Performance of Co-Mo/Al$_2$O$_3$ Nano Catalyst for CAMERE Process in a Batch Reactor

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Reverse Water Gas Shift (RWGS) reaction is one of the main reactions that can be used to reduce greenhouse gas emissions. Through this reaction CO_2 is converted to CO to produce beneficial chemicals such as methanol. In the present study, Mo/Al$_2$O$_3$ and Co-Mo/Al$_2$O$_3$ catalysts were synthesised using impregnation method. The structures of the catalysts were studied using XRD, XRF and TEM techniques. Activity and selectivity of both catalysts were investigated in a batch reactor and the results indicate that addition of cobalt promoter to Mo/Al$_2$O$_3$ catalyst increased its activity and CO selectivity. Co-Mo/Al$_2$O$_3$ can be a suitable candidate for RWGS reaction in CAMERE (carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction) process.

Key words:
Reverse water gas shift (RWGS) reaction, Co-Mo/Al$_2$O$_3$ catalyst, selectivity, CAMERE process

Introduction

The amount of carbon dioxide in the atmosphere is increasing continuously. Its accumulation in the air is one of the major causes of global warming and the change at equilibrium condition of weather and the environment. Utilization of carbon dioxide and other greenhouse gases to produce useful chemicals could be a suitable solution to this problem. CO_2 is not just a greenhouse gas, but also an important source of carbon for producing organic chemicals, materials, carbohydrates, and fuels such as methanol, carboxylic acids and ethylene.[1–6]

It is important to note that the amount of CO_2 emitted as the concentrated CO_2–rich flue gases from electric power plants and effluent gases from industrial manufacturing plants have become much higher than the amount of carbon used for making most chemicals, organic materials and liquid transportation fuels.[7]

The conversion of CO_2 into chemical resources has been attempted by several methods to mitigate the greenhouse effects.[8,9] The RWGS can be used in some cases for control of CO_2 emission. In this reaction CO_2 is used to produce CO. The products of this reaction can be used in production of clean fuels such as methanol and dimethyl carbonate (DMC). The catalytic hydrogenation of CO_2 to form

methanol is one of the efficient processes being able to treat a large quantity of CO_2 and the produced methanol can be consumed in the conventional chemical industry.[10,11]

In recent years, most of the authors [12–15] considered carbon dioxide to be the direct source of methanol production but the yield of methanol produced from CO_2 is lower than CO.[16] The reverse water gas shift (RWGS) reaction,

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H = +41.3 \text{ kJmol}^{-1} \quad (1)$$

produces CO from CO_2; therefore, the yield of methanol production increases when RWGS reaction takes place upstream of methanol synthesis in a chemical plant. The commercial catalyst, Fe_2O_3/Cr_2O_3, is a logical candidate for the RWGS reaction for the purpose of methanol production. But, Fe_2O_3 in this catalyst is easily reduced into iron metal under high reaction temperature for the RWGS reaction.[17–19]

The products of RWGS reaction are CO and H_2O. However, at some level of CO, it may react with hydrogen in reaction medium to form methane according to the following side reaction:

$$CO + 3H_2 \leftrightarrow CH_4 + 3H_2O \quad (2)$$
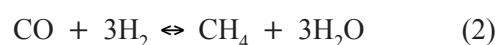
Using impregnation method instead of precipitation method in catalyst synthesis enhances CO selectivity in RWGS.[20] Also, addition of metals such as Fe, K and Pd supported on Al, Si and Ce can change CO selectivity in RWGS reaction.[20–22]

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Light hydrocarbons are by-products of RWGS reaction over many catalysts, and development of catalyst for this reaction also concerns its catalyst selectivity. In the present study, two catalysts (Mo/Al$_2$O$_3$ and Co-Mo/Al$_2$O$_3$) were compared in terms of their activity and CO selectivity for RWGS reaction in a batch reactor and better catalyst was proposed to CAMERE (carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction) process.

Experimental

Catalyst preparation

One-tenth mole of (NH$_4$)$_6$Mo$_7$O$_{24}$ ·4H$_2$O (Merck) was dissolved in one litre of distilled water. 11 grams of γ-Al$_2$O$_3$ (East Nano Material Co. Inc., 170 m^{2}g^{-1}, 99 % pure) per 3 grams of Molybdate complex, was added to the solution. The solution was stirred by a high speed mechanical stirrer for 10 h at 308 K, as molybdate anion was chemisorbed on the surface of γ-Al$_2$O$_3$ particles and Mo/Al$_2$O$_3$ catalyst was formed. The Co-Mo/Al$_2$O$_3$ catalyst was prepared by dropwise addition of Co(NO$_3$)$_2$ ·6H$_2$O (Merck Co., 99 % pure) solution (0.1 molar) to Mo/Al$_2$O$_3$ slurry. Impregnated samples were subsequently air-dried at 323 K for 10 h and calcined in air at 923 K for 5 h. All catalysts were reduced in H$_2$ at 600 °C and 2.5 MPa for 5 h before use in a batch reactor.

