Promotion effect of iron on Mo/Al$_2$O$_3$ catalyst for the CAMERE process

Abolfazl Gharibi Kharaji and Ahmad Shariati

Petroleum University of Technology, Ahwaz Faculty of Petroleum Engineering,
Gas Engineering Department, Ahwaz, Iran. Corresponding author: A. Shariati,
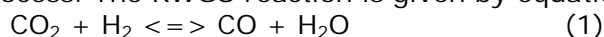shariati@put.ac.ir

Abstract. Reverse Water Gas Shift (RWGS) reaction is one of the main reactions that can be used to reduce greenhouse gases emissions. Through this reaction CO_2 is converted to CO to produce beneficial chemicals such as methanol. In this paper Mo-Al$_2$O$_3$ catalyst was prepared and then promoted with Fe ions through co-impregnation method to produce Fe-Mo-Al$_2$O$_3$ catalyst. XRD tests were taken to determine the structure of the catalysts. Activity, selectivity and stability of both catalysts were investigated in a batch reactor and the results indicate that addition of Fe promoter to Mo-Al$_2$O$_3$ catalyst increased its activity and CO selectivity. Fe-Mo-Al$_2$O$_3$ showed acceptable catalytic stability during RWGS reaction. As a whole, Fe-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: RWGS reaction, Fe-Mo-Al$_2$O$_3$ catalyst, methanol process, greenhouse gases.

Introduction. The anthropogenic emissions of greenhouse gases (GHGs) are due mainly to the fossil energy utilization. The major challenges in the 21st century supply clean fuels and eliminate environmental pollution problems and stabilize GHG emissions due to energy utilization. The mitigation of emissions of GHGs, particularly CO_2, and their effective utilization present to the world both a difficult challenge and a major opportunity for sustainable development in energy and environment. 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 (Melillo et al 1993; Halmann & Stainberg 1999; Park et al 2001; Maroto-Valer et al 2002; Song 2006).

It is important to note that the amounts 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 amounts of carbon used for making most chemicals, organic materials and liquid transportation fuels (Song et al 2002).

In recent years, most of the authors (Rozovskii & Lin 1990; Bussche & Froment 1996; Sun et al 1997; Sahibzada et al 1998; Ostrovskii 2002) consider carbon dioxide to be the direct source of methanol production but the yield of methanol produced from CO_2 is lower than CO (Edwards et al 1995). The RWGS can produce CO from CO_2; therefore the yield of methanol production is increased when RWGS reaction is used before methanol synthesis process. The RWGS reaction is given by equation:

$$CO_2 + H_2 <=> CO + H_2O \qquad (1)$$

The endothermic reverse water gas shift reaction can be used to produce CO from CO_2 at high temperatures over Fe, FeSi, Fe$_3$O$_4$, Fe-Cu, ZnO, Pt, Pt-Ca and Pt-Mg based catalysts (Roman-Martinez et al 1994; Kaspar et al 1994; Spencer 1995; Park et al 2001; Chen et al 2004) and this reaction was used at low temperatures over Cu, Cu-ZnO and Pd based catalysts (Koeppel et al 1992; Pettigrew et al 1994; Spencer 1995).

The commercial catalyst, Fe$_2$O$_3$/Cr$_2$O$_3$, was a logical candidate for the RWGS of the methanol production process. But, the Fe$_2$O$_3$/Cr$_2$O$_3$ catalyst was easily reduced into the iron metal under high reaction temperature for the RWGS reaction (Twigg 1989; Joo et al 1999; Joo & Jung 2003). In this study activity, stability and CO selectivity of both

catalyst systems ($Mo-Al_2O_3$ and $Fe-Mo-Al_2O_3$ catalysts) were investigated in RWGS reaction and better catalyst was proposed to methanol production from CO_2 by using RWGS reaction.

Material and Method. This experimental study was conducted in laboratory of Gas Engineering Department of Petroleum University of Technology in November 2011.

