Co_3O_4 (JCPDS #42-1467) [21,46–48] in all prepared catalysts. The crystalline phase of the catalysts prepared by KOH contained some spinel $\text{Co}_2\text{MnO}_{4.5}$, with higher reduction temperatures and lower catalytic activities.

The scanning electron microscope (SEM) images of the CoMn-HTC catalysts after drying are shown in Figure 6. The effects of catalyst preparation methods on the catalyst morphology were investigated. The prepared CoMn hydrotalcites were formed by the accumulation of aggregated nanoparticles. The CoMn-HTC-III catalyst showed a more obvious plate-like layered structure than the other catalysts. This result showed that using a mixture of $\text{KOH} + \text{K}_2\text{CO}_3$ and the addition of H_2O_2 have a positive effect on the preparation of hydrotalcite structured catalysts. In addition, the CoMn-HTC-III catalyst had the lowest reduction temperature possible because of its better layered structure. The distributions of metals were examined by performing the energy-dispersive X-ray spectroscopy (EDX) mapping of the catalysts (Figure 7). Mn and Co were homogeneously distributed over the entirety of the catalyst particles. The dispersion of cobalt and manganese particles could be promoted by the addition of hydrogen peroxide during the catalyst preparation and enhances crystal grain growth. Cui et al. [49] and Liu et al. [42] also reported that the addition of H_2O_2 could promote the dispersion of metal particles and improve the crystal grain growth, and this consequently resulted in the formation of mixed oxides with good thermal stability.

Figure 6. Scanning electron microscope (SEM) images of the CoMn-HTC catalysts.

Figure 7. Energy-dispersive X-ray spectroscopy (EDX) mapping of the CoMn-HTC catalysts.

2.2. Catalytic Evaluation

Generally, FT synthesis products consist of light gaseous hydrocarbons (C_1 – C_4), liquid fuels (C_5 – C_{22}), and waxes (C_{23+}). The catalytic performance of calcined CoMn-HTC catalysts in FT reaction at $H_2/CO = 2$, with a reaction temperature of 240 °C, pressure of 7 MPa, and reaction time of 6 h are shown in Figure 8. The product distribution over two different groups of catalysts, (I, II, III) and (IV, V, VI), were different. The catalysts I, II, and III, which were prepared by a mixture of KOH + K_2CO_3 as the precipitating agent, showed a higher potential in the production of liquid fuels including gasoline (C_5 – C_{10}) (Figure 8a) and jet fuel range hydrocarbons (C_8 – C_{16}) (Figure 8b), whereas the other catalysts (IV, V, VI) showed a higher potential in the formation of heavier hydrocarbons.

Figure 8. Product distribution in the Fischer-Tropsch (FT) reaction over CoMn-HTC catalysts: (a) gasoline range hydrocarbons (C₅–C₁₀), and (b) jet fuel range hydrocarbons (C₈–C₁₆). Reaction conditions: H₂/CO = 2, 240 °C, 7 MPa, 6 h.

The CoMn-HTC-I catalyst exhibited 48.6% selectivity to C₅–C₁₀ and 30.5% to jet fuel. The CoMn-HTC-III catalyst had the highest selectivity of 61.2% to gasoline range hydrocarbons with the methane selectivity of 7.4%. The simultaneous addition of H₂O₂ during the precipitation process also leads to an increase in the CO conversion, from 35.2% to 38.9%. The CoMn-HTC-II catalyst had the highest selectivity (49.7%) for jet fuel range hydrocarbons. The product distributions on catalysts IV, V, and VI revealed that the methane selectivity decreased to less than 1%, and selectivities to C₅–C₁₀ and C₈–C₁₆ also decreased to 17–40% and 17–25%, respectively. The selectivity to C₁₇+ in these catalysts was considerably higher than those in catalysts of group I, which were prepared by a mixture of KOH + K₂CO₃ as the precipitating agent. Very small amounts of olefins were detected over the CoMn-HTC catalysts at the given reaction conditions. The CO conversion did not change

considerably over different catalysts, and it was in the range of 35–39% for all catalysts. The CO₂ formation rates in all catalysts were less than 2%, implying that the CoMn-HTC catalysts had extremely poor activity for the water–gas shift reaction (WGS: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$).

