# Selectivity and Performance of Ni-Mo/γ-Al₂O₃ Catalyst for Methanol Production with Reverse Water Gas Shift (RWGS) Reaction

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**Abstract:** One of the main reactions that can be used to reduce greenhouse gases emissions is Reverse Water Gas Shift (RWGS) reaction. Through this reaction $CO_2$ is converted to CO to produce beneficial chemicals such as methanol. In this paper Mo/Al₂O₃ catalyst was prepared and then promoted with Ni ions through impregnation method to produce Ni-Mo/Al₂O₃ catalyst. The structures of the catalysts were studied using XRD, XRF and TEM techniques. Activity, selectivity and stability of both catalysts were investigated in a batch reactor and the results indicate that addition of Ni promoter to Mo/Al₂O₃ catalyst increased its activity and CO selectivity. Ni-Mo/Al₂O₃ showed acceptable catalytic stability during RWGS reaction. As a whole Ni-Mo/Al₂O₃ can be a suitable candidate for methanol production process from $CO_2$ using RWGS reaction.

## 1. Introduction

Emissions of pollutants from combustion of fuels in energy systems as well as manufacturing plants have caused major global problems involving not only the pollutants such as $NO_x$, $SO_x$, and particulate matter, but also the greenhouse gases (GHG) such as carbon dioxide ($CO_2$ ) and methane ($CH_4$). There are increasing concerns for global climate change (Levin, 1992; Melillo et al, 1993; Schimel, 1995) and thus heightened interest worldwide for reducing the emissions of GHG, particularly $CO_2$ (Halamann et al, 1999; Song, 2006; Gharibi Kharaji et al, 2011). Reduction in carbon dioxide ($CO_2$) emissions is one of the most important challenges of today Sahibzada et al, 1998).

The conversion of $CO_2$ into chemical resources has been attempted by several methods to mitigate the greenhouse effects (Kitamura and Tazuke, 1983; Jessop et al, 1995; Gharibi Kharaji et al, 2011). 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 (Joo and Jung, 2003; Gharibi Kharaji et al, 2011).

Methanol yield become high if the conversion of $CO_2$ to CO in the RWGSR is high because the CO can react with water on the methanol synthesis catalyst, chemically removing the water on the catalyst and forwardly driving methanol synthesis

reaction (Edwards, 1995). In this process, carbon dioxide and hydrogen were converted to CO and $H_2O$ by the RWGS Reaction, and then the mixture gas of $CO/CO_2/H_2$ was fed into the methanol reactor after removing the water. The RWGS reaction is given by equation,

$$CO_2 + H_2 \longleftrightarrow CO + H_2O \qquad (1)$$
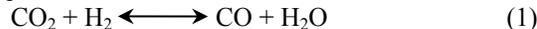
The development of an active and stable catalyst for the RWGSR was important for the Methanol production process (Joo and Jung, 2003). Methanol synthesis from a mixture of $CO/CO_2/H_2$ is an industrially important process, and Cu/ZnO-based catalysts are generally used for the reaction (Lee et al, 1993; Muhler et al, 1994; Liu et al, 1985; Chinchen et al, 1987). In this study activity, stability and CO selectivity of Mo/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts were investigated in RWGS reaction and better catalyst was proposed to methanol production from $CO_2$ by using RWGS reaction.

## 1. Experimental

### 1.1. Catalyst Preparation

One-tenth mole of $(NH_4)_6Mo_7O_{24}.4H_2O$ (Merck) was dissolved in one litre of distilled water. 11 grams of γ-Al₂O₃ (East Nano Material Co. Inc., 170 m²/g, 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-Al₂O₃ particles and Mo/Al₂O₃ catalyst was formed. The Ni-Mo/Al₂O₃ catalyst was prepared by dropwise addition of $Ni(NO_3)_2.6H_2O$ (Merck Co., 99% pure) solution (0.1 molar) to Mo/Al₂O₃ slurry.

Impregnated samples were subsequently air-dried at 323 K for 10 h and they were 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.

