Metal organic framework-mediated synthesis of potassium-promoted cobalt-based catalysts for higher oxygenates synthesis

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ABSTRACT

Syngas to higher oxygenates conversion was carried out on a series of potassium-promoted cobalt-based catalysts. Catalysts with different potassium composition were prepared by metal organic framework-mediated synthesis, which is the calcination of the ZIF-67 metal organic framework (MOF). Cobalt skeleton structure that originated from the MOF is preserved after the calcination. The calcined catalysts consist of Co_3O_4 nanoparticles and surface carbon. The catalysts were reduced by H_2/He prior to the reaction. CO hydrogenation was carried out at various temperatures (270 °C, 300 °C and 325 °C) and at 40 bar, with H_2/CO = 1/1. The formation of methane and higher hydrocarbons is suppressed by potassium, and cobalt carbide is formed from metallic cobalt during the reaction. Thus, the K-promoted cobalt based catalyst synthesized by the MOF-mediated synthesis shows higher selectivity to ethanol, acetaldehyde and higher oxygenates, even at high temperatures.

1. Introduction

The increasing energy consumption and the limited fossil fuels supplies have spurred the search for alternative energy sources. Ethanol and higher oxygenates are such substitutes which can be used as fuels or fuel additives. Ethanol and higher oxygenates can be added to gasoline to reduce the emission of CO_2, NO_x, and unburned hydrocarbons and to improve the octane rating of the fuel [1–3]. Ethanol is produced commercially by following two methods: (1) fermentation of sugars, (2) hydration of ethylene [4]. Fermentation route is the dominant process, and can interfere with the food supplies. The hydration of ethylene can be limited in some cases. Therefore, there is a need to find new routes for the mass production of ethanol and higher oxygenates. One new method is the catalytic conversion of syngas, which is derived from coal, natural gas or biomass [4,5]. The studies to convert syngas into higher alcohols has been conducted for decades. Forming higher oxygenates requires the catalyst to have dual sites in close proximity: one to adsorb CO associatively and one to adsorb CO dissociatively, forming the C—C bond between the adsorbed C_xH_y and CO [6,7]. The catalysts for higher oxygenate synthesis contains metals like rhodium, cobalt, copper, iron or a combination of more than one metal to provide these two types of sites [2,3,8–14].

Cobalt-based catalysts are one type of material with the potential to produce higher alcohols [8,15]. Metallic cobalt is capable of dissociating CO, and the dissociated CO is hydrogenated to CH_x and steam, e.g.,

in Fischer-Tropsch [16]. Typically one or more transitional metals, such as Cu, Cr or Pd [17,18], are doped with cobalt to associatively adsorb CO and form higher oxygenates. However, it is extremely difficult to reach the "atomic adjacency" between Co and the other metal [19]. Therefore, the catalyst favors carbon chain polymerization rather than CO insertion [20]. Recently, several studies on cobalt-based Fischer-Tropsch catalysts or higher alcohol synthesis catalysts have reported the formation of cobalt carbide in the presence of syngas [20–26]. Pei et al. [23] and Bian et al. [27] claim that cobalt carbide (Co_2C) can adsorb CO nondissociatively, and insert the CO to adjacent C_xH_y species. Once CO is inserted onto the hydrocarbon chain, the intermediates can be hydrogenated to produce corresponding oxygenates such as aldehydes and alcohols [28–30]. Forming Co_2C on the surface of a cobalt catalyst can provide both metallic cobalt and Co_2C sites in close proximity, as is required for oxygenate formation. Although the role of Co_2C in CO hydrogenation is not certain, there are several studies that detected the formation of cobalt carbide on catalysts with high oxygenate yields [20,31–34].

Metal organic frameworks (MOFs) are novel materials as catalysts due to their unique highly ordered structures and high thermal and chemical stability [35,36]. One example is the zeolitic imidazolate framework 67 (ZIF-67), which is constructed from tetrahedrally coordinated divalent cobalt cations (Co^{2+}) linked by uninegative imidazolate ligands (im-) [37–39]. In this study, a MOF-mediated synthesis method is used for the preparation of Co_3O_4 nanoparticles.