The reduction temperature of easily reducible species of CoMn composite oxide decreased in both air-bubbled and H₂O₂ added catalysts, and this decrease resulted in a slight increase in catalytic activity because of the formation of additional Mn³⁺ and more CoMn species, which are easy to reduce. In addition to the reducibility of the catalyst, accessible catalyst acid sites can greatly affect the product distribution. The in situ cracking of the FT products may have been affected by the surface acidity of the catalysts. In general, Brønsted acidity leads to the cracking/isomerization of FT waxes [12]. The integrated synthesis of gasoline, jet fuel, and diesel range hydrocarbons using cobalt catalysts supported on mesoporous Y-type zeolites were studied by Li et al. [12]; they found that the porosity and acidic properties of zeolites play an important role in product distribution, mainly affecting the chain growth and cracking of heavier hydrocarbons. The NH₃-TPD analysis revealed that the CoMn-HTC-III catalyst had higher Brønsted acid sites, which promoted the cracking of heavy hydrocarbons and the formation of C₅–C₁₀ fraction. Catalysts I, II, and III, owing to the accessibility of their Brønsted acid sites and higher possibility for the cracking of heavy hydrocarbons, showed high selectivity to the gasoline range hydrocarbons (C₅–C₁₀) and jet fuel range hydrocarbons (C₈–C₁₆). However, excessive Brønsted acidity on the catalysts may have resulted in low catalyst stability and overcracking of heavy hydrocarbons and a subsequent increase in the fraction of lighter hydrocarbons and methane. Catalytic activity is strongly related to the types of precursor and precipitant agent. As it can be seen in Figure 8, a very small amount of olefinic products was produced during the reaction, the highest O/P ratio of C₂–C₄ hydrocarbon range of 1 was observed for catalyst II, and the highest O/P ratio in the whole range of produced hydrocarbon was less than 0.05. Oxygenated products were not detected in the products of the reaction for all catalysts.

According to Cai et al. [50], the activity of the copper manganese oxides catalysts prepared using sodium carbonate (Na₂CO₃) as the precipitating agent was higher than the catalyst precipitated by sodium hydroxide (NaOH) for the CO oxidation reaction. The crystalline phase of catalysts prepared using strong electrolyte (OH[−]) was found to be mainly spinel Cu_{1.5}Mn_{1.5}O₄; catalysts prepared using weak electrolyte (CO₃^{2−}) mainly consisted of MnCO₃, Mn₂O₃, and CuO. The catalytic activities of the multiphase catalysts (containing CuO and Mn₂O₃) were several times higher than those of single-phase oxides, especially at low temperature ranges [50].

It is worth mentioning that the available cobalt active sites of the catalyst are responsible for the chain growth, and the accessible acid sites are responsible for the cracking and isomerization. In this study, it was observed that the first group of catalysts (I, II, and III), with more available active sites at lower temperatures and more available acid sites (mainly medium strength acid sites), showed higher selectivity to C₅–C₁₀ and C₈–C₁₆ hydrocarbons than the second group of catalysts. Owing to their lower acidic properties and the inferior cracking rates of the heavy hydrocarbons, catalysts IV, V, and VI revealed higher selectivity for the production of hydrocarbons heavier than the gasoline or jet fuel range of hydrocarbons, and they also showed a considerably lower selectivity to methane.

3. Materials and Methods

3.1. Catalyst Preparation

CoMn-HTC catalysts (Co/Mn molar ration = 2) with layered structures were synthesized by the co-precipitation method. Solution A was prepared by mixing cobalt nitrate (Co(NO₃)₂·6H₂O), manganese nitrates (Mn(NO₃)₂·4H₂O), and ammonium fluoride (NH₄F) in a 2000 mL beaker at room temperature. The mixture was continuously stirred for 60 min. Two different basic solutions (solution B) containing (1) (KOH (2 mol/L) + K₂CO₃ (0.2 mol/L)) and (2) (KOH (2 mol/L)), were used as precipitating agents. Solution B was added dropwise to solution A with vigorous stirring, at pH = 9 and room temperature. Details of the catalyst preparation conditions are provided in Table 3.

Table 3. Catalyst preparation conditions.

Catalyst	Precipitating Agent
CoMn-HTC-I (Group 1)	KOH + K ₂ CO ₃
CoMn-HTC-II (Group 1)	KOH + K ₂ CO ₃ + air bubbling
CoMn-HTC-III (Group 1)	KOH + K ₂ CO ₃ + H ₂ O ₂
CoMn-HTC-IV (Group 2)	KOH
CoMn-HTC-V (Group 2)	KOH + air bubbling
CoMn-HTC-VI (Group 2)	KOH + H ₂ O ₂

Catalysts I, II, and III were precipitated as hydrotalcite precursors with a KOH + K₂CO₃ solution, and catalysts IV, V, and VI were precipitated by KOH. In catalysts II and V, air was bubbled through precipitation for the oxidation of Mn²⁺ to Mn³⁺. Catalysts III and VI were precipitated by the simultaneous addition of 100 mL of H₂O₂ (30 vol.%). The resulting solution was aged for 24 h at room temperature. The solid product was filtered and washed with deionized water to a neutral pH, then dried at room temperature. The dried products were then calcined at 300 °C for 5 h in air (3 °C/min). The obtained catalysts were denoted as CoMn-HTC I to VI.

3.2. Catalyst Characterizations

The bulk metal contents in the prepared catalysts were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES; Agilent 725/Agilent Technologies Inc., Santa Clara, CA, USA). Before analysis, approximately 0.5 g of catalyst was dissolved in 10 mL aqueous solution of H₂SO₄ (1:1) and heated. Then, the solution was cooled down and diluted with demineralized water and heated to 100 °C for 2 min. The obtained solution was then used for ICP analysis.

