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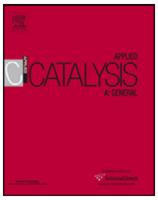

Influence of porous characteristics of the carbon support on alkali-modified trimetallic Co–Rh–Mo sulfided catalysts for higher alcohols synthesis from synthesis gas

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ABSTRACT

Alkali-modified trimetallic Co–Rh–Mo sulfided catalysts supported on commercial activated carbons with different textural characteristics were tested for the synthesis of higher alcohols from synthesis gas and compared with a similar catalyst supported on multi-walled carbon nanotubes (MWCNTs). Addition of metals (Co, Rh, and Mo) to the microporous and mesoporous activated carbons, and the MWCNT supports increased the mean pore diameter and % mesoporosity of the catalysts. The N_2 adsorption–desorption isotherms of the MWCNTs support and the MWCNT-supported alkali-modified trimetallic C–Rh–Mo catalyst revealed that the mesoporous structural integrity of the catalyst was unchanged from the support after impregnation of the catalyst species. The formation of large particles took place due to the agglomeration of metal species on the microporous activated carbon supports. The metal dispersion of the sulfided catalysts on different supports is: MWCNTs < AC-CGP Super < AC-Fluid Coke < AC-RX$_3$ Extra < AC-Darco. The total alcohols STY and selectivity of 0.296 g/(g of cat./h) and 35.6%, respectively were found to be on the MWCNTs-supported alkali-modified trimetallic C–Rh–Mo catalyst compared to similar catalysts supported on activated carbon. The % CO conversion as well as alcohols space time yield are not related to the BET surface area and pore volume of the support, whereas, textural properties of the support such as pore size and mesoporosity has direct influence on the synthesis of mixed alcohols from synthesis gas. Little or no sintering of metal species was observed on the spent catalyst supported on MWCNTs, whereas, the agglomeration of catalytic species is high on the microporous activated carbon support compared to that of the mesoporous activated carbon supported catalysts.

1. Introduction

Mixture of higher alcohols is a potential gasoline blending stock to improve the octane number of the motor gasoline and reduces the emissions of NO$_x$, ozone, CO, and aromatic vapours. Catalytic conversion of synthesis gas derived from waste biomass and coal gasification to higher alcohols is an alternative approach that remains economically attractive for making fuels and chemicals [1–3]. Synthesis gas obtained from coal or biomass contains sulfur contaminant in the form of H_2S, which can deactivate the catalyst. Molybdenum sulfide catalysts have been recognized to be effective for the CO hydrogenation reactions because of their sulfur resistance and activity for water–gas shift (WGS) reaction. This saves the cost of ultra-desulfurization for feed gas and water separation [4]. Addition of alkali to MoS_2 catalysts increases the formation of alcohols and suppresses the formation of hydrocarbons [5].

The higher alcohols space time yield (STY) and selectivity are found to be low over the K-modified MoS_2 catalysts due to the formation of methanol, hydrocarbons and carbon dioxide. The Rh promotion to this catalyst system increased the activity towards the formation of oxygenates, due to the strong interaction between the rhodium modifiers with Mo species [6]. The incorporation of Co resulted substantial changes in the structure of K-modified MoS_2 catalysts and enhanced the $C_1 \rightarrow C_2$ homologation step that leads to the formation of ethanol as the dominant product [7]. The formation of hydrocarbons can be greatly reduced using alkali-modified trimetallic Co–Rh–Mo catalyst due to the formation of Co (Rh)–Mo–S species, evident in the X-ray absorption near-edge structure (XANES) spectra [8]. This catalyst was found to be attrac-

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Abbreviations: MWCNTs, multi-walled carbon nanotubes; AC, activated carbon; TPR, temperature programmed reduction; GHSV, gas hourly space velocity; ICP-MS, inductively coupled plasma-mass spectroscopy; XRD, X-ray diffraction; TEM, transmission electron microscopy; STY, space time yield.

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tive to reduce Rh content and increase the activity and selectivity of the catalyst for the formation of higher alcohols [9].

