

## Research Article

# Novel Ni-Co-Mo-K Catalysts Supported on Multiwalled Carbon Nanotubes for Higher Alcohols Synthesis

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Alkali-promoted Ni-Co-Mo catalysts supported on multiwalled carbon nanotubes (MWCNTs) were prepared using 9 wt% K, 4.5 wt% Co, and 15 wt% Mo, whereas Ni content was varied from 0 to 6 wt%. The catalysts were extensively characterized and studied for higher alcohols synthesis from synthesis gas. Alkali-promoted trimetallic catalyst with 3 wt% Ni showed the highest total alcohols yield of 0.284 gm/(gm of cat./h), ethanol selectivity of 20%, and higher alcohols selectivity of 32% at 330°C and 9.0 MPa using gas hourly space velocity (GHSV) of 3.8 m<sup>3</sup> (STP)/kg of catalyst/h and H<sub>2</sub> to CO molar ratio of 1.25.

## 1. Introduction

Ethanol has been used as an additive for reformulated gasoline as unleaded gasoline has become the standard, and short ether compounds (MTBE, ETBE, etc.) have been banned as gasoline octane continues to improve in North America [1]. The catalytic conversion of syngas to ethanol, and other higher alcohols, is generally recognized as an interesting route for the production of clean fuels and petrochemical feedstocks from coal, natural gas, and hydrocarbon wastes via gasification [2]. The catalysts for higher alcohol synthesis (HAS) are divided into two main groups based on the product distribution [3]. Alkali-doped high-temperature ZnCrO-based and low-temperature Cu-based catalysts produce mainly methanol and higher branched alcohols [4, 5]. Methanol synthesis catalysts modified with Fischer-Tropsch (FT) elements and modified Mo-catalysts are the second group of HAS catalysts. These catalysts yield a series of linear primary alcohols and gaseous hydrocarbons both with Anderson-Schulz-Flory (ASF) carbon number distribution [6, 7]. Comparatively, molybdenum-sulfide-based catalysts showed a high proportion of higher alcohols at lower pressure and high temperature. MoS<sub>2</sub>-based catalysts can tolerate sulfur and coke-buildup as a result of higher alcohols synthesis.

When MoS<sub>2</sub> is promoted with K<sub>2</sub>CO<sub>3</sub>, the same performance of the catalysts is achieved at a significantly lower temperature [8].

The alkali-promoted MoS<sub>2</sub> catalysts promoted with Co showed high activity to alcohols and can also produce alcohols with a variable ratio of methanol to higher alcohols by changing the operating conditions [9, 10]. The CO hydrogenation was studied over K/Co/Mo/Al<sub>2</sub>O<sub>3</sub> and K/Co/Mo/SiO<sub>2</sub> catalysts and found that all three elements are necessary for higher activity. Hydrocarbons and alcohols were produced in approximately equal amounts over both the catalysts [11]. Copromotion on alkali-modified MoS<sub>2</sub> catalysts leads to the shrinking of MoS<sub>2</sub> species, while Co exists mainly in the form of Co-Mo-S phase at low Co loading and partly in a Co<sub>9</sub>S<sub>8</sub>-like structure at high Co loading [12]. This structural modification leads to the enhanced C<sub>1</sub> → C<sub>2</sub> homologation step that improves the formation of ethanol as the dominant product [13].

Ni is known as Fischer-Tropsch element which has strong methanation tendency in CO hydrogenation reaction. The effect of Ni for the production of higher alcohols was studied using La-promoted Ni/K<sub>2</sub>CO<sub>3</sub>/MoS<sub>2</sub> catalysts [14]. The authors found that Ni enhanced not only the CO hydrogenation activity but also C<sub>2+</sub>OH selectivity. This

enhancement effect might be related to the improvement structure morphology of Ni and unique surficial chemical environment of the alkali-promoted MoS<sub>2</sub> catalyst. Moreover Hedrick et al. [15] concluded that nickel was unique in keeping high activity after sulfur treatment on the Group VIII metals, which is advantageous for the H<sub>2</sub>S-contained feed gas. Chung and Pien [16] concluded that nickel showed an excellent ability for CO insertion, which has an important significance for higher alcohol synthesis. The formation of Ni-Mo-S phase is related to the electron donation from Ni to Mo, decreasing the Mo-S bond strength to an optimum range, and thus significantly increasing the activity of the catalyst [17].

