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Syngas conversion to higher alcohols: A comparative study of acid and base-treated mesoporous carbon-supported $KCoRhMoS_2$ catalysts

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ABSTRACT

Ordered mesoporous carbons (OMC) of desirable textural properties have been synthesized by the novel one-pot soft-templating synthesis approach. Prior to catalyst metals loading, the OMC supports were functionalized using the wet chemical oxidation technique to introduce surface oxygen-containing functional groups for metals anchorage. In this regard, the crucial role functionalizing agents (acidic and basic) on the morphology & structural integrity of the parent OMC support was also investigated. It was observed that the structural integrity of the parent OMC material remained intact as confirmed by the TEM analyses. Moreover, less defective sites were generated as evidenced from the Raman spectroscopic analysis; suggesting that non-acidic oxidative treatment could be a mild way of introducing oxygen functionalities as metal anchoring sites on the surface of pristine OMC support. Based on the defective sites generated on the OMC supports, the severity of chemical oxidative treatment was observed to follow the trend: $HNO_3 > NH_4OH/H_2O_2 > KOH$. The HNO_3, NH_4OH/H_2O_2 and KOH treated-OMC supports were used to prepare a series of $KCoRhMoS_2$ catalysts with nominal compositions of 9%K, 4.5%Co, 15%Mo, & 1.5 wt.%Rh, respectively. Catalytic performance evaluations of these catalysts for syngas conversion to higher alcohols were also studied at similar reaction conditions: $T = 300–340\,^{\circ}C$, $P = 8.3$ MPa, GHSV = 3600 mL (STP)/h.g_{cat}, and $H_2/CO = 1.25$. The HNO_3-treated OMC-supported $KCoRhMoS_2$ catalyst showed superior total alcohol productivity as compared to its NH_4OH/H_2O_2 and KOH counterparts; probably due to the greater number of surface oxygen-containing functional groups, thereby, enhancing its metal-oxygen anchorage properties in the catalyst formulation. All catalysts showed an increase in CO conversion with incremental temperature with a maximum of 40.2% recorded for the KCoRhMo/OMC-HNO_3 catalyst at $T = 330\,^{\circ}C$ as opposed to 26.1 and 19.6% for the catalysts with KOH and NH_4OH/H_2O_2 treatment, respectively.

1. Introduction

The price volatility of crude oil on the world market, the dwindling of crude oil reserves, as well as environmental concerns resulting from its utilization among other factors have led to increased and extensive research on alternative feedstocks such as biomass, coal, natural and shale gas and their plausible conversion routes into syngas [1]. Syngas as an alternative feedstock is versatile with opportunities for development since it finds application in the direct synthesis of olefins, ultra-clean gasoline and diesel, high quality waxes, valuable oxygenates and chemicals, and higher alcohols [2]. Higher alcohols (C_2 and $C_{2+}OH$), commonly refer to short-chain alcohols higher than methanol, and can be used as automotive fuels, fuel additives for octane enhancement, and value-added chemicals in fine chemical synthesis [3,4]. These oxygenated fuels burn more cleanly than fossil fuels, mitigating environmental footprints such as noxious CO emissions and net atmospheric CO_2 content [1]. It is also worth mentioning that in order to obtain these valuable chemical products and alternative green fuels from syngas conversion, the catalyst used therein the process becomes pivotal. Among the four typical catalysts with potential application for Higher Alcohol Synthesis (HAS) namely; Rh-based catalysts [5], modified high-temperature (ZnO/Cr_2O_3) and low-temperature ($Cu/ZnO/Al_2O_3$) methanol catalysts [6], modified Fischer Tropsch (FT) catalysts (based on Fe, Co and Ru) [7], and MoS_2-based catalysts [8], the latter is the most promising catalytic systems due to its high resistance to sulfur poisoning, deactivation by coking, and high selectivity for C_1-C_5 linear primary alcohols when secondary promoters (such as Co & Rh) are incorporated [9].

Carbon-based supported MoS_2 catalysts, promoted with Co and Rh have garnered immense attention in the conversion of syngas to higher alcohols via the Fischer Tropsch synthesis process [10]. Car-

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bonaceous materials such as ordered mesoporous carbons (OMC) have received considerable focus due to their potential applications in a wide range of fields including catalysis, adsorption or sensor technology. Though, these porous carbon materials possess desirable textural properties (tunable pore sizes, high surface areas, and large pore volumes), applications in catalysis becomes limited as a result of their chemical inertness, minimal surface functionality and their hydrophobic nature [11]. Thus, to enhance their surface chemistry for practical catalysis application, carbon materials are usually subjected to post-synthesis treatment techniques including chemical oxidation (liquid or gas phase), polymer coating and grafting [12,13] in order to improve their hydrophilicity as well as generate the necessary surface oxygen groups for interacting with catalytic species. Regarding surface chemistry modification via oxidation, the most studied carbon-based materials include activated carbon and carbon nanotubes [13].

