Direct synthesis of long-chain alcohols from syngas over CoMn catalysts

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\section*{Abstract}
CoMn model catalysts were prepared by co-precipitation and evaluated for higher alcohol synthesis (HAS) via syngas. The selectivity to oxygenates (mainly alcohols and aldehydes) was found to be higher than 20\% for the Na-promoted CoMn catalyst. Among the oxygenates, \textit{C}_2\textsuperscript{+} and \textit{C}_6\textsuperscript{+} fractions accounted for \textless{} 90 wt\% and \textless{} 50 wt\%, respectively. Metallic Co\textsuperscript{0} particles and Mn\textsubscript{3}O\textsubscript{4} were found in both Na-promoted and un-promoted CoMn catalysts after the reaction, whereas Co\textsubscript{2}C nanoparticles could only be observed in the spent Na-promoted catalyst. The addition of Na benefited the carbonization of cobalt and increased the selectivity to oxygenates and CO\textsubscript{2}. Our studies thus suggested that Co/Co\textsubscript{2}C were the bifunctional dual-sites for the oxygenates formation over the Na-promoted CoMn catalyst, where Co catalyzed CO dissociation and chain propagation, while Co\textsubscript{2}C was responsible for CO non-dissociative activation and subsequent insertion. In addition, the sole Co\textsubscript{2}C nanoparticles with certain exposed facets may also act as another kind of active dual-sites for oxygenates formation.

\section*{1. Introduction}
Higher alcohol synthesis (HAS) via syngas derived from coal, biomass or natural gas has attracted much attention due to the wide potential applications of higher alcohols [1–3]. When higher alcohols are used as fuels, less NO\textsubscript{x} and SO\textsubscript{x} are released compared with traditional fuels from petroleum [4,5]. When used as fuel additives, an enhanced activity. Rh-based catalysts a

For the modified FT catalysts, the CO insertion mechanism proposed by Xu et al. [11] is widely accepted. Bifunctional dual-sites play an important role in higher alcohol formation. Two types of active sites are needed, where one type dissociates CO to form alkyl species while the other activates non-dissociatively adsorbed CO for its insertion. Among modified FT catalysts, Cu-modified Co catalysts for HAS have been widely investigated since the first report in the late 1970s [12] and some significant progress has been achieved [13–21]. It is generally accepted that Cu and Co metallic species in intimate contact as active dual-sites are responsible for alcohol formation. Metallic Co\textsuperscript{0} is suggested to be the active site for CO dissociation and chain growth for \textit{C}_2\textsuperscript{+} alkyl chain while Cu for CO insertion to generate \textit{C}_2\textsuperscript{+} oxygenates in including alcohols and aldehydes. However, Cu-modified Co catalysts for HAS exhibit low activity and low stability due to the accumulation of Cu over Co on the catalyst surface during the reaction [22,23]. In addition, the carbon chain growth for the CuCo catalysts is rather weak and little \textit{C}_6\textsuperscript{+}OH can be obtained. Therefore, it is highly desirable to find a substitute to Cu as an effective active site for CO insertion and to improve the stability and the \textit{C}_6\textsuperscript{+}OH selectivity. Recently, several studies disclosed that the formation of cobalt carbide during syngas exposure would improve the oxygenates selectivity [24–30]. Pei et al. [26] and Wang et al. [27] claimed that the Co\textsubscript{2}C was capable of...
catalyzing CO non-dissociative adsorption and subsequent insertion to the adjacent C,H₄ species to form oxygenates. Xiang et al. [24] prepared potassium-promoted CoMn catalysts by co-precipitation using oxalate as the precipitant, and they found that the sum selectivity to aldehydes and alcohols was usually up to 50 wt%. The synergic interaction between Mn₅O₈ and bulk Co₂C, promoted by potassium, was considered to be responsible for the high selectivity towards oxygenates. The presence of Mn was found to be helpful in promoting the formation of weak acid sites and to enhance the adsorption of linear and bridge-type CO significantly, which contributed to the formation of alcohol and growth of carbon chain [31]. Very recently, a Na-promoted CoMn catalyst for Fischer-Tropsch to olefins (FTO) was reported by our group [32]. A strong factor effect of CO₂C was illustrated and Co₂C nanoparticles with specifically exposed facets of (101) and (020) exhibited extremely high olefins selectivity (80 C%) with incredibly low methane selectivity, indicating that Co₂C was also capable of dissociative CO adsorption. The addition of alkalis has been proved to promote the carbonization rate of Co and the stabilization of the Co₂C specie [33]. Further studies found that the increase in the reaction pressure would result in increasing oxygenates selectivity. Thus, it was presumed that this Na-promoted CoMn catalyst may be suitable for higher alcohol synthesis under higher reaction pressure.

In this paper, CoMn catalysts were prepared by co-precipitation using Na₂CO₃ or (NH₄)₂CO₃ as the precipitant and evaluated for higher alcohol synthesis from syngas. The influence of the Na content and the reaction conditions were investigated. The structure of the bifunctional dual-sites and catalytic mechanism for oxygenates formation were also discussed.