In our previous research, we have studied the effects of different loadings of active metals (Mo), alkali (K) promoters, and metal promoters (Co and Rh) on higher alcohols synthesis from synthesis gas using K-promoted monometallic, bimetallic, and trimetallic MoS<sub>2</sub> catalysts [8, 13, 18, 19]. The formation of hydrocarbons and methanol was significantly less over the K-promoted trimetallic catalyst compared to that of monometallic and bimetallic catalysts. It is important to prepare K-promoted trimetallic catalysts using inexpensive metals such as Ni, as explained in the literature, to replace Rh for higher alcohols synthesis from synthesis gas.

A multiwalled carbon nanotube (MWCNT) is a new form of carbon material which is drawing special attention as a catalyst support [18]. MWCNTs provide a relatively inert support and high-temperature stability, which is similar to that of activated carbon (AC) support [20]. MWCNTs exhibit well-defined hollow interiors and display exceptionally high mechanical strength, thermal stability, and electrical conductivity [21]. Their unique characteristics, such as appropriate pore-size distribution, and nanosized channels, make them a promising support in CO hydrogenation reactions [22]. In our previous research, we have compared higher alcohols synthesis from synthesis gas using alkali-promoted trimetallic Co-Rh-Mo-sulfided catalysts that are supported on AC and MWCNTs [19]. It was found that total alcohols space time yield (STY) and selectivity were higher on the MWCNTs-supported catalyst compared to catalysts supported on activated carbon. These results proved that support pore-size influenced particle size distribution, dispersion, and extent of reduction and plays an important role in diffusing the reactant molecules to the catalytically active centers that are located inside the pores [23]. The microporous structure of activated carbon-supported catalysts caused pore plugging due to the formation of coke and deactivation of the catalyst, which results in transport limitation in the reaction [24].

In the present paper, a series of MWCNTs-supported Ni-promoted catalysts with 9 wt% K, 4.5 wt% Co, and 15 wt% Mo are prepared by varying Ni content from 0 to 6 wt%, and the catalytic performance for higher alcohols synthesis over these catalysts is investigated at optimum operating conditions.

## 2. Experimental Method

**2.1. Preparation of Catalysts.** Commercially available MWCNTs are used as catalyst supports and the catalysts were prepared by conventional incipient wetness method, as described in our preceding papers [8, 13, 18, 19, 23–26].

Ammonium heptamolybdate tetrahydrate (AHM), potassium carbonate, cobalt acetate tetrahydrate, and nickel nitrate hexahydrate are used as precursors for Mo, K, Co, and Ni, respectively. At the first step, the support was impregnated with an aqueous solution of K<sub>2</sub>CO<sub>3</sub>, followed by drying at 120°C for 2 h, and stabilizing in an argon flow of 50 mL/min at 300°C, at a heating rate of 10°C/min for 4 h. The support was further impregnated with aqueous solutions containing the required amounts of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, Co(CH<sub>3</sub>COO)<sub>2</sub>, and Ni(NO<sub>3</sub>)<sub>2</sub>, followed by drying at 120°C for 2 h and stabilizing in an argon flow of 50 mL/min at 450°C, at a heating rate of 10°C/min for 12 h.

To obtain samples in sulfided form for characterization techniques, the catalysts were first sulfided for 6 h at 450°C and 500 psi, at a heating rate of 2°C/min using a gaseous mixture containing 10 mole% H<sub>2</sub>S in H<sub>2</sub> at a flow rate of 50 mL/min. The catalysts were then cooled to room temperature in a flow of He, and the sample was transferred to sample holders under protection of He.

**2.2. Catalyst Characterization.** The surface area, pore volume, and average pore diameter of sulfide samples were measured by N<sub>2</sub>-physisorption at 77 K using a Micromeritics ASAP 2000. Approximately 0.2 g of sample was used for each analysis. The moisture and other adsorbed gases present in the sample were removed before analysis by degassing the sample at 200°C for 2 h under 66.7 \* 10<sup>-6</sup> MPa (500 mmHg). The sample was then evacuated at 2.67 \* 10<sup>-6</sup> MPa (0.02 mmHg) before N<sub>2</sub> adsorption.