Table 1
Catalyst composition by ICP-OES and BET surface area.

Catalyst	Conc. Of Co wt%	Conc. Of K mg/kg	Surface Area m^2/g
1K-Co3O4	79.4	52	13.9
5K-Co3O4	70.4	429	14.7
10K-Co3O4	69.9	634	17.4

Different loadings of potassium were added into these precursors. The Co_3O_4 nanoparticles were reduced by H_2/He flow and used for higher oxygenate synthesis reaction at 40 bar and at varying temperatures (270 °C, 300 °C and 325 °C). The catalysts are characterized by Scanning Electron Microscopy, X-ray photoelectron spectroscopy, BET analysis, X-ray powder diffraction. The objective is to use the MOF-mediated synthesis method to prepare a highly-dispersed Co_3O_4 polyhedral nanoparticles as catalysts for higher oxygenate synthesis.

2. Experimental

ZIF-67 with different potassium concentrations were synthesized by mixing two different salt solutions of methanol. In system (1), 3 g Cobalt (II) nitrite hexahydrate $(Co(NO_3)_2 \cdot 6H_2O)$ + potassium carbonate (K_2CO_3) were dissolved in 100 mL methanol. The weight of K_2CO_3 was adjusted so as to yield the desired weight percent of potassium as shown in Table 1. In system (2), 7.05 g of 2-methylimidazole $(CH_3C_3H_2N_2H)$ were dissolved in another 100 mL methanol. The two systems resulted in two clear solutions on continuous magnetic stirring. The latter solution was then poured into the former under continuous stirring. Stirring was kept for 5 mins. After settling down for 3 h, the solid was collected from the colloidal dispersion by centrifugation. The solid was then washed with anhydrous ethanol and centrifuged several times, and the precipitate was dried at 60 °C overnight. The dried precursors were calcined in the air flow at 500 °C for 2 h with a ramp rate of 3 °C/min.

Co and K composition of the calcined samples are determined using a Perkin Elmer 2000 DV inductively coupled plasma-optical emission spectrometer. BET surface area test is performed on an Altamira AMI-200 system using a flow BET adsorption procedure with 10%, 20% and 30% N_2. The morphology of the ZIF-67 MOF and the calcined catalyst samples were studied by Scanning electron microscopy (SEM) on a Quanta 3D DualBeam FEG FIB-SEM. The accelerating voltage is set at 20 kV

A Kratos AXIS 165 X-Ray Photoelectron Spectrometer using monochromatic Al $K\alpha_1$ radiation (hν = 1486.6 eV, intrinsic linewidth 0.3 eV) was used to collect the XPS spectra on calcined catalysts. Survey spectra with a pass energy of 160 eV were taken on each sample prior to the measurement to check correct sample alignment. High resolution scans of Co 2p, C 1s, O 1s, and K 2p were recorded with a pass energy of 40 eV. C 1s peak at 284.8 eV were used as known standard to calibrate binding energy scale.

XRD analysis was conducted on calcined samples using an Empyrean X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm). Data is collected at 2θ from ~5° to 70°. The patterns were analyzed using the X'pert HighScore Plus software with the Search & Match feature.

Temperature-programmed reduction was carried out using the Altamira AMI-200 system. Typically 25 mg of calcined samples are loaded into a U-shape quartz tube reactor. The samples were heated to 150 °C under helium flow and kept for 30 mins to remove the moisture. Then 10%H_2/Ar gas flowed through the reactor, and the temperature is increased to 650 °C with a ramp rate of 5 °C/min. A thermal conductivity detector (TCD) is used to detect the hydrogen consumption. The TPR patterns of 20, 35 and 50 mg Ag_2O are used as standards to quantify the hydrogen consumption of the catalysts.

