Preparation and Characterization of Co–Mo/γ-Al$_2$O$_3$, Ni–Mo/γ-Al$_2$O$_3$ and (Co/Ni)–Mo/γ-Al$_2$O$_3$ Metal Oxides by Sol–Gel Process

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In this study, Co–Mo/γ-Al$_2$O$_3$, Ni–Mo/γ-Al$_2$O$_3$ and (Co/Ni)–Mo/γ-Al$_2$O$_3$ metal oxides have been prepared by the sol–gel process using citric acid and calcined at 800 °C for 5 h. Phases of synthesized materials were characterized with X-ray diffraction. Morphological analysis and elemental composition of oxides were determined by scanning electron microscope and energy dispersion spectroscopy. Surface analyses of the metal oxides have been studied using the Brunner–Emmett–Teller surface analyzer. Effects of substitution of cobalt and nickel together on the physical properties of the synthesized oxides were also investigated.

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1. Introduction

Hydrogen production has gained great importance in parallel with the spread of fuel cell technology in the last quarter century complementary to the development of alternative energy technologies [1]. Although water electrolysis is the best option to produce clean hydrogen, steam reforming and partial oxidation of hydrocarbons are the most common and economical processes for hydrogen production. Although carbon dioxide is a byproduct during hydrogen generation with these processes, methane has significant advantage due to its high H/C ratio. In general, catalytic hydrogen production process can be expressed in terms of the following reaction [2, 3]:

$$C_nH_mO_z + y(O_2 + 3.76N_2) + 2\left(n - y - \frac{z}{2}\right)H_2O$$
$$\rightarrow nCO_2 + 2\left(n - y - \frac{z}{2} + \frac{m}{4}\right)H_2 + 3.76yN_2. \quad (1.1)$$
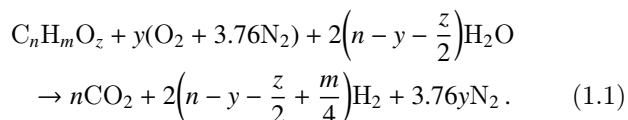
Hydrogen can be produced from hydrocarbon fuels such as natural gas, LPG, gasoline, diesel fuel, methanol and ethanol through steam reforming, partial oxidation and autothermal reforming. All of these processes can be operated at lower temperatures when catalysts are used [4]. Metal oxide catalysts are one of the most important and widely used categories of solid catalysts, either as active phases or supports. In addition to catalytic applications, these oxides are also in demand as photoconductive thin films, gas sensors, and in fuel cell and ceramic technologies. Literature indicates that nickel and cobalt-containing catalysts are very successful for fuel processing [4–6].

Molybdenum (Mo) is also an important component, and its physical and catalytic properties have been investigated in detail by Borowiecki et al. [7, 8]. In practice, Mo-based materials have been used as catalysts for hydrodesulphurization of petroleum feed stocks and the selective oxidation of alkenes in industrial processes. Unique catalytic functions of molybdenum oxides have recently been reported [7–9]. There are many studies that are focused on γ-Al$_2$O$_3$ supported catalysis, although there are only a few studies which involve molybdenum added γ-Al$_2$O$_3$ catalysts for the purpose of hydrogen production reaction. In this study, Ni–Mo/γ-Al$_2$O$_3$, Co–Mo/γ-Al$_2$O$_3$ and Co–Ni–Mo/γ-Al$_2$O$_3$ catalysts were prepared that can be suitable for hydrocarbon processing. Structural characterization was carried out using X-ray diffraction (XRD), scanning electron microscopy and energy dispersion spectroscopy (SEM-EDS) and the Brunauer–Emmett–Teller (BET) instrumental analysis techniques.

2. Experimental
2.1. Preparation of metal oxides

The Al$_2$O$_3$ supported Ni–Mo (M11), Co–Mo (M18) and Co–Ni–Mo (M24) catalysts were prepared by the sol–gel method. In the preparation procedure, aluminum nitrate hydrate was chosen as the support phase reagent and cobalt nitrate hydrate, nickel nitrate hydrate and ammonium molybdate hydrate as the metal precursors of the catalyst materials. After that 1 M aqueous solutions of citric acid — C$_6$H$_8$O$_7$ (Carlo Erba), and Al(NO$_3$)$_3$·9H$_2$O (Merck) were pre-mixed, and 0.25 M aqueous solutions of Ni(NO$_3$)$_2$·6H$_2$O (Carlo Erba), Co(NO$_3$)$_2$·6H$_2$O (Carlo Erba), and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (Riedel–De Haen) solutions were added to the mixture.