The 30 wt.% Mo/Al_2O_3 was prepared by one step co-impregnating γ-Al_2O_3 (Merck Co., 170 m^2/g, 99% pure) and with an aqueous solution of $Mo_7O_{24}.4H_2O$ (Merck Co., 99% pure). The $Fe-Mo-Al_2O_3$ catalyst with 15wt.% $Fe(NO_3)_2.6H_2O$ (Merck Co., 99% pure) and 15 wt.% Mo was prepared by two step co-impregnation method using the same γ-Al_2O_3 and Mo solutions. In the first step $Mo-Al_2O_3$ was formed and in the second step Fe ions were added to $Mo-Al_2O_3$ slurry. The resulting slurry solution was under stirring for 10 hours and then dried at 50°C for 5 hours. All catalysts were reduced in H_2 at 873 K and 2.5 MPa for 5 hours before use.

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 reaction was performed under the H_2/CO_2 at a total pressure of 1 MPa. The amounts of both catalyst systems used in the reaction were 5 g each. Activity tests of both catalyst systems were taken in the temperature range of 573-973 K. All products were analyzed by gas chromatography (Young Lin) equipped with 30 m Q and MS columns and an HID detector. CO, H_2, CO_2, and CH_4 were detected by GC and their respective mole fractions were calculated with a third order calibration function. Initial stability and activity tests were repeated 5 times with both catalysts and the results lead to an estimated accuracy of ± 3% in our measurements.

The structures of the prepared catalysts were determined from their X-ray diffraction (XRD) patterns with 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°.

Results and Discussion. The XRD patterns only indicated the specific Al_2O_3 peaks. Mo with impregnation method affected only slightly the textural properties of γ-Al_2O_3. The same result is also seen in the literature (Luna & Iriarte 2008; Wang et al 2009). The lines corresponding to Fe are not observed either, probably because it is found in very low proportion.

According to the results shown in Figure 1, the CO_2 conversions for $Fe-Mo-Al_2O_3$ is close to equilibrium conversions, at low temperature the difference in activity of the catalysts becomes more apparent. $Fe-Mo-Al_2O_3$ catalyst reached the equilibrium conditions at temperatures above 673 K after 5 min of reaction time but $Mo-Al_2O_3$ catalyst did not reach the equilibrium conditions during this reaction time.

Figure 2 shows the catalytic activity as function of time for both catalyst systems 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 5 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 proceeded further the difference between their conversions becomes more significant. Also the results show that, the methane conversion of $Mo-Al_2O_3$ is 30.9 times larger than $Fe-Mo-Al_2O_3$ after 60 minutes of reaction time, this difference can be originated from division of CO selectivity over each catalyst. On the other hand, methane was formed during RWGS reaction as the by-product and its formation for $Mo-Al_2O_3$ was greater than $Fe-Mo-Al_2O_3$ throughout reaction time, so this verifies division of CO conversion of $Mo-Al_2O_3$ from its equilibrium condition.