### 1.2. 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.

### 1.3. RWGS Reactors 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. Both catalysts were reduced under hydrogen 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. The sketch of the batch reactor is shown in Figure 1.

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.

### 2. Results and Discussion

Figure 2 shows the X-ray diffraction patterns for both catalysts ($Mo/Al_2O_3$ and $Ni-Mo/Al_2O_3$). The phases $Al_2O_3$ (PDF 073-1512), $NiMoO_4$ (PDF 031-0902), $MoO_3$ (PDF 01-0706) and $NiAl_{32}O_{49}$ (PDF 020-0777) were identified in the X-ray diffraction pattern of the $Ni-Mo/Al_2O_3$ catalyst. Whereas, the

phases $Al_2O_3$ (PDF 073-1512) and $MoO_3$ (PDF 01-0706) were recognized in the pattern of the $Mo/Al_2O_3$ catalyst. The XRD results indicate that $NiMoO_4$ phase was apparent, when nickel was added to $Mo/Al_2O_3$. Existence of $NiMoO_4$ phase in $Ni-Mo/Al_2O_3$ catalyst after calcination shows that this phase was formed by solid state reaction between NiO and $MoO_3$. The XRF analysis confirms the presence of Ni and Mo in the $Ni-Mo/\gamma-Al_2O_3$ catalyst.
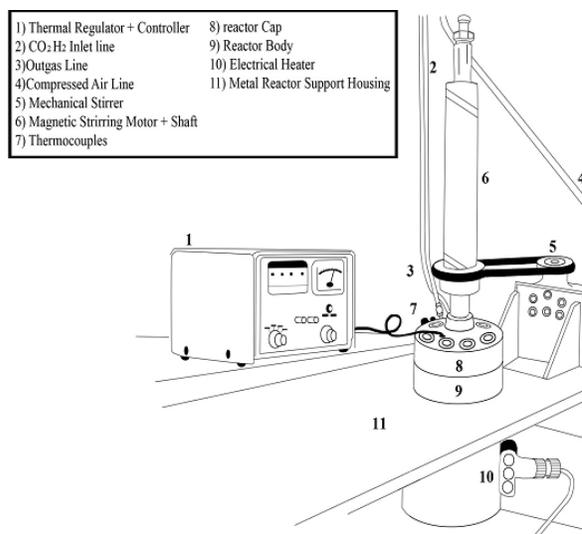


Figure 1: A schematic diagram of the batch reactor.
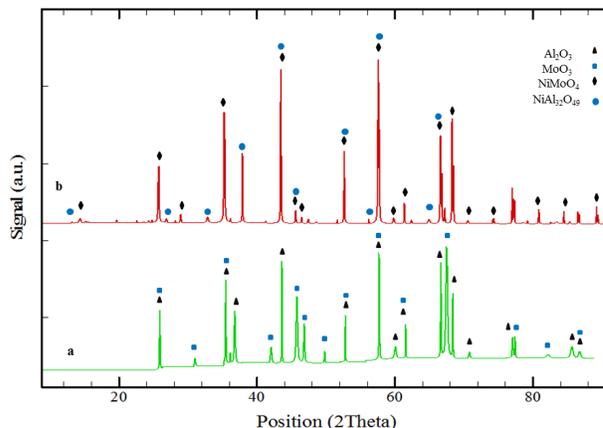


Figure 2: The XRD patterns for $Mo/Al_2O_3$ (a) and $Ni-Mo/Al_2O_3$ (b) catalysts.

According to the results shown in figure 3, at low temperatures the $CO_2$ conversions for both catalysts are close to each other and far from equilibrium conversions, but as the temperature increases, the differences in activity of the catalysts become more apparent. $Ni-Mo/Al_2O_3$ catalyst