In the preparation procedure, first an aqueous solution of aluminum hydrate was added dropwise to the citric acid solution under vigorous stirring at room temperature for approximately 30 min. Subsequently, nickel and/or cobalt and molybdenum solutions were added dropwise to this pre-mixture, and after stirring for 1 h, the pH value was adjusted to 6 with 2 M NH$_4$OH solution. Resulting hydrogel was aged overnight at room temperature, and the excess water was removed by a rotary evaporator at 75 °C until the catalyst gel was obtained. This gel was dried in an oven at 120 °C overnight.

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Dried precursor was kept in an oven with its temperature slowly increasing to 230 °C. At this stage, a significant yellow/brown vapor output was observed. After releasing the citrate–nitrate–ammonium vapor, the precursor was milled, and calcined in air atmosphere at 800 °C for 5 h, at 5 °C/min heating rate.

2.2. Characterization

Instrumental analysis with XRD, SEM-EDS and BET techniques were used for structural study of the samples. Characterization of crystal structure and determination of crystallographic parameters of the metal oxide catalysts were performed by XRD analyses. Samples were ground in an agate mortar and settled in an aluminum sample holder. X-ray diffraction analyses were carried out at ambient temperature using a Philips Panalytical X'Pert-Pro diffractometer in a diffraction angle range of 10° to 90° with Cu K_α radiation (λ = 0.15418 nm) at operating parameters of 40 mA and 45 kV with step

a size of 0.02° and speed of 1°/min. Phase identification of samples were performed by powder diffraction file (PDF) database which is available in X'Pert High Score Plus in Pan Analytical XRD equipment. Specific surface area of the catalysts were characterized by using the BET technique under N_2 adsorptive gas and He carrier gas at 77 K after outgassing at 0.6 Pa and 473 K, using Quantachrome, Nova 400E multi point BET Instrument. Microstructure and surface morphology of the catalysts were observed by field-emission gun scanning electron microscopy (CamScan Apollo 300 FEG-SEM equipment) and semi-quantitative elemental analyses were carried out with X-ray energy dispersive spectroscopy (Oxford EDS apparatus).

3. Results and discussion

XRD patterns of prepared metal oxide catalyst are given in Fig. 1 and parameters are listed in Table I.

TABLE I

Crystalline phase properties of catalysts sample.

Phase	$NiMoO_4$	$NiMoO_4$	$CoMoO_4$	Al_2O_3	Al_2O_3
reference code	00-031-0902	00-045-0142	00-021-0868	00-050-0741	00-047-1292
crystal system	monoclinic	monoclinic	monoclinic	cubic	cubic
space group	$C2/m$	$C2/m$	$C2/m$	$Fd-3m$	$Fd-3m$
a [Å]	9.5920	10.1840	10.2100	7.9390	7.9448
b [Å]	8.7550	9.2410	9.2680	7.9390	7.9448
c [Å]	7.6550	7.0189	7.0220	7.9390	7.9448
alpha (°)	90.0000	90.0000	90.0000	90.0000	90.0000
beta (°)	114.2400	107.0946	106.9000	90.0000	90.0000
gamma (°)	90.0000	90.000	90.0000	90.0000	90.0000

TABLE II

Surface areas of metal oxide catalysts according to BET methods and comparison by theoretical and EDS analysis.

Catalyst code	Catalyst	Surface area [m²/g]	Theoretical atomic ratio	EDS atomic ratio
M-11	Ni–Mo/γ-Al_2O_3	30.071	1–1–5	0.98–1.05–4.97
M-18	(Co/Ni)-Mo/γ-Al_2O_3	40.420	(0.5/0.5)–1–5	(0.52/0.51)–1.02–4.95
M-24	Co–Mo/γ-Al_2O_3	37.579	1–1–5	1.00–1.10–4.90

Characteristic crystalline peak of the sample M-11 (Ni–Mo/γ-Al_2O_3) represents two different monoclinic $NiMoO_4$ crystal structures (PDF number: 00-031-0902 and 00-045-0142) and cubic Al_2O_3 crystal structure (γ-Al_2O_3 structure) (PDF number: 00-050-0741). Characteristic crystalline peak of M-18 (Co/Ni–Mo/γ-Al_2O_3) represents only one monoclinic $NiMoO_4$ crystal structure (PDF number: 00-045-0142) and monoclinic $CoMoO_4$ crystal structure (PDF number: 00-021-0868) and cubic

Al_2O_3 crystal structure (γ-Al_2O_3 structure) (PDF number: 00-050-0741). The sample M-24 (Co–Mo/γ-Al_2O_3) represents monoclinic $CoMoO_4$ crystal structure (PDF number: 00-021-0868) and cubic Al_2O_3 crystal structure (γ-Al_2O_3 structure) (PDF number: 00-047-1292).