According to the Figures 1 and 2, $Fe-Mo-Al_2O_3$ catalyst reached the equilibrium conditions after 5 minutes of reaction at a temperature of 873 K whereas for the same conditions, CO production for $Mo-Al_2O_3$ catalyst reached 76% but after 15 minutes of reaction reaches 86% of equilibrium conversion and remained constant after that.
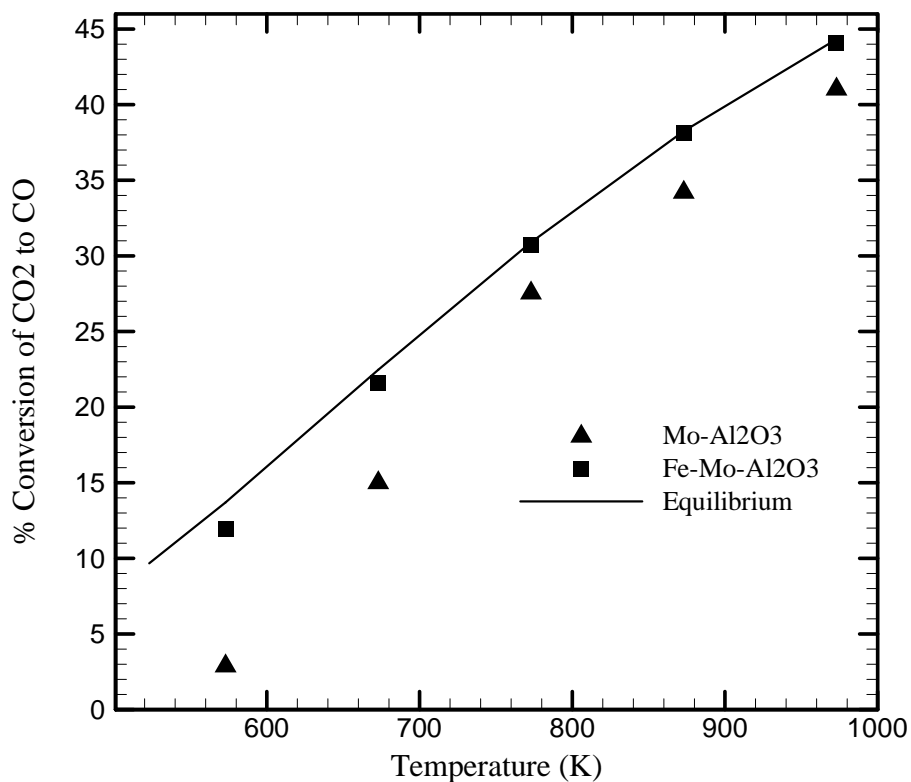
Figure 1. Conversion of CO_2 to CO versus temperature after 15 min of reaction time for Mo-Al$_2$O$_3$ and Fe- Mo-Al$_2$O$_3$.
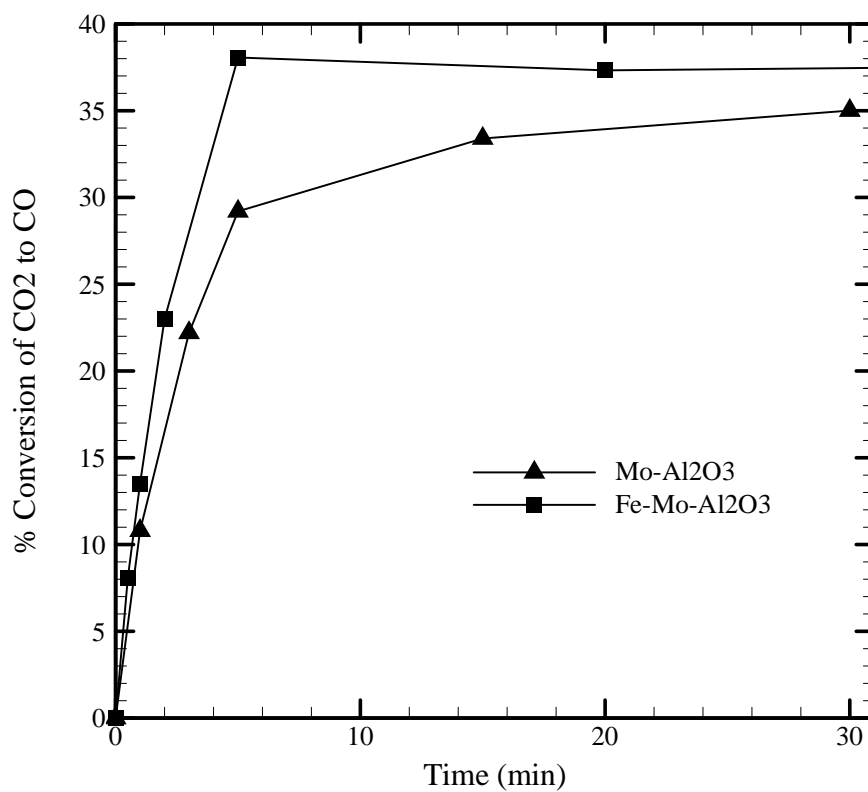

Figure 2. Conversion of CO_2 versus time at temperature of 873 K for both catalyst systems.