reached the equilibrium conditions at temperatures above 773 K after 15 min of reaction time but $Mo/Al_2O_3$ catalyst did not reach the equilibrium conditions during this reaction time.
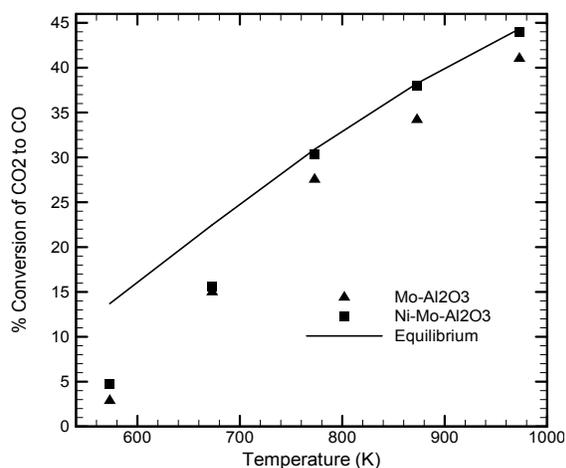


Figure 3: Conversion of $CO_2$ to CO versus temperature after 15 min of reaction time for $Mo/Al_2O_3$ and Ni- $Mo/Al_2O_3$.

Figure 4 shows the catalytic activity as function of time for $Mo/Al_2O_3$ and $Ni-Mo/Al_2O_3$ catalysts at 873 K. Reactions were performed in $H_2/CO_2$ stream with 1:1 ratio and 1 MPa pressure. For both catalysts $CO_2$ conversion to CO increased with reaction time until 15 minutes of reaction and after that no significant change in the CO content of the reactor was observed. Soon after the reaction started both catalysts had nearly the same conversions and as reaction preceded further, the difference between their conversions became more significant.
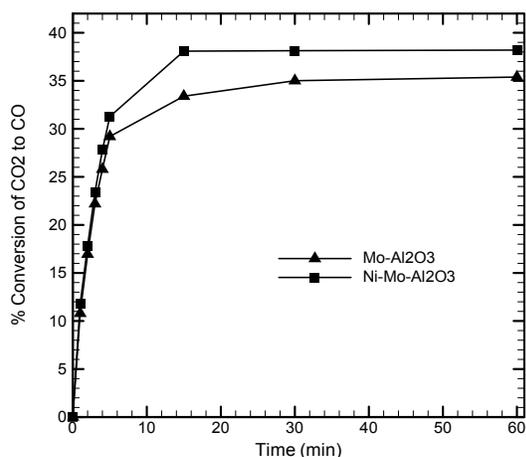


Figure 4: Conversion of $CO_2$ versus time at temperature of 873 K for $Ni-Mo/Al_2O_3$ and $Mo/Al_2O_3$ catalysts.

To investigate the reasons for the observed difference in conversions, the conversion of $CO_2$ to methane versus time was plotted in figure 5. The results show that at reaction times less than 15 min, both catalysts had same conversions to methane but after that time the methane conversion of $Mo/Al_2O_3$ started to deviate from that of $Ni-Mo/Al_2O_3$ and it became 1.9 times larger than $Ni-Mo/Al_2O_3$ methane conversion after 60 minutes of reaction.
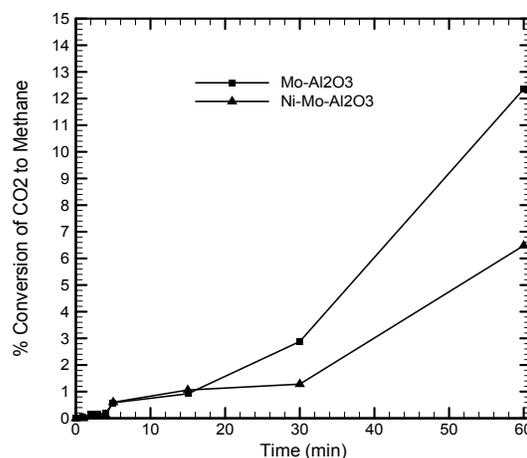


Figure 5: Conversion of $CO_2$ to Methane versus time at temperature of 873 K for $Ni-Mo/Al_2O_3$ and $Mo/Al_2O_3$ catalysts