2. Experimental

2.1. Catalyst preparation

Two CoMn catalysts with the same Co/Mn atomic ratio of 1/1 were prepared by co-precipitation using sodium carbonate anhydrous (Na₂CO₃) or ammonium carbonate anhydrous ((NH₄)₂CO₃) as the precipitant, which were denoted as CoMn-SC (Na-promoted CoMn) and CoMn-AC (unpromoted CoMn), respectively. Co(NO₃)₂·6H₂O and 50% Mn(NO₃)₂ aqueous solutions were used as metal precursors. All reagents were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further processing. During the co-precipitation process, the 2 M metal ion (including Co²⁺ and Mn²⁺) solution and 2 M Na₂CO₃ or (NH₄)₂CO₃ solution were added simultaneously into a beaker containing 200 mL deionized water under continuous stirring. All solutions were prepared using deionized water. A constant pH of 8 ± 0.1 was used during the precipitation process, and the temperature was kept at 65 °C and 30 °C for Na₂CO₃ and (NH₄)₂CO₃ as the precipitant, respectively. The as-prepared suspension solution was aged for 2 h, and then centrifuged with deionized water for 6 times. After drying at 100 °C for 5 h, the samples were calcined in a muffle furnace at 330 °C for 3 h under static air. CoMn catalysts with different Na loadings were prepared by wet impregnation of CoMn-AC using sodium carbonate anhydrous followed by similar procedures and denoted as CoMn-xNa, in which x stands for the weight percentage of Na in the sample.

The calcined catalysts were reduced by 10 vol% H₂/N₂ (200 mL/min) at 300 °C for 300 min in a tube furnace. The reactor was then cooled to the room temperature (ca. 19 °C), followed by passivation in 1 vol% O₂/Ar for 60 min. The as-prepared samples were then characterized to reveal the structural properties of the fresh reduced catalyst.

2.2. Characterisation

An inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8000, Perkin Elmer) was used to determine the bulk compositions of the CoMn catalysts. Nitrogen adsorption measurements were performed on a Micromeritics TriStar 3020 instrument at −196 °C. All samples were degassed at 200 °C in vacuum overnight. The specific area was calculated using the adsorption isotherm in relative pressure (P/Po) ranging from 0.04 to 0.3 by the Brunauer-Emmett-Teller (BET) equation. The total pore volume was calculated by the Barrett-Joyner-Halenda (BJH) method and the average pore size was determined using the BJH desorption isotherm.

XRD patterns for the CoMn catalysts were recorded on a Rigaku diffractometer using Cu Kα radiation with the wavelength of 1.54056 Å at 40 kV and 40 mA. All the measurements were performed at ambient temperature. The samples were loaded into a shallow glass holder and levelled on the surface before measurements. The data was collected with a rate of 1°/min in a continuous scanning mode.

H₂-TPR experiments were carried out on a Micromeritics AutoChem 2920 instrument. About 30 mg of sample was purged with 30 mL (STP) min⁻¹ He at 120 °C for 100 min. After cooling to 50 °C, the catalyst was exposed to 30 mL (STP) min⁻¹ of 5% H₂/Ar flow as the temperature ramped to 800 °C. The exhaust was analyzed by a thermal conductivity detector (TCD).

Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM 2011 electron microscope with 200 kV accelerating voltage. Samples for TEM were prepared by dispersing the nanoparticles in ethanol followed by ultrasonication. One droplet of dispersion was placed on carbon-coated molybdenum or nickel grids for measurement.

2.3. Catalytic evaluation

Higher alcohol synthesis reaction was carried out in a stainless steel continuous flow fixed-bed reactor with an inner diameter of 10 mm. 1.5 g of the catalyst (40-60 meshes) was mixed with 3.0 g of silica (blank experiment proved that silica had no catalytic activity for HAS under current conditions), and then loaded into the reactor. The catalyst was reduced in-situ in 10 vol% H₂/N₂ with GHSV (gas hourly space velocity) of 8000 mL (gcat.⁻¹ h⁻¹) at the atmosphere pressure at 300 °C for 300 min. The gas flow was controlled by a Brooks mass flow meter. After the reactor was cooled to 200 °C, the system was pressurized to 2.0 MPa with 10 vol% syngas/N₂. Then the feed gas was changed into syngas (H₂/CO/N₂ = 65/32/3) with GHSV of 6000 mL (gcat.⁻¹ h⁻¹). 3 v% of nitrogen was included in the feed gas as an internal standard. The outlet gas was analyzed on-line by GC after passing through a hot trap (120 °C) and a cold trap (0 °C) and the liquid and wax products were collected and analyzed off-line by GC. The details of GC analysis were shown in our previous study [10]. All the data were collected after 48 h of time-on-stream.

3. Results

3.1. ICP and textural structures

The ICP results of the various CoMn samples are shown in Table 1. The Co/Mn atomic ratios in calcined CoMn catalysts were close to 1, suggesting the complete precipitation of the Co²⁺ and Mn²⁺ species during the preparation process. The Na content in CoMn-SC was 0.79 wt%, much higher than that in CoMn-AC (no detection of sodium). As shown in Table 1, the specific surface area (S_BET) and pore volume were similar after the calcination for all samples. The specific surface area decreased and pore size increased after the reduction, while no obvious changes were found in the pore volume among all samples. Both the pore volume and the diameter of CoMn-AC were higher than those of CoMn-SC. After addition of Na, the pore volume and diameter decreased for the CoMn catalysts.

3.2. XRD

Fig. 1 shows XRD patterns of the CoMn catalysts at different stages.