An Altamira AMI-200R-HP system was used to carry out our

reactions at different conditions. During each run, 75 mg of freshly-calcined sample was put inside a ¼ in. glass-lined stainless steel tubular reactor. The gas lines were heated to 200 °C to maintain the hydrocarbon and oxygenate products in vapor phase. The catalysts were heated in a 10% H_2/He flow with a ramp rate of 10 °C/min from RT to 400 °C. The catalyst was then reduced at 400 °C for 3 h. After the reduction, the reactor was pressurized to 40 bar under continuous He flow and the temperature was set to 270 °C. A mixed flow of hydrogen and CO (CO:H2 ratio = 1:1) flowed through the reactor to carry out the CO hydrogenation reaction. The gas hour space velocity (GHSV) for the reaction is 36000 scc/g_{cat}/h. Products were then analyzed by a Shimadzu GC-2014 gas chromatograph which has one flame ionization detector (FID) for hydrocarbon and oxygenate products, and two thermal conductivity detectors (TCDs) for CO, CO_2, CH_4 and H_2. The reaction was ran for around 24 h so as to attain steady state at 270 °C. The catalyst was subsequently tested at 300 °C and 325 °C for 24 h each to evaluate the reaction performance at higher temperatures.

The CO conversion and the product selectivity are calculated using the following equations:

$$X_{CO} = \frac{\sum N_C \times moles(C_n)}{\sum N_C \times moles(C_n) + moles(CH4)} \times 100\% \quad (1)$$

$$S_{C_n} = \frac{N_C \times moles(C_n)}{\sum N_C \times moles(C_n)} \times 100\% \quad (2)$$

Where X_{CO} = CO conversion. N_c = carbon number of the product C_n. S_{Cn} = carbon selectivity of the product C_n.

After the reaction, the catalysts are passivated under 1% O_2/Argon for 30 mins before taken out of the reactor. The catalyst samples are characterized by XRD using the same instrument and method as for the calcined catalysts.

3. Results and discussion

Fig. 1 shows the Scanning Electron Microscope images at 80,000 Magnification on ZIF-67 before and after the calcination. The uncalcined sample is composed of polyhedral-shaped particles with < 500 nm in size. ZIF-67 is reported to form a stable suspension in methanol, and the average size of the particle ranges from 228 nm to 500 nm [37,40,41]. In this study, ZIF-67 serves as the precursors to the cobalt-based catalysts and the sample is calcined under air flow at 500 °C for 2 h. After the calcination in air (Fig. 1b), the organic linkers between cobalt metallic nodes are removed. The sample is composed of cobalt oxide skeletons, while some of the polyhedron structures are maintained. XRD pattern of the calcined sample in Fig. 1C detects Co_3O_4 phase in the catalyst (JCPDS 01-076-1802). Therefore, the organic ligands are removed and the catalyst consists of only cobalt oxide after calcination. This agrees with previous reported decomposition of ZIF-67 using Thermo-gravimetric analysis and XRD [40–42]. The XPS spectra of the calcined samples at Co ($2p_{3/2}$) are shown in Fig. 1(d). The calcined samples with different potassium concentration show no major changes at Co ($2p_{3/2}$). The binding energy at 779.8 eV indicates cobalt is in the form of Co_3O_4 on the surface.

ICP-OES composition and BET surface area results are listed in Table 1. The catalysts were denoted as xK-Co3O4 where x = 1,5,10 because the target wt% of K in the catalyst should be 1%, 5% and 10% of the final calcined catalyst, respectively. However, the incorporation of potassium in the ZIF-67 is not successful, as the wt% in 1K-Co3O4 is even much lower than 1%. 5K-Co3O4 showed ~10 folds higher concentration of potassium than 1K-Co3O4, but still much lower than the target composition. Doubling the potassium loading in the synthesis of 10K-Co3O4 did not yield twice the potassium concentration than 5K-Co3O4 in the final composition. The concentration of 10K-Co3O4 is 634 mg/kg catalyst, which is slightly higher than 5K-Co3O4. The surface area of the catalyst is below 20 m^2/g, which is much lower