According to the figures 3 and 4, Ni-$Mo/Al_2O_3$ catalyst reached the equilibrium conditions after 15 minutes of reaction at a temperature of 873 K whereas for the same condition, CO production for $Mo/Al_2O_3$ catalyst reached 86% of equilibrium conversion and remained constant after that.
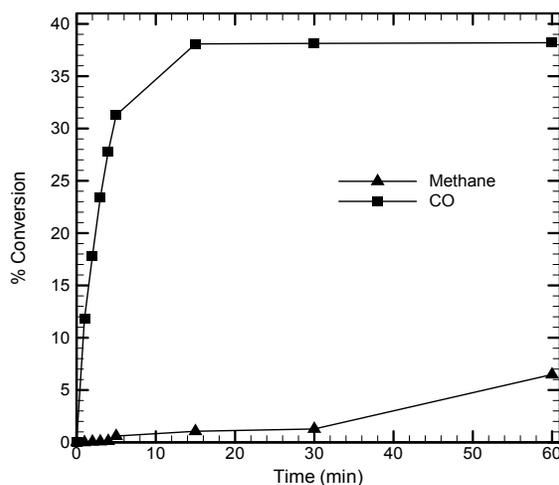


Figure 6: Methane and CO conversions versus time for $Ni-Mo/Al_2O_3$ at 873 K.

To better understand the catalytic behavior of both catalysts, the CO and $CH_4$ productions were analyzed at a temperature of 873 K during reaction time. Both catalysts had similar trends in variations of conversion for CO and $CH_4$ production. As an example this trend for Ni-Mo/$Al_2O_3$ is shown in figure 6.

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 the following reaction:

$$CO + 3H_2 \longrightarrow CH_4 + 3H_2O \qquad (2)$$

For both catalysts after 5 minutes of reaction, the slope of CO production curve decreases and at the same time methane production increases. At this time $CO_2$ conversions to CO for Mo/$Al_2O_3$ and Ni-Mo/$Al_2O_3$ Catalysts reach 76% and 82% of the equilibrium condition, respectively. This difference could be due to selectivity of each catalyst. Selectivity is defined as follows.

$$CO \text{ selectivity} = \frac{\text{moles of produced CO x l00}}{\text{moles of used } CO_2} \qquad (3)$$

CO selectivity for Ni-Mo/$Al_2O_3$ after 1 minute and 60 minutes of reaction time were 100% and 85% respectively and for Mo/$Al_2O_3$ they were 99% and 74% respectively. By comparing Mo/$Al_2O_3$ and Ni-Mo/$Al_2O_3$ catalysts in the presence of $H_2$, $CO_2$ and CO, it is found that Ni-Mo/$Al_2O_3$ has higher reaction progress for RWGS (equation 2) than Methanation reaction (equation 3).

Table 1 shows $CO_2$ conversion for fresh and used catalysts after 10 hours of reaction time. Mo/$Al_2O_3$ did not show any sign of deactivation during this time and Ni-Mo/$Al_2O_3$ showed a negligible sign of deactivation. Both catalysts maintained good stability after using it in 10 hours of reaction time but Ni-Mo/$Al_2O_3$ had a better activity for CO production. According to Table 1, used Mo/$Al_2O_3$ had lower CO selectivity than its fresh type, but Ni-Mo/$Al_2O_3$ showed the reverse behavior.

Pettigrew et al. (1994) in their study on Pd-$CeO_2$/$Al_2O_3$ catalyst for RWGS found out that used type of this catalyst had better CO selectivity than its fresh form. The same results for Ni-Mo/$Al_2O_3$ catalyst were observed in this study.

By addition of nickel, the initial rate of CO production over Ni-Mo/$Al_2O_3$ catalyst increased to 9.2%. In spite of the difference in initial rate of CO formation over Ni-Mo/$Al_2O_3$, the variation in rate of CO formation is the same for both catalysts.

