

## Selectivity and Performance of Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Nano Catalyst for Methanol Production with Reverse Water Gas Shift (RWGS) Reaction

A. Gharibi Kharaji<sup>1</sup>, A. Shariati<sup>1</sup>, M.A. Takassi<sup>\*2</sup>

<sup>1</sup>Department of Chemical Engineering, Petroleum University of Technology, Ahwaz 6198144471, Iran

<sup>2</sup>Department of Science, Petroleum University of Technology, Ahwaz, Iran,  
takassi@put.ac.ir

**Abstract:** Reverse Water Gas Shift (RWGS) reaction is one of the reactions in which CO<sub>2</sub> is transformed to other useful chemicals such as methanol. The RWGS reaction was carried out at a total pressure of 10 bars and at a temperature range of 573-973 K in a batch reactor using V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst and its iron promoted form. Both catalysts were activated by hydrogen at a pressure of 20 bars and at a temperature of 873 K in a batch reactor. The structures of these catalysts were studied using XRD, XRF and BET techniques. In present study, the effect of iron on the activity of V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and also CO selectivity of the promoted catalysts were investigated in the reverse water gas shift reaction. The results showed that the promoted Fe-V<sub>2</sub>O<sub>5</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst exhibits a better catalytic activity in RWGS reaction. The iron promoted V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst demonstrated the best catalytic activity for CO<sub>2</sub> conversion to CO for methanol production, at a reaction time of 45 seconds and at a reaction temperature of 773K. Stability test of Fe-V<sub>2</sub>O<sub>5</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was also carried out in a fixed bed reactor. This catalyst showed a high CO<sub>2</sub> conversion for 60 h of time on stream.

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**Keywords:** Global Warming; Fe-V<sub>2</sub>O<sub>5</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst; Methanol Production; RWGS Reaction, selectivity.

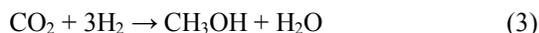
### 1. Introduction

The most energy utilization in the modern societies today is based on combustion of fossil fuels such as coal, crude oil and natural gas. Carbon dioxide is the product of complete oxidation or combustion of any material that contains carbon. 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 (Pettigrew et al, 1994; Edwards, 1995; Wainwright et al, 1995; Souma et al, 1995; Park et al, 1995; Ihm et al, 2001; Song, 2006).

Carbon dioxide is a very stable molecule thermodynamically. Therefore, a large input of energy, efficient reaction condition, and often active catalysts are required for the conversion of CO<sub>2</sub> into useful chemicals. In other words, many reactions for CO<sub>2</sub> conversion require positive changes in enthalpy and hence they are endothermic (Lange's HDBK, 1985; CRC Handbook, 1994). It is more energy-demanding if one could use only CO<sub>2</sub> as a single reactant, but it becomes easier thermodynamically if CO<sub>2</sub> is used as a co-reactant with another substance that has higher Gibbs free energy, such as CH<sub>4</sub>, graphite and H<sub>2</sub> (Song, 2002; Song, 2006).

It is important to note that the amounts of CO<sub>2</sub> sent out from electric power plants and effluents 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, 2002).

Several synthetic methods have been proposed for the conversion of CO<sub>2</sub> to useful chemicals (Lehn and Ziesel, 1990; Jessop et al, 1995; Doz and Leitner, 1995). Among all different reactions, the catalytic hydrogenation of CO<sub>2</sub> to form methanol seems to be an efficient process to treat a large quantity of CO<sub>2</sub>, minimizing the hydrogen loss contrasted with that of hydrocarbon production. Carbon dioxide hydrogenation is used in a large scale to form methanol via a reverse water gas shift reaction. In this process, at first the carbon dioxide and hydrogen react together to form CO and H<sub>2</sub>O (Equation 1). Then the mixture of CO/CO<sub>2</sub>/H<sub>2</sub> gases is fed into the methanol reactor after removing the water produced in the first step. The reactions for production of methanol are shown in equations 2 and 3. The higher conversion of CO<sub>2</sub> to CO in the first step (RWGS reaction) causes the higher yield of methanol in the process (Park et al, 2001; Joo et al, 2003).



In present study, two catalyst systems ( $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$  and  $\text{Fe-V}_2\text{O}_5/\text{Al}_2\text{O}_3$  catalysts) were compared in term of their activity and CO selectivity for RWGS reaction in a batch reactor. A batch reactor was chosen for better assessment of CO selectivity. Because in a batch reactor all products and reactants are available to the catalyst surface so catalyst selectivity can be studied in sufficient time for any by-product formation. The stability test of  $\text{Fe-V}_2\text{O}_5/\text{Al}_2\text{O}_3$  catalyst system which had better activity and CO selectivity was conducted in a fixed-bed reactor.