To a large extent, the introduced oxygen-containing groups play the role as weak acids or bases, which possess ion exchange properties. For instance, acidic groups such as carboxyl, phenolic hydroxyl, lactone and quinone can be introduced to the surface of the carbon material leading to significant changes of the surface chemistry; hence, its application as catalyst support or adsorbent [14]. Commonly used treatment protocols include oxidative treatment (wet or dry), plasma treatment, and electrochemical modifications [15,16] where as dry chemical oxidation employs gaseous oxidizing agents (e.g. oxygen, ozone and carbon dioxide), its wet counterpart uses individual solutions of nitric acid, sulfuric acid, phosphoric acid or a mixture with hydrogen peroxide, sodium hypochlorite, permanganate etc., to accomplish a similar purpose [13–16]. Among the series of different oxidants studied (including HNO_3 and H_2O_2), Pradhan and coworkers observed HNO_3 treatment as the most effective regarding modification of the surface area and porosity of activated carbons [15]. Also, treatment of CNT with 68% HNO_3 under reflux conditions introduced carboxylic groups on the surface and ends of the nanotubes as reported by Tsang et al. [17]. Similarly, chemical oxidation treatments as reported recently by Ryoo and coworkers evidenced that the carbon framework remained intact after surface modification of CMK-1 and CMK-5 by oxidation with concentrated nitric acid at 110 °C for 15 min [18]. Moreso, the same workers reported in a previous study that OMC can maintain an ordered structure even in boiling 5 M aqueous solution of NaOH, KOH, or H_2SO_4 over a week, showing strong resistance to attack by acids and bases [19]. However, Lu and co-workers modified the surface chemistry of CMK-5 carbon using the mild oxidizing agent H_2O_2 in order to introduce surface oxygen groups while its ordered structure was maintained, but surprisingly a structural collapse occurred [16].

In this study, surface modification of pristine OMC (i.e. not functionalized) supports via wet chemical oxidation treatments using HNO_3, NH_4OH/H_2O_2, and KOH have been investigated and subsequently evaluated for their catalytic performance for the conversion of syngas to higher alcohols at similar metals loading using laboratory-scale fixed bed reactor under industrial conditions. In addition, the untreated OMC-supported-KCoRhMo catalyst were also evaluated at similar conditions to benchmark performance via screening with syngas feedstock for the HAS reaction.

2. Experimental

2.1. Synthesis of pristine OMC support with F127 as template

Synthesis of the pristine OMC support followed procedure described in the literature [20] with some modification. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer (F127) was used as the starting soft template and phloroglucinol was employed as the phenolic compound to enhance the polymerization reaction of phenols with formaldehyde under acidic conditions [21]. The block copolymer Pluronic F127 (M_{av} = 12,600, $EO_{97}PO_{67}EO_{97}$) and phloroglucinol were procured from Sigma-Aldrich and used as received. The nominal molar ratio of the chemicals used in the synthesis medium was 0.0008 F127: 0.008 Phloroglucinol: 0.0099 Formaldehyde: 0.004 HCl: 0.435 Ethanol. In a typical synthesis protocol, 1.0 g each of phloroglucinol and F127 template were dissolved in 20 g of ethanol solution at 15 °C under mechanical stirring. After the solid was completely dissolved, 0.39 g of 37% HCl was added to the solution as a catalyst and stirring continued at the same temperature for an additional 2 h until a light pink color appeared. Subsequently, 0.8 g of 37% formaldehyde solution was added to the obtained solution and stirring continued for approximately 50 min until the mixture turned turbid. The solution was then poured into petri dishes to facilitate the evaporation of ethanol at room temperature (for about 12 h), followed by heating in an oven at 100 °C for 24 h. The as-made products were scraped out of the petri dishes and crushed into chunks. To carbonize the obtained product, the sample was pyrolyzed in a tubular furnace at 600 °C for 4 h using a heating rate of 1 °C/min under N_2 atmosphere (at a flow rate of 50 mL/min).

2.2. Chemical oxidation of pristine OMC supports

Chemical oxidation of the pristine OMC was necessary in order to modify the surface chemistry of the material. In this work, the oxidizing agents used include 30 wt.% nitric acid, a mixture of NH_4OH/H_2O_2 and KOH. Pristine OMC support treatments followed procedure described in the literature [22] with modification. In a typical treatment, 2 g of the pristine OMC support was dispersed in 215 mL of the nitric acid (70 wt%) in a 500 mL round bottom flask equipped with a condenser and immersed in an oil bath maintained at 100 °C. The mixture was kept under reflux condition with magnetic stirring for 12 h and subsequently diluted with de-ionized water, filtered, and washed multiple times until a neutral pH was attained. The resulting solid sample was then oven dried at 120 °C for 12 h. For the NH_4OH/H_2O_2 treatment, 2 g of pristine was dispersed in 215 mL of a mixture of 25 wt% NH_4OH and 30 wt% H_2O_2 (in ratio 50:50) in a 500 mL round bottom flask and similar treatments was followed as described above. Finally, for the KOH treatment, 30 wt% KOH solution was made by dissolving the required amount of KOH pellets in 500 mL of de-ionized water in a round bottom flask and reaction proceeded as in above. Henceforth, the chemically treated supports can be designated as OMC-HNO3, OMC-NH_4OH/H_2O_2, and OMC-KOH for the HNO_3, NH_4OH/H_2O_2, and KOH treatments, respectively.

2.3. Preparation of K-promoted CoRhMo/OMC catalysts

The preparation of OMC-supported K-CoRhMo catalysts (chemically treated or untreated) followed a similar procedure described previously [23,24]. In brief, the pre-treated supports were alkalized using the required amount of aqueous solution of K_2CO_3, dried at 100 °C for 6 h, followed by stabilization at 300 °C in argon flow of 50 mL/min at a heating rate of 10 °C/min for 4 h. Consequently, co-impregnation of the respective metal (Co, Mo, Rh) species was performed using ammonium heptamolybdate tetrahydrate (Alfa-Aesar), potassium carbonate (Sigma-Aldrich), cobalt acetate tetrahydrate (Alfa-Aesar), and rhodium chloride hydrate (Sigma-Aldrich) as precursors for Mo, K, Co, and Rh, respectively. The oxidic form of the dried powder K-doped CoRhMo samples were obtained after 4 h of oven drying at 100 °C, followed by stabilization at 450 °C under argon flow of 50 mL/min at a heating rate of 10 °C/min for 12 h. The final catalyst composition (wt.%) of 9% K, 15% Mo, 4.5% Co and 1.5% Rh, respectively,

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