Characterization

The structures of these catalysts were studied using X-ray diffraction (XRD) patterns. The (XRD) patterns were obtained by a PW1840 X-ray powder diffractometer using Cu tube anode operated at 40 kV and 30 mA with step size 0.02 from 5° to 90°. The chemical composition of the promoted catalyst was determined by X-ray fluorescence using a XRF-1800 Shimadzu X-ray analyzer.

TEM images were obtained by a Phillips CM-120 scanning transmission electron microscopy at 120 kV. After pre-treatment, the catalyst samples were dispersed in methanol, and the solutions were mixed ultrasonically at room temperature. Samples of this solution were dropped on the grid to obtain TEM images.

RWGS reactor system

Reverse water gas shift reaction was carried out in a batch reactor. A thermocouple connected to a PID temperature controller was used for adjusting the temperature of the reaction. The reactor is cylindrical and had 1 litre volume. The length of reactor was 20 cm. Both catalysts were reduced under hydrogen (99.99 %) gas at a temperature of 873 K and a pressure of 2.5 MPa for 5 hours before use in batch reactor system. The reaction was performed in hydrogen to carbon dioxide ratio of 1 under 1 MPa of pressure. The catalyst loading was 5 g for each catalyst systems. The activities of both catalysts were studied at a temperature range of 573–973 K. An ice-water cold trap was placed at the outlet of the reactor to condense out any water from the product gas stream.

All products were analyzed by gas chromatography (Young Lin) equipped by Q and MS capillary columns and a HID detector. CO, H$_2$, CO$_2$, and CH$_4$ were detected by GC and their respective mole fractions were calculated from peak area with a third order calibration function. The initial yield of CO and CH$_4$ were repeated five times for each catalyst system. The results led to an estimated accuracy of ±3 % in our measurements.

Results and discussion

Fig. 2 shows the X-ray diffraction patterns for both catalysts (Mo/Al$_2$O$_3$ and Co-Mo/Al$_2$O$_3$). The phases Al$_2$O$_3$ (PDF 073–1512), CoMoO$_4$ (PDF 021–0868), MoO$_3$ (PDF 01–0706) and Al$_2$(MoO$_4$)$_3$ (PDF 023–0764) were identified in the X-ray diffraction pattern of the Co-Mo/Al$_2$O$_3$ catalyst. Whereas, the phases Al$_2$O$_3$ (PDF 073–1512) and MoO$_3$ (PDF 01–0706) were recognized in the pattern of the Mo/Al$_2$O$_3$ catalyst. The XRD results indicate that CoMoO$_4$ phase was apparent, when cobalt was added to Mo/Al$_2$O$_3$. Existence of CoMoO$_4$ phase in Co-Mo/Al$_2$O$_3$ catalyst after calcination shows that this phase was formed by solid state reaction between CoO and MoO$_3$. The XRF analysis confirms the presence of Co and Mo in the Co-Mo/γ-Al$_2$O$_3$ catalyst. This catalyst is in spherical particles form at 55–60 micrometre.
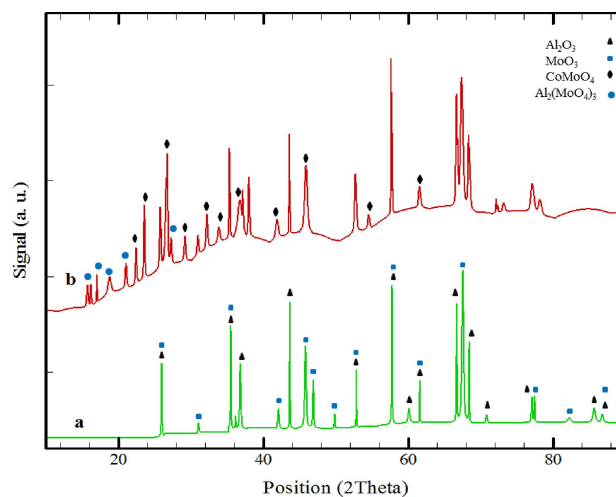

F i g . 1 – *The XRD patterns for calcined Mo/Al2O3(a) and Co-Mo/Al2O3(b) catalysts*