The contents of Mo, Co, and Ni of the sulfide catalysts were determined using a Perkin-Elmer ELAN 5000 inductively coupled plasma mass spectroscopy (ICP-MS) instrument.

Powder X-ray diffraction (XRD) analysis patterns of sulfide forms of samples were recorded on a Rigaku X-ray diffraction instrument with nickel filtered Cu K $\alpha$  radiation ( $\lambda = 0.1541$  nm). Each sample was scanned at a rate of 0.05°/s, with  $2\theta$  varying from 10 to 80°.

The morphology of the sulfided samples was characterized by transmission electron microscopy (TEM) investigations, using a Philips CM20 (100 kV) transmission electron microscope equipped with a NARON energy-dispersive spectrometer with a germanium detector.

**2.3. Catalytic Studies.** The catalytic conversion of synthesis gas to higher alcohols was performed using the feed gas mixture CO (40 mole%), H<sub>2</sub> (50 mole%), and Ar (10 mole%) in a single-pass tubular downflow fixed-bed reactor under the reaction conditions of 330°C, 9.1 MPa (1320 psig), and 3.8 m<sup>3</sup> (STP)/hr/(kg of catalyst) over a period of 48 h, including an induction period of 24 h. The detailed description about the high-pressure reaction set-up used in this study was discussed in our previous papers [8, 13, 18, 19, 23–26]. Prior to the reaction, the catalyst was reduced and sulfided for 6 h at 450°C at a heating rate of 2°C/min using a gas mixture containing 10 mol% H<sub>2</sub>S in H<sub>2</sub> and a flow rate of 50 mL/min. The product gas was cooled to 0°C and separated into gas and liquid phases at the reaction pressure. The liquid

TABLE 1: Elemental compositions of sulfided catalysts.

Catalyst	Targeted composition (wt%)				Measured composition (wt%)		
	K	Mo	Co	Ni	Mo	Co	Ni
Acid Treated MWCNT	—	—	—	—	—	—	—
Co-Mo-K/MWCNT	9	15	4.5	—	14.3	4.3	—
1.5 wt% Ni-Co-Mo-K/MWCNTs	9	15	4.5	1.5	13.9	4.1	1.2
3.0 wt% Ni-Co-Mo-K/MWCNTs	9	15	4.5	3.0	13.7	4.0	2.5
4.5 wt% Ni-Co-Mo-K/MWCNTs	9	15	4.5	4.5	14.1	3.8	3.9
6 wt% Ni-Co-Mo-K/MWCNTs	9	15	4.5	6.0	13.6	4.3	5.7

TABLE 2: Textural characteristics of catalysts in sulfide form.

Catalyst	BET surface area (m <sup>2</sup> /g)	Total pore volume (cc/g)	Average pore diameter (nm)
Acid Treated MWCNT	220	0.66	10.9
Co-Mo-K/MWCNT	89	0.36	15.7
1.5 wt% Ni-Co-Mo-K/MWCNTs	80	0.30	16.9
3.0 wt% Ni-Co-Mo-K/MWCNTs	72	0.25	17.4
4.5 wt% Ni-Co-Mo-K/MWCNTs	65	0.19	18.1
6 wt% Ni-Co-Mo-K/MWCNTs	57	0.12	18.8

products were collected at the end of the reaction and analyzed with a Varian 3400 gas chromatograph equipped with a capillary column and a flame ionization detector (FID). The gaseous products were analyzed online on a Shimadzu gas chromatograph through a sampling valve for every 1 h. The experiments were repeated at least twice to check reproducibility and to confirm that the results obtained were within the experimental error of  $\pm 2.5\%$ .

Mass balance calculations similar to those proposed by Bahome et al. [27] were used to calculate the % CO conversion, % CO<sub>2</sub> produced, product space time yield (STY), and alcohol selectivity (wt.%) and are given as follows:

% CO Conversion

$$= \frac{\text{Moles}(\text{CO}_{\text{in}} - \text{CO}_{\text{out}}) \times \text{gas contraction}}{\text{Moles}(\text{CO}_{\text{in}})} \times 100, \quad (1)$$

where the gas contraction was determined from the  $\text{Ar}_{\text{in}}/\text{Ar}_{\text{out}}$  calibration. Consider

$$\% \text{CO}_2 \text{ produced} = \frac{\text{Moles of CO}_2 \text{ produced}}{\text{Moles of CO}_2 \text{ converted}} \times 100, \quad (2)$$

$$\text{Product STY} = \frac{\text{Wt. of the product produced}}{\text{Wt. of cat./hr}}, \quad (3)$$