To better understand the catalytic behaviour of both catalysts, the CO and CH_4 productions were analyzed after 15 minutes of reaction time versus reaction temperature. Both catalysts had similar trends variations of conversion for CO and CH_4 production but $Mo-Al_2O_3$ had higher CH_4 production and lower CO production at each temperature. As an example this trend for $Fe-Mo-Al_2O_3$ is shown in Figure 3.
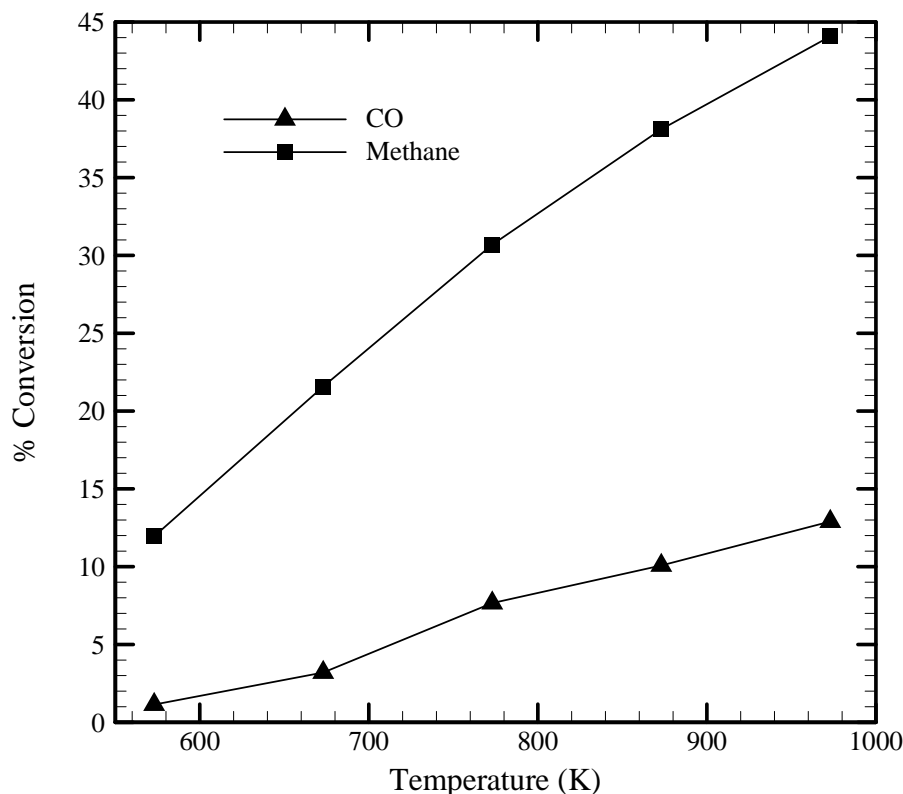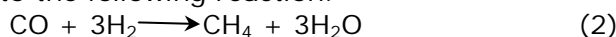

Figure 3. Methane and CO conversions versus time for $Fe-Mo-Al_2O_3$ at 873 K.

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 $Fe-Mo-Al_2O_3$ catalysts reach 76% and 99% of the equilibrium condition, respectively. This difference could be due to selectivity of each catalyst. Selectivity is defined as follows:

$$CO \text{ selectivity} = \frac{\text{moles of produced CO x } 100}{\text{moles of used } CO_2} \qquad (3)$$

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

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 reaction time and $Fe-Mo-Al_2O_3$ showed a negligible sign of deactivation. Both catalysts maintained good stability in 10 hours of reaction time but $Fe-Mo-Al_2O_3$ 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 $Fe-Mo-Al_2O_3$ showed the reverse behaviour. 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 $Fe-Mo-Al_2O_3$ catalyst were observed in this study.

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
$Mo-Al_2O_3$	Fresh	34.2	97
	Used	34.2	93
$Fe-Mo-Al_2O_3$	Fresh	38.1	98
	Used	37.5	99