Fig. 3 shows CO$_2$ conversion of both catalysts after 15 minutes of RWGS reaction at 4 different temperatures in the batch reactor. As expected, CO$_2$ conversion increases as temperature increases. It is also apparent that the CO$_2$ conversion for Co-Mo/Al$_2$O$_3$ is higher than that of Mo/Al$_2$O$_3$ catalyst. Co-Mo/Al$_2$O$_3$ catalyst is more active than Mo/Al$_2$O$_3$; therefore cobalt can improve catalytic activity in RWGS reaction.
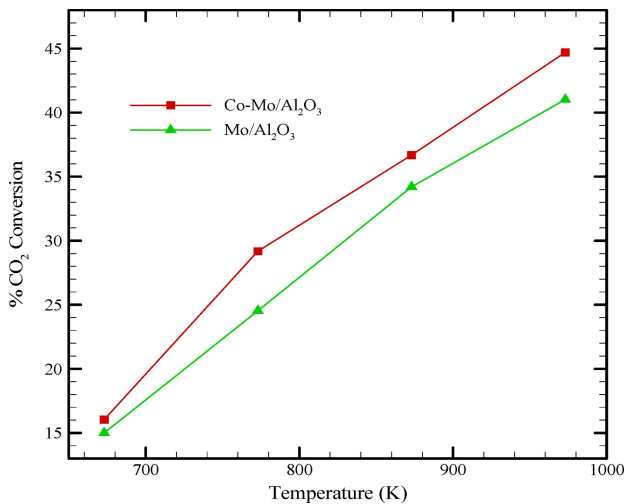

F i g. 3 – *CO$_2$ conversion versus temperature for both catalysts (reaction time = 15 min., H$_2$/CO$_2$ = 1, total pressure = 1 MPa)*

Fig. 4 demonstrates the CO$_2$ conversion versus time for both catalysts at 873 K. Upon the start of the reaction, all catalysts had nearly the same CO$_2$
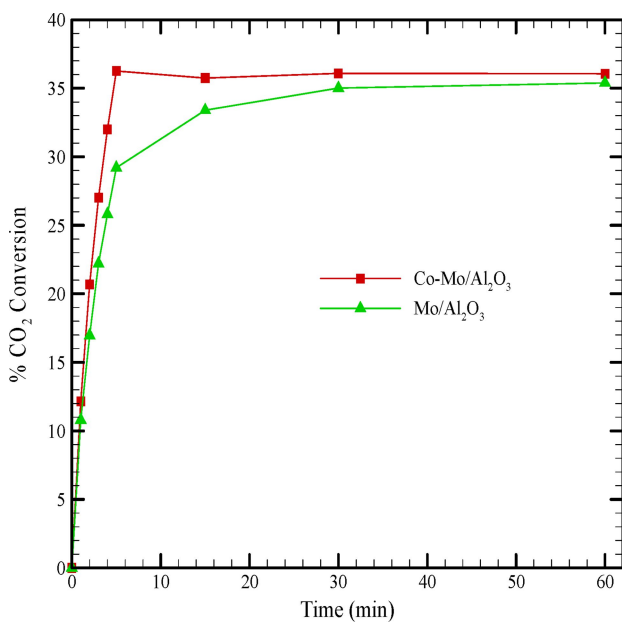

F i g. 4 – *CO$_2$ conversion versus time for both catalysts (reaction temperature = 873 K, H$_2$/CO$_2$ = 1, total pressure = 1 MPa)*

conversion. It takes 5 minutesfor the reaction to reach the maximum conversion on Co-Mo/Al$_2$O$_3$ catalyst, and after that a small decrease in CO$_2$ conversion is seen, which may be due to production of by-products such as methane.

Based on the results obtained, as long as the CH$_4$ formation is low, a rapid change in conversion of CO$_2$ to CO is observed, and as CH$_4$ formation for each catalysts increases, the change in CO production decreases. In other words, when the CO concentration reaches a definite amount, which is different for each catalyst, methane production starts to proceed according to equation 2. This difference could be due to selectivity of each catalyst. Selectivity is defined as follows.

$$\text{CO selectivity} = \frac{\text{moles of produced CO x l00}}{\text{moles of used CO}_2} \quad (3)$$

The CO selectivity of both catalysts versus temperature is demonstrated in Fig. 5. The CO selectivity of Co-Mo/Al$_2$O$_3$ gradually decreases as temperature increases. CO selectivity of Mo/Al$_2$O$_3$ monotonically increased when temperature was below 773 K. After reaching a maximum at 773 K, it slowly descended.
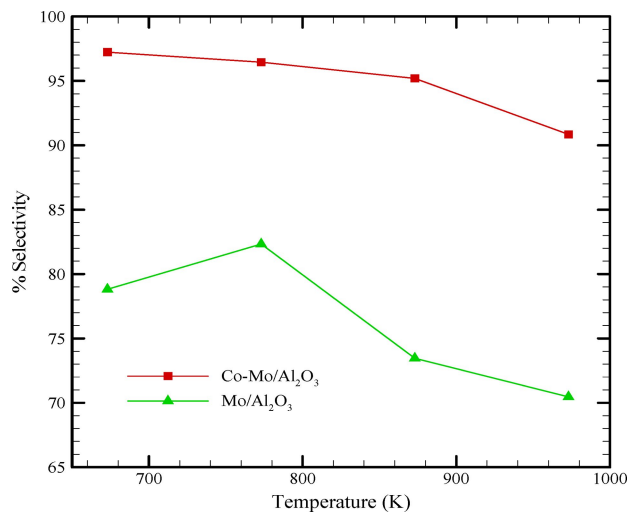