Catalyst support has great influence on alcohols synthesis from CO hydrogenation. Over the unsupported catalysts, molybdenum species exists in much reduced state. The activity of the catalyst is found to be high on Mo species with lower oxidation state and the catalyst becomes more selective to hydrocarbons [10,11]. The surface acidity of acid metal oxide supports, like Al_2O_3, SiO_2 and ZrO_2 suppress the reaction rate of alcohols by favouring the formation of hydrocarbons and results the deactivation of the catalyst by coke formation [12]. In catalysis, carbon based supports such activated carbon, carbon nanotubes, carbon nanohorns have been attracting attention as potential supports for precious metals containing catalysts used for hydrogenation reactions [13]. These materials hold several advantages as a catalyst support for higher alcohols synthesis from synthesis gas. Activated carbon support has intriguing properties such as, large surface area, inert graphitic surface, resistance to acidic or basic media, and high thermal stability. The alcohols selectivity is found to be higher on the MoS_2 catalysts that are supported on activated carbon compared to the SiO_2, Al_2O_3, and CeO_2 supported catalysts [14–16]. Carbon in the form of multi-walled carbon nanotubes (MWCNTs) display unique properties such as meso/macro porous structures that mitigate transport limitations, uniform and straight pores that allow great metal dispersion, high mechanical strength that can be useful in terms of the industrial problems experienced by the Oryx gas-to-liquid (GTL) facility, and high thermal conductivity that is important in exothermic reactions [17,18].

Conventional activated carbons being microporous (pore diameter <2 nm) causes pore plugging due to the formation of coke and deactivation of the catalyst, which results in transport limitation in the reaction [19]. The problems related to internal diffusion can be eliminated by using mesoporous supports with pore diameter in the range of 2–50 nm. Most of the research on higher alcohols synthesis was done using microporous activated carbon supported catalysts that had significantly smaller surface area (350–820 m^2/g) than commercially available activated carbons (950 m^2/g and higher) and long time activity of these catalysts does not meet the commercial levels. The textural properties of the support, such as average pore diameter, pore volume and surface area, could significantly influence the extent of reduction, morphology, adsorption and activity/selectivity properties of the active phase, especially in well-dispersed catalysts [20]. The effects of pore size and surface area of activated carbon support on the catalytic performance of higher alcohols synthesis from synthesis gas have not been elucidated yet.

A good understanding of the relationship between porous characteristics and performance of the support is important for designing and selecting a catalyst system with a suitable pore structure for a particular application. The goal of the present research is to study the influence of the porous characteristics of commercially available activated carbons on the physico-chemical properties of the catalyst, as well as, the performance of higher alcohols synthesis from synthesis gas using alkali-modified trimetallic Co–Rh–Mo sulfided catalysts supported on various activated carbons. The higher alcohols synthesis reaction was also performed under similar reaction conditions using the Co–Rh–Mo–K/MWCNTs catalyst for comparing the MWCNTs support with that of different activated carbons.

Table 1
Textural properties of pure supports and catalysts.

Catalyst support	Pure support						Catalyst						
	S_{BET} (m^2/g)	S_{me} (m^2/g)	V_{tot} (cm^3/g)	V_{me} (cm^3/g)	D (nm)	% Me	S_{BET} (m^2/g)	S_{me} (m^2/g)	BE	V_{tot} (cm^3/g)	V_{me} (cm^3/g)	D (nm)	% Me
AC-Darco	658	197	0.93	0.35	1.95	38	97	41	0.79	0.16	0.08	7.21	50
AC-RX_3 Extra	1249	483	0.66	0.31	1.58	47	292	140	0.67	0.34	0.19	4.61	56
AC-Fluid Coke	245	161	0.17	0.13	2.81	76	127	87	0.26	0.10	0.08	3.03	80
AC-CGP Super	1739	1534	1.33	1.25	3.07	94	816	642	0.33	0.60	0.57	3.92	95
MWCNTs	188	162	0.53	0.52	11.34	98	68	59	0.48	0.24	0.24	17.91	100

S_{BET} – BET surface area; S_{me} – mesopore surface area; V_{tot} – total pore volume; V_{me} – mesoporous volume; D – average pore diameter; % Me – percentage of mesoporosity; and BE – blocking extent of the pores of the support due to metal loading.

2. Experimental

2.1. Preparation of MWCNTs supported catalysts

Four catalysts listed in Table 1 were prepared using different activated carbons. AC-Darco, brand named activated carbon was