Figure 4 illustrates the CO production rate versus time at 873 K for both catalyst systems. As it can be seen, the trend for CO formation of both catalyst systems is the same. However, the initial rate is 70% higher for $Fe-Mo-Al_2O_3$ catalyst system. After 20 minutes of reaction time no CO was formed for both catalyst systems.
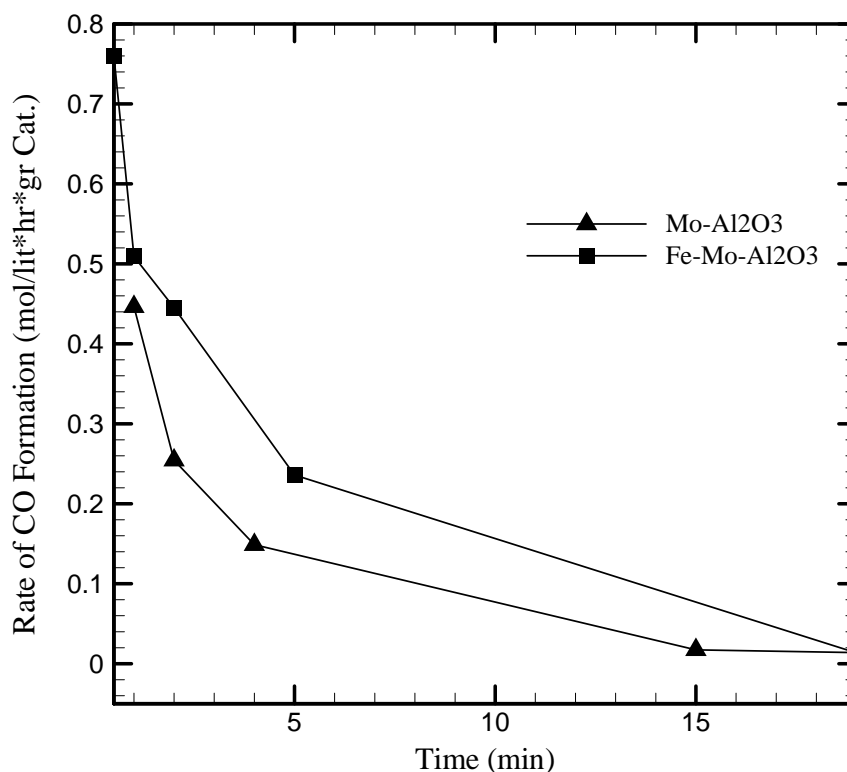

Figure 4. Methane and CO conversions versus time for both catalyst systems at 873 K.

In a similar study (Joo & Jung 2003) in temperature range of 673 K to 973 K, 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 (Pettigrew et al 1994; Yan et al 2000; Perez -Alonso et al 2008).

Conclusions. Fe-Mo-Al$_2$O$_3$ catalyst reached the equilibrium conditions at temperatures above 673 K after 5 min of reaction time but Mo-Al$_2$O$_3$ catalyst did not reach the equilibrium conditions during this reaction time. Soon after the reaction proceeded, both catalysts had nearly the same conversions and the difference between their conversions becomes more significant. CO production for Mo-Al$_2$O$_3$ catalyst reaches 86% of equilibrium conversion and remains constant as the time passes. 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. Fe-Mo-Al$_2$O$_3$ catalyst had good stability during the reaction and its CO selectivity improved as the reaction proceeded. In conclusion Fe-Mo-Al$_2$O$_3$ has better activity, CO selectivity and good stability in RWGS reaction and it is an appropriate candidate for converting CO$_2$ to CO and using the produced CO in Methanol synthesis process.

References

Bussche K. M. V., Froment G. F., 1996 A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al$_2$O$_3$ catalyst. Journal of Catalysis 161:1-10.

Chen C.-S., Cheng W.-H., Lin S.-S., 2004 Study of iron-promoted Cu/SiO$_2$ catalyst on high temperature reverse water gas shift reaction, Applied Catalysis A. 257:97-106.

Edwards J. H., 1995 Potential sources of CO$_2$ and the options for its large-scale utilisation now and in the future. Catalysis Today 23:59-66.

Halmann M. M., Steinberg M., 1999 Green house gas carbon dioxide mitigation: science and technology. Lewis Publishers. Boca Raton, pp. 563-568.

Joo O.-S., Jung K. D., Moon I., Rozovskii A. Ya., Lin G. I., Han S. H., Uhm S. J., 1999 Carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction. Industrial & Engineering Chemistry Research 38:1808-1812.

Joo O.-S., Jung K.-D., 2003 Stability of ZnAl$_2$O$_4$ catalyst for reverse-water-gas-shift reaction. Bull Korean Chem Soc 24:86-90.

Kaspar J., Graziani M., Rahman A. H., Trovarelli A., Vichi E. J. S., da Silva E. C., 1994 Carbon dioxide hydrogenation over iron containing catalysts. Applied Catalysis A. 117:125-137.

Koeppel R. A., Baiker A., Wokaun A., 1992 Copper/zirconia catalysts for the synthesis of methanol from carbon dioxide: influence of preparation variables on structural and catalytic properties of catalysts. Applied Catalysis A. 84:77-79.