Alcohol Selectivity (wt.%)

$$= \frac{\text{Wt. of the alcohol produced}}{\text{Total wt. of the producted}} \times 100. \quad (4)$$

### 3. Results and Discussion

**3.1. Catalyst Characterization.** The Ni, Co, and Mo contents of the stabilized catalysts are measured by ICP-MS after sulfidation and are reported in Table 1 along with the targeted

compositions. The measured contents of the prepared catalysts are slightly lower compared to targeted values, which may be due to the hygroscopic nature of precursors.

Table 2 shows the results for surface area, total pore volume, and average pore diameter of the stabilized catalysts in sulfide form. The BET surface area of the MWCNTs increased from 178 to 220 m<sup>2</sup>/g after acid treatment. Acid treatment opens the nanotube caps and removes impurities from the MWCNTs. The MWCNT-supported bimetallic (4.5 wt% Co and 15 wt% Mo) catalyst promoted with 9 wt% K showed a BET surface area of 89 m<sup>2</sup>/g and a total pore volume of 0.36 cm<sup>3</sup>/g, increasing the amount of Ni from 1.5 to 6 wt% and decreasing the BET surface area of the MWCNT-supported alkali-promoted trimetallic catalysts from 80 to 57 m<sup>2</sup>/g and the total pore volume from 0.30 to 0.12 cm<sup>3</sup>/g.

The typical XRD patterns of the second screening catalysts are shown in Figure 1. Apart from the peaks for the support, MWCNTs ( $2\theta = 27$  and  $43.5^\circ$ ), there are no peaks with significant intensity indicating that the metal particles are finely dispersed and smaller than the detection limit of the XRD instrument.

TEM images of the catalysts were recorded and the representative image of a 3.0 wt% Ni-promoted Mo-K/MWCNT catalyst was selected from several micrographs and is shown in Figure 2. The carbon nanotube size and particle size are measured using imaging particle analyzer. The carbon nanotubes are multi-walled, with inner diameters in the range of 8–15 nm and wall thickness in the range of 5 to 10 nm. Most of the nanotube caps are found to be open. No amorphous carbon or other impurities are observed in and around the tubes. The particle sizes of the metal species that are inside ( $\sim 60\%$ ) and outside ( $\sim 40\%$ ) of the tubes are in the range of 3–5 nm. This revealed that the catalyst particles are well dispersed both inside the carbon nanotubes and on the outside of the tube walls.

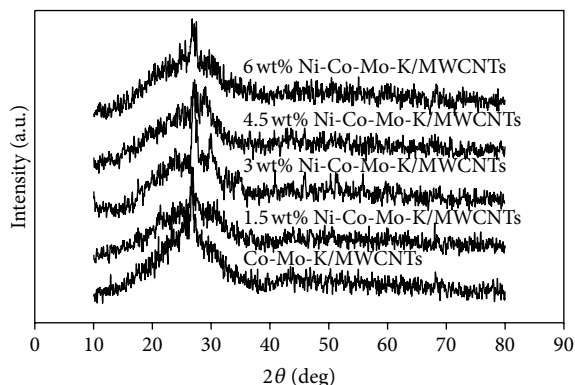


FIGURE 1: XRD patterns of catalysts in sulfide form.

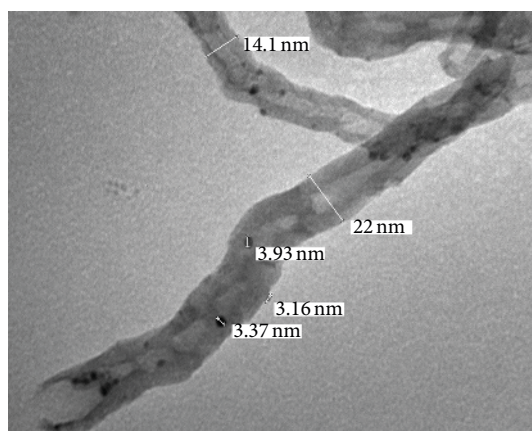


FIGURE 2: TEM image of 3 wt% Ni-Co-Mo-K/MWCNT.