Physicochemical properties of the prepared catalysts are summarized in Table II. Although the catalysts have quite similar surface areas, the sample containing three metals (M-18) has the largest one.
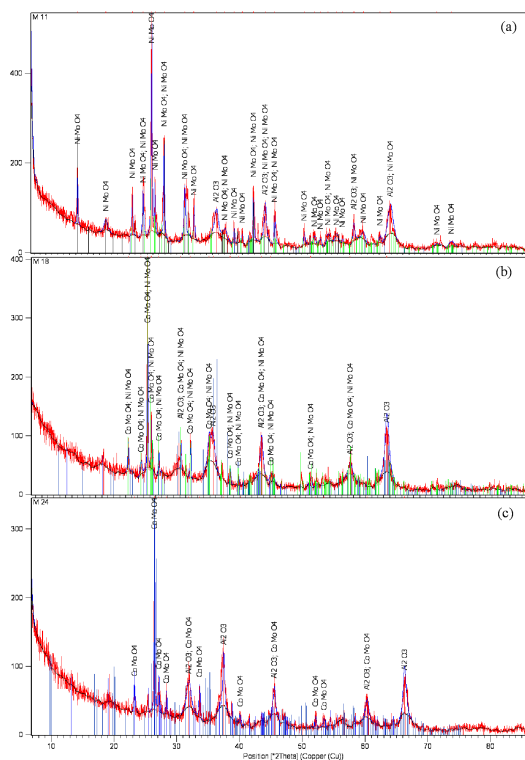
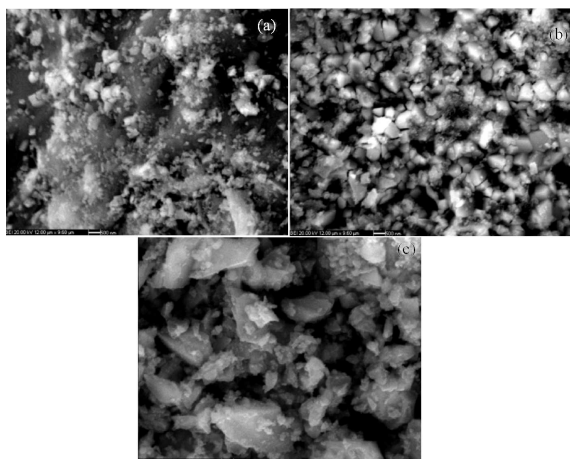Fig. 1. XRD spectra of metal oxide catalysts: (a) M-11, (b) M-18, (c) M-24.

Fig. 2. SEM images of metal oxide catalysts (a) M-12, (b) M-18, (c) M-24.

The microstructures of prepared catalysts were determined using a SEM. The samples were fixed to the sample holder with carbon sticky band. Figure 2 shows SEM micrographs at $10000\times$ magnification obtained by backscattered electron detector. It can be easily seen that the sample M-18 has a more homogeneous structure in terms of particle size. Moreover, the images clearly show that the addition of a third metal ion improves dispersion in the metallic layer of the γ-Al_2O_3 surface.

Semi-quantitative elemental X-ray analysis (EDS) results are also given in Table II. These results indicate that the theoretical preparation ratios of Ni:Mo:Al, (Ni/Co):Mo:Al and Co:Mo:Al are compatible with the EDS results.

4. Conclusion

Metal oxide type catalysts with three different compositions were prepared with sol–gel method. XRD results showed the existence of monoclinic $NiMoO_4$, monoclinic $CoMoO_4$ and cubic Al_2O_3 also known as γ-Al_2O_3 crystal phases. BET surface area measurements indicated that the surface areas of prepared catalysts are quite close, and EDS analysis results are compatible with the theoretical ratios. SEM micrographs indicate that the third metal ion addition has promoted more homogeneous dispersion on the γ-Al_2O_3 support. In view of the results obtained, it can be concluded that the sol–gel process is quite satisfactory as a method for the catalyst preparation.

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