Luna A. E. C., Iriarte M. E., 2008 Carbon dioxide reforming of methane over a metal modified Ni-Al$_2$O$_3$ catalyst. Applied Catalysis A. 343:10-15.

Maroto-Valer M. M., Song C. S., Soong Y., 2002 Environmental challenges and greenhouse gas control for fossil fuel utilization in the 21st Century. Kluwer Academic/Plenum Publishers. New York, pp. 203-274.

Melillo J. M., Mcguire A. D., Kicklighter D. W., Moore B., Vorosmarty C. J., Schloss A. L., 1993 Global climate-change and terrestrial net primary production. Nature 363:234-240.

Ostrovskii V. E., 2002 Mechanisms of methanol synthesis from hydrogen and carbon oxides at Cu–Zn-containing catalysts in the context of some fundamental problems of heterogeneous catalysis. Catalysis Today 15:141-160.

Park S.-W., Joo O-S., Jung K.-D., Kim H., Han S.-H., 2001 Development of ZnO/Al$_2$O$_3$ catalyst for reverse-water-gas-shiftreaction of CAMERE process. Applied Catalysis A. 211:81-90.

Perez-Alonso F. J., Ojeda M., Herranz T., Rojas S., González-Carballo J. M., Terreros P., Fierro J. L. G., 2008 Carbon dioxide hydrogenation over Fe–Ce catalysts. Catalysis Communications 9:1945-1948.

Pettigrew D. J., Trimm D. L., Cant N. W., 1994 The effects of rare earth oxides on the reverse water-gas-shift reaction on palladium/alumina. Catalysis Letters 28:313-315.

Roman-Martinez M. C., Cazorla-Amoros D., Linares-Solano A., Salinas-Martínez de Lecea C., 1994 Carbon dioxide hydrogenation catalyzed by alkaline earth and platinum-based catalysts supported on carbon. Applied Catalysis A. 116:187-204.

Rozovskii A. Ya., Lin G. I., 1990 Theoretical grounds of the process of methanol synthesis. Khimiya. Moscow (in Russian), pp. 107-189.

Sahibzada M., Metalfe L. S., Chadwick D., 1998 Methanol synthesis from $CO/CO_2/H_2$ over $Cu/ZnO/Al_2O_3$ at differential and finite conversions. Journal of Catalysis 174:111-118.

Song C. S., Gaffney A. M., Fujimoto K., 2002 CO_2 conversion and utilization. American Chemical Society, Washington DC, ACS Symposium Series 809:2-30.

Song C., 2006 Global challenges and strategies for control, conversion and utilization of CO_2 for sustainable development involving energy, catalysis, adsorption and chemical processing. Catalysis Today 115:2-32.

Spencer M. S., 1995 On the activation energies of the forward and reverse water-gas shift reaction. Catalysis Letters 32:9-13.

Sun Q., Zhang Y.-L., Chen H.-Y., Deng J.-F., Wu D., Chen S.-Y., 1997 A novel process for the preparation of Cu/ZnO and $Cu/ZnO/Al_2O_3$ ultrafine catalyst: structure, surface properties, and activity for methanol synthesis from CO_2+H_2. Journal of Catalysis 167:92-105.

Twigg M. V., 1989 Catalyst Handbook. Wolfe Publication. London. pp. 283-339.

Wang C. M., Tsai T. C., Wang I., 2009 Deep hydrodesulfurization over Co/Mo catalysts supported on oxides containing vanadium. Journal of Catalysis 262:206-214.

Yan S. R., Jun K. W., Hong J. S., Choi M. J., Lee K. Wan., 2000 Promotion effect of Fe–Cu catalyst for the hydrogenation of CO_2 and application to slurry reactor. Applied Catalysis A. 194:63-70.

Abolfazl Gharibi Kharaji, Petroleum University of Technology, Ahwaz Faculty of Petroleum Engineering, Gas Engineering Department, Ahwaz 6198144471, Iran, Telefax: (98)611-555-1754, e-mail: abolfazl.gharibi@yahoo.com

Ahmad Shariati, Petroleum University of Technology, Ahwaz Faculty of Petroleum Engineering, Gas Engineering Department, Ahwaz 6198144471, Iran, Telefax: (98)611-555-1754, e-mail: shariati@put.ac.ir