**3.2. Catalytic Studies.** The catalyst activity studies towards higher alcohol synthesis reaction were carried out under similar conditions at 330°C, 9.1 (1320 psig), and 3.8 m<sup>3</sup> (STP)/hr/(kg of catalyst) over a period of 48 h, including an induction period of 24 h. Figure 3 gives the results of the percentage CO conversion as time-on-stream during 48 h of higher alcohols synthesis over MWCNT-supported alkali-modified Ni-promoted Co-Mo catalysts. CO conversion sharply reduced in the first 18 h and then levelled off, indicating that the catalyst was quite stable after 18 h of time-on-stream during the 48 h alcohol synthesis. A 43% CO conversion is observed on the alkali-modified bimetallic Co-Mo catalyst supported on MWCNTs. % CO conversion increased from 47% to 56% with increased Ni content from 1.5 to 6 wt% over the alkali-modified Ni-Co-Mo trimetallic catalysts supported on MWCNTs. The catalytic activity and product selectivity data were calculated after an induction period of 24 h.

The analysis of the liquid products indicates that linear alcohols are formed and no branched alcohols were observed in the GC trace corresponding to the higher alcohols. This analysis confirmed that higher alcohols synthesis from CO hydrogenation over alkali-modified trimetallic Ni-Co-Mo

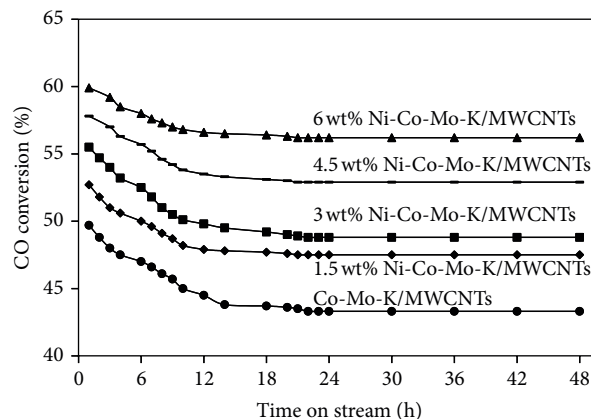


FIGURE 3: % CO conversion with time-on-stream (wt. of the catalyst = 2 g,  $P = 9.0$  MPa (1300 psig),  $T = 330^\circ\text{C}$ , GHSV = 3.8 m<sup>3</sup> (STP)/h/kg of catalyst, H<sub>2</sub>/CO molar ratio = 1.25).

catalysts likely follow a CO insertion mechanism as suggested by Santiesteban [31]. Methanol, ethanol, n-propanol, and n-butanol are the major products, together with other higher alcohols. The analysis of exit gas indicates that methane is the major component apart from CO<sub>2</sub> and unconverted gases, such as, CO, H<sub>2</sub>, and Ar.

Table 3 shows the activity and selectivity results obtained from CO hydrogenation over the sulfided alkali-modified Ni-Co-Mo catalysts. The term higher alcohols represents the ethanol and alcohols with a carbon number greater than 2 (C<sub>2+</sub> alcohols). The total alcohols and total hydrocarbons space time yields (STYs) of 0.239 and 0.352 gm/(gm of cat./h), respectively, are observed over the nickel-free MWCNT-supported catalyst. With the addition of 1.5 wt% Ni on the MWCNT-supported 4.5 wt% Co, 15 wt% Mo, and 9 wt% K catalyst, the total alcohols and total hydrocarbon STY increased to 0.262 and 0.361 gm/(gm of cat.)/h, respectively. The methanol, ethanol, and higher alcohols selectivity increased from 5.3%, 16.8%, and 26.6% over the alkali-modified bimetallic Co-Mo/MWCNT catalyst to 7.1%, 18.9%, and 29.4% on the MWCNT-supported alkali-modified trimetallic catalyst promoted with 1.5 wt% Ni. By increasing the Ni loading from 1.5 to 3 wt% on the MWCNT-supported trimetallic catalyst, the total alcohols STY increased from 0.262 to 0.284 gm/(gm of cat.)/h and total hydrocarbons STY increased from 0.361 to 0.375 gm/(gm of cat.)/h. These results confirmed that nickel promoter not only improved the formation of alcohols but also benefited the formation of hydrocarbons.