Table 1: CO activity and selectivity for fresh and used catalysts at 873 K after 15 minutes of reaction time.

| Catalysts | Type | % $CO_2$ conversion to CO | %CO selectivity |
|---|---|---|---|
| Mo | Fresh | 34.2 | 97 |
| | Used | 34.2 | 93 |
| Ni-Mo | Fresh | 38 | 97 |
| | Used | 37 | 99 |

Throughout the reaction the rate of $CO_2$ conversion to CO for MO/$Al_2O_3$ was lower than that of Ni-Mo/$Al_2O_3$ and finally for both catalysts, $CO_2$ conversion decreased to nearly zero within 30 minutes of reaction. Figure 7 illustrates the results obtained for CO production rate versus time at 873 K for Ni-Mo/$Al_2O_3$ catalyst.
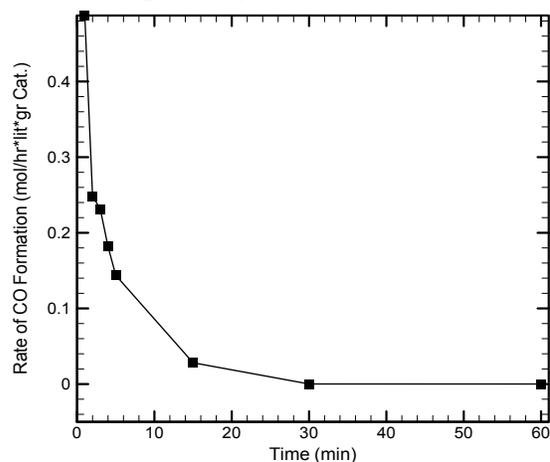


Figure 7: Methane and CO conversions versus time for Ni-Mo/$Al_2O_3$ at 873 K.

High-resolution TEM image of Ni-Mo/$Al_2O_3$ catalyst is shown in figure 8. The results indicated that the average particle size is 17 nm and the catalyst particles are in spherical form.
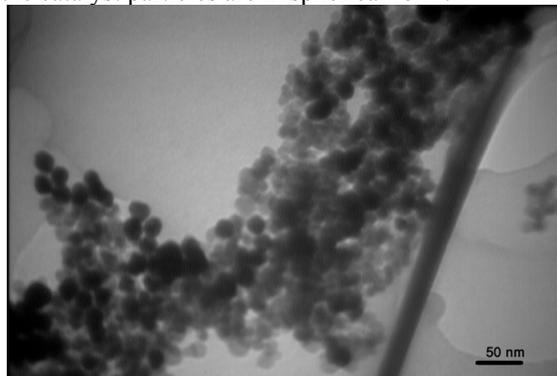


Figure 8: TEM image of Ni-Mo/$Al_2O_3$ catalyst.

In a similar study by joo et al (2003) in temperature range of 400 $^o$C to 700 $^o$C, it was shown that addition of ZnO to $Al_2O_3$ support will increase the activity of the catalyst but increases its deactivation rate. The deactivation is caused by conversion of Zinc Oxide molecules to Zinc ions. As a result it is anticipated that depositing metal ions on alumina support with co- impregnation method will prevent the deactivation of the catalyst. Using impregnation method instead of precipitation method in catalyst preparation can enhance CO selectivity in RWGS (Yan et al, 2000). Also addition of metals such as Fe, K and Pd supported on Al, Si and Ce can change CO selectivity in RWGS reaction (Pettigew et al, 1994; Yan et al, 2000; Perez-Alonso et al, 2008; Gharibi Kharaji et al, 2011).

### 3. Conclusion

The Ni-Mo/$Al_2O_3$ catalyst reached the equilibrium conditions at temperatures above 773 K after 15 min of reaction time but Mo/$Al_2O_3$ catalyst did not reach the equilibrium conditions during this reaction time. Soon after the reaction preceded both catalysts had nearly the same conversions and as time passed the difference between their conversions became more significant. CO production for Mo/$Al_2O_3$ catalyst reached 86% of equilibrium conversion and remained constant to the end of reaction. Since the initial conditions of reaction for both catalysts were the same, the difference in CO formation can be attributed to CO selectivity and activity of the catalyst. Ni-Mo/$Al_2O_3$ catalyst had good stability during the reaction and its CO selectivity improved as the reaction proceeded. In conclusion Ni-Mo/$Al_2O_3$ has a good activity, stability and CO selectivity in RWGS reaction and it is an appropriate candidate for converting $CO_2$ to CO and using the produced CO in Methanol synthesis process.

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6/8/2012