F i g. 5 – *CO selectivity versus temperature for both catalysts (reaction time = 60 min, H$_2$/CO$_2$ = 1, total pressure = 1 MPa)*

Fig. 6 illustrates the CO selectivity of both catalysts versus time. CO selectivity of Mo/Al$_2$O$_3$ catalyst is higher than Co-Mo/Al$_2$O$_3$ up to 30 minutes of reaction time and both catalysts have the same selectivity at 30 minutes of reaction time. As the reaction proceeds, the selectivity of Mo/Al$_2$O$_3$ catalyst significantly decreases. According to obtained results, Co-Mo/Al$_2$O$_3$ catalyst has higher overall CO selectivity in RWGS reaction.
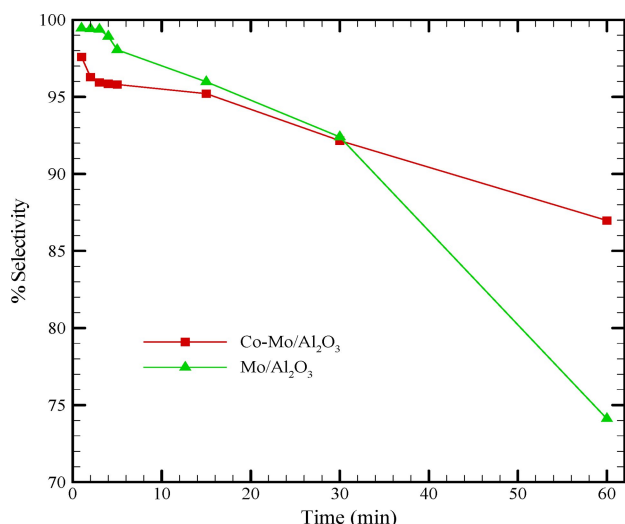
F i g .   6 – *CO selectivity versus time for both catalysts (reaction temperature = 873 K, H$_2$/CO$_2$ = 1, total pressure = 1 MPa)*

The stability of catalyst was conducted in a fixed bed reactor in a continuous period of time. Fixed bed contains catalyst in 55–60 micron particle size. The results indicate that catalyst deactivation was lower than 3 % at 40 hours of time. High-resolution TEM image of Co-Mo/Al$_2$O$_3$ catalyst is shown in Fig. 7. The results indicate that the average particle size is 20 nm and the catalyst particles are in spherical form.
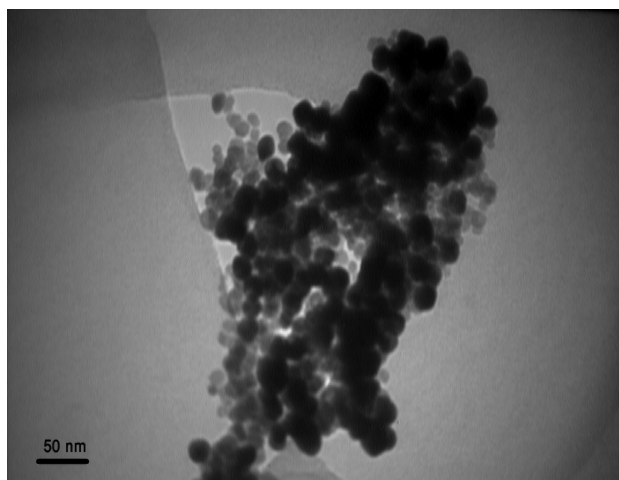

F i g .   7 – *TEM image of Co-Mo/Al$_2$O$_3$ catalyst*

Conclusions

Co-Mo/Al$_2$O$_3$ catalyst is more active than Mo/Al$_2$O$_3$; therefore cobalt can improve catalytic activity in RWGS reaction. According to obtained results, Co-Mo/Al$_2$O$_3$ catalyst also has higher overall CO selectivity in RWGS reaction. Finally, Co-Mo/Al$_2$O$_3$ can be a suitable candidate for RWGS reaction in CAMERE process.

List of symbols and abbreviations

CAMERE – CArbon dioxide hydrogenation to form MEthanol via a REverse-water-gas-shift reaction

XRD – X-Ray Diffraction

XRF – X-Ray Fluorescence

TEM – Transmission Electron Microscopy

RWGS – Reverse-Water-Gas-Shift

DMC – Dimethyl carbonate

HID – Helium Ionization Detector

GC – Gas Chromatography

MS – Molecular Sieve

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