The total alcohols STYs are comparatively low over 4.5 and 6 wt% Ni-promoted alkali-modified trimetallic catalysts supported on MWCNTs, than that of the catalyst with 3 wt% Ni content. Chung and Pien [16] observed the formation of NiO species at higher Ni content in H<sub>2</sub>-TPR studies. Hydrocarbon STYs of 0.388 and 0.403 gm/(gm of cat.)/h are observed over the alkali-modified trimetallic catalysts supported on MWCNTs promoted with 4.5 and 6 wt% Ni, respectively, which may be due to increased formation of

TABLE 3: Catalytic performance of sulfided MWCNT-supported catalysts (wt. of the catalyst = 2 gm,  $P = 9.0$  MPa (1300 psig),  $T = 330^\circ\text{C}$ , GHSV =  $3.8\text{ m}^3$  (STP)/hr/kg of catalyst,  $\text{H}_2/\text{CO}$  molar ratio = 1.25).

Catalyst	CO conversion (%)	Product STY (gm/(gm of cat.)/h)		CO <sub>2</sub> produced (mol. %)	Alcohol selectivity (wt %)			
		Total alcohols	Total Hydrocarbons		Methanol	Ethanol	Higher alcohols	Total alcohols
Co-Mo-K/MWCNTs	43.3	0.239	0.352	36.6	5.3	16.8	26.6	31.9
1.5 wt% Ni-Co-Mo-K/MWCNTs	47.5	0.262	0.361	37.1	7.1	18.9	29.4	36.5
3 wt% Ni-Co-Mo-K/MWCNTs	48.8	0.284	0.375	38.2	7.9	20.2	32.8	40.7
4.5 wt% Ni-Co-Mo-K/MWCNTs	52.9	0.275	0.388	40.1	7.5	19.5	32.1	39.6
6 wt% Ni-Co-Mo-K/MWCNTs	56.2	0.269	0.403	41.5	6.8	18.1	29.9	36.7

TABLE 4: Comparison of the activities of alkali-modified molybdenum-based catalysts promoted with transition metals.

Reference	Li et al., 2001 [28]	Li et al., 2001 [29]	Qi et al., 2003 [30]	Surisetty et al., 2010 [13]	Present work
Catalyst	Mo-K/AC	Co-Mo-K/AC	Ni-Mo-K	Co-Mo-K/MWCNT	Ni-Co-Mo-K /MWCNT
Temperature ( $^\circ\text{C}$ )	330	330	315	330	330
Pressure (MPa)	5.0	5.0	9.5	8.3	9.0
H <sub>2</sub> /CO molar ratio	2.0	2.0	2.0	1.0	1.25
GHSV (L/kg <sub>cat.</sub> /h) * ( $\text{h}^{-1}$ )	7200	*4800	6000	3600	3800
CO conversion (%)	13	14 (CO <sub>2</sub> -free)	23	45	49
STY of total alcohols † (g/g <sub>cat.</sub> /h)	†23.1	††0.199	0.220	0.236	0.284
†† (g/mL <sub>cat.</sub> /h) (mL/g <sub>cat.</sub> /h)					
STY of higher alcohols (g/g <sub>cat.</sub> /h) ‡ (CO mol/kg <sub>cat.</sub> /h) ‡‡ (mL/g <sub>cat.</sub> /h)	‡12.1	‡‡0.114	—	0.171	0.228
STY of hydrocarbon (g/g <sub>cat.</sub> /h) ††† (% of CO)	†††38	—	—	0.395	0.375
Total alcohols selectivity (wt%)	—	47 (CO <sub>2</sub> -free)	60 (CO <sub>2</sub> -free)	32	43

NiO species. These results confirmed that the methanation activity of the catalyst is increased at higher Ni (4.5 and 6 wt.%) contents. The selectivity of methanol, ethanol, and higher alcohols is found to be low on the 4.5 and 6 wt% Ni-promoted catalysts compared to that of catalysts with less Ni content, which can be explained due to the formation of hydrocarbons. The water-gas-shift reaction rate increased from 37% to 42% with increased Ni content from 0 to 6 wt% over the alkali-modified trimetallic catalysts supported on MWCNTs.