Thermogravimetric analysis (TGA) was carried out using the TGA Discovery series (TA Instruments, Lukens Drive, NW, USA). Approximately 20 mg of the catalyst was placed in an open aluminum crucible and heated from 50 °C to 900 °C at 10 °C/min in a nitrogen atmosphere (20 mL/min). The fragments were detected using an OmniStar GSD320 quadrupole mass detector (Pfeiffer Vacuum Austria GmbH, Vienna, Austria).

The surface morphology of the prepared catalysts was studied using a scanning electron microscope (SEM) (JEOL JSM-IT500HR; JEOL Ltd., Tokyo, Japan) accessorized with energy-dispersive X-ray spectroscopy (EDX) for elemental analysis and map analysis. Representative backscattered electron or secondary electron images of microstructures were taken in high vacuum mode, using an accelerating voltage of 15 kV.

The X-ray diffraction (XRD) patterns of the prepared catalysts were measured using a D8 Advance ECO (Bruker AXG GmbH, Karlsruhe, Germany) with CuK α radiation (λ = 1.5406 Å). The step time was 0.5 s, and the step size was 0.02° in a 2 θ angle ranging from 10° to 70°. The diffractograms were evaluated using the Diffrac.Eva software with the Powder Diffraction File database (PDF 4+ 2018, International Centre for Diffraction Data).

Hydrogen temperature-programmed reduction (H₂-TPR) and ammonia temperature-programmed desorption (NH₃-TPD) analysis were performed using an Autochem 2950 HP (Micromeritics Instrument Corporation, Norcross, GA, USA). In H₂-TPR analysis, 50 mg of catalyst was placed in the quartz tube. The catalyst sample was pretreated under argon flow at 450 °C (10 °C/min) for 30 min to remove traces of water and impurities from the catalyst pores, and it was then cooled to 40 °C. H₂-TPR was performed using 10% H₂/Ar with a flow rate of 30 mL/min and heating from 40 °C to 800 °C (10 °C/min). In NH₃-TPD analysis, approximately 0.1 g of catalyst was pretreated with He (25 mL/min) at 450 °C (10 °C/min) for 1 h. After cooling to 80 °C, ammonia adsorption was carried out, and the catalyst was saturated with 10% NH₃/He (25 mL/min) at 80 °C for 1 h. The physically bound molecules of ammonia were removed by purging with He (25 mL/min) at 100 °C for 1 h. Finally, NH₃ desorption

was performed by increasing the temperature from 100 °C to 800 °C, at a heating rate of 10 °C/min under He, with a flow rate of 25 mL/min. A thermal conductivity detector (TCD) was used to detect desorbed NH₃ in the outlet gas.

3.3. Catalytic Evaluation

The FT test was carried out in a 1 L stainless steel autoclave batch reactor (Parr instruments). In a typical experiment, 500 mg of catalyst and 50 mL of cyclohexane as a solvent were added to the reactor vessel. For the in-situ reduction of catalyst, the reactor was sealed and purged with N₂ five times and with H₂ three times. The reactor was then heated to 300 °C at a ramping rate of 3 °C/min, then pressurized with H₂ to 5 MPa for 5 h. After reduction, the reactor system was cooled to room temperature and purged three times with premixed syngas (H₂/CO = 2). The reactor temperature was raised to 240 °C at a ramping rate of 3 °C/min, then pressurized to 7 MPa to conduct the reaction in batch mode under a constant stirring speed of 800 rpm to eliminate the diffusion control region. A constant temperature was maintained during the reaction for 6 h. The conversion rate was measured according to the decrease in pressure during the reaction. After the reaction was terminated, the products were analyzed using different chromatographic procedures. The resultant gas sample was transferred to a gas bag and analyzed with a gas chromatograph, Agilent 7890A, with three parallel channels which collect data at the same time. The channels are equipped with two thermal conductivity detectors (TCD), CO, H₂, N₂, and CO₂ gases, and a flame ionization detector (FID) for the detection of hydrocarbons. The liquid samples were analyzed, without prior preparation steps, on chromatograph Agilent 7890A with FID detector using non-polar column HP PONA.

4. Conclusions

The effects of catalyst preparation methods on the physicochemical properties of CoMn-HTC catalysts derived from hydrotalcite-like precursors were investigated. The characterization results showed that the catalysts precipitated with KOH as a strong electrolyte (OH[−]) had higher reduction temperatures and lower reducibility, reduced and readily reducible species, and less accessible acid sites on the surface than the catalysts prepared with the KOH + K₂CO₃ mixture as precipitating agent and thus had better catalyst reducibility and more accessible medium and strong acid sites. The catalytic performance of the prepared CoMn catalysts was evaluated for FT synthesis at 240 °C, 7 MPa, and H₂/CO = 2 in a batch autoclave reactor. The highest selectivity (61%) was obtained after using the catalyst prepared with KOH + K₂CO₃ mixture and the addition of H₂O₂ (CoMn-HTC-III). The selectivity to gasoline range hydrocarbons decreased from 61% to 36% after the precipitating agent was changed from mixed solution to KOH only. The CO conversion did not greatly change by variations in catalyst preparation methods and remained in the range of 35–39% in all catalysts. CO₂ formation was less than 2% regardless of the catalyst used, indicating the extremely poor and negligible activity of the catalysts for the water-gas shift reaction.

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