Figure 4 represents the molar percentage distribution of alcohols on 3 wt% Ni-promoted Co-Mo-K/MWCNTs catalysts. Ethanol is the major product (41%) together with methanol (22%), propanol (15%), and butanol (12%). A little amount of higher alcohols ( $C_n > 4$ ) up to octanol is also detected over these Ni-promoted CoMo-K/MWCNTs catalysts. These results confirmed that Ni promotes the activity

and selectivity toward higher alcohols (particularly ethyl alcohol).

Table 4 compares the activities of sulfided 3 wt.% Ni, 4.5 wt.% Co, 15 wt.% Mo, and 9 wt.% K supported on MWCNTs with those of other catalysts discussed in the literature. It can be observed from this table that the addition of transition metals such as Ni and Co to alkali-modified molybdenum-based catalysts improved CO hydrogenation which enhanced space time yield of methanol, higher alcohols, and hydrocarbons [13, 28–30, 32]. The catalyst with the highest activity from each work was selected for comparison purposes. From Table 4 it can be observed that the alcohol STY of 0.285 gm/(gm of cat./h) over sulfided alkali-modified Ni-Co-Mo catalysts supported on MWCNT at 1300 psig, 330 $^\circ\text{C}$ , 3.8 m<sup>3</sup> (STP)/hr/kg of catalyst and H<sub>2</sub>/CO molar ratio of 1.25 is better than that the catalyst performance reported in the literature.

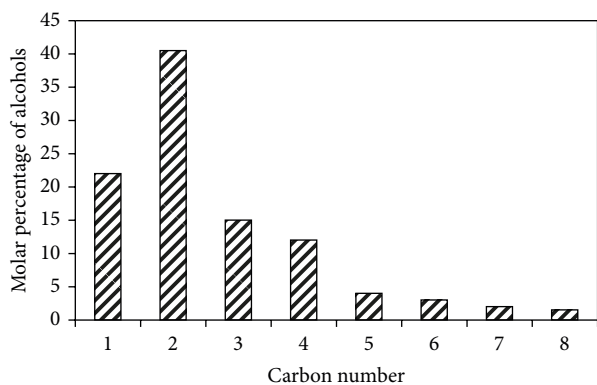


FIGURE 4: Molar percentage of alcohols over the catalyst 3 wt% Ni-Mo-K/MWCNTs (wt. of the catalyst = 2 g,  $P = 9.0$  MPa (1300 psig),  $T = 330^{\circ}\text{C}$ , GHSV =  $3.8\text{ m}^3$  (STP)/h/kg of catalyst,  $\text{H}_2/\text{CO}$  molar ratio = 1.25).

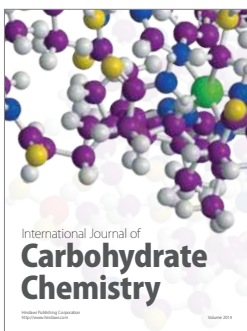
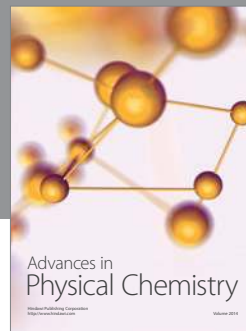
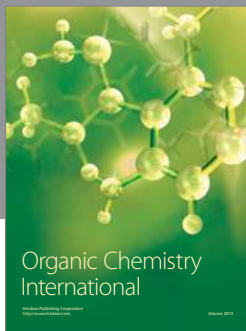
#### 4. Conclusions

The incorporation of Ni to the alkali-promoted bimetallic Co-Mo catalyst resulted in substantial changes in both structure properties and catalytic performance. Metal species were uniformly distributed both inside the tubes and on the outside of the tubes, with particle sizes in the range of 1 to 2 nm. The MWCNT-supported alkali-promoted trimetallic catalyst with 3 wt% Ni showed the highest total alcohols yield of  $0.284\text{ gm}/(\text{gm of cat.}/\text{h})$ , ethanol selectivity of 20.2%, and higher alcohols selectivity of 32.8% at  $330^{\circ}\text{C}$  and 8.96 MPa using gas hourly space velocity (GHSV) of  $3.8\text{ m}^3$  (STP)/kg of catalyst/h and  $\text{H}_2$  to CO molar ratio of 1.25. Ni-promotion to K-modified Co-Mo catalysts supported on MWCNTs improved the activity and selectivity toward higher alcohols (particularly ethyl alcohol).

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