## 1. Experimental

### 1.1. Catalyst Preparation

Nano  $\gamma\text{-Al}_2\text{O}_3$  powder was purchased from East Nano Material Co. Inc. and used as a catalyst support.  $\text{Fe-V}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$  supported nano  $\gamma\text{-Al}_2\text{O}_3$  catalyst were prepared using impregnation method. The procedure is as follows: 0.05 mole of anhydrous vanadium pentoxide (Sigma Aldrich) was dissolved in 0.3 M sodium hydroxide (Kanto Chemical Co. Inc) solution. Then, 0.01 mole of hydrogen peroxide (Merck) was added to this solvent to complete oxidation. The solution was filtered. Then, it was acidified slowly with nitric acid down to PH equal to 6. At this time, the decavanadate anion was deposited on the nano  $\gamma\text{-Al}_2\text{O}_3$  powder (for each 1 g of complex 4 g nano  $\gamma\text{-Al}_2\text{O}_3$  powder).

In the first step, for each 1 gram of complex, 4 grams of nano (10-20 nm)  $\gamma\text{-Al}_2\text{O}_3$  was added to the decavanadate solution. It was stirred for 10 hours using a magnetic stirrer. Then the slurry solution was filtered to formation of  $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$  catalyst. It was washed with distilled water to remove the ionic co-products, and then it was dried at air. 0.01 mole of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck) was dissolved in sufficient distilled water and it was added drop wise to the chemisorbed  $\text{V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$  slurry. In the second step, the slurry solution was filtered. It was washed with distilled water to remove the ionic co-products, and then it was air dried to formation of  $\text{Fe-V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$  catalyst.

### 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  $5^\circ$  to

$90^\circ$ . The chemical composition of the promoted catalyst was determined by X-ray fluorescence using a XRF-1800 Shimadzu X-ray analyzer.

The specific surface areas of the samples were determined using the Brunauer–Emmett–Teller (BET) method with adsorption of nitrogen at liquid nitrogen temperature and subsequent desorption at room temperature after initial pretreatment of the samples by degassing at 573 K for 1 h. The BET surface area was obtained with a Quanta Chrome Quantasorb.

### 1.3. RWGS Reactors System

Tests of Selectivity of catalysts were carried out in a batch reactor for RWGS reaction. 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 activity of both catalyst systems 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.

Stability test of  $\text{Fe-V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$  catalyst system was conducted in a fixed-bed reactor. A schematic diagram of the experimental apparatus and the configuration of the fixed-bed reactor are shown in Figure 1. The reaction tube (20mm ID and 150mm length) was made from stainless steel. The mass flow rate was controlled and measured using mass flow controllers (Hitachi). The stability of the  $\text{Fe-V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$  catalyst was investigated under the reaction condition of 873 K and GHSV of 30,000 (ml/h.gcat.) with molar ratio of 1 under atmospheric pressure. Before the reaction take place, the catalyst was reduced in situ at 923 K for 4 h in 200 ml/min flow of hydrogen and nitrogen with hydrogen to nitrogen ratio of 1/5. The stability test was carried out at 873 K for the  $\text{Fe-V}_2\text{O}_5/\gamma\text{-Al}_2\text{O}_3$  catalyst. A cold trap at the outlet of the reactor was used to condense out any water from the gas product stream.

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

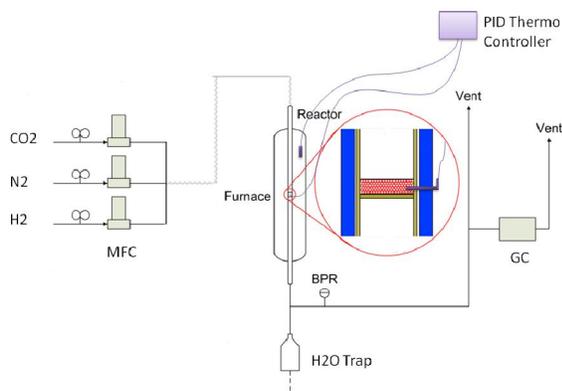


Figure 1: A schematic diagram of the stability experimental apparatus and the configuration of the fixed-bed reactor.

## 2. Results and Discussion

Figure 2 shows the XRD pattern for Fe- $V_2O_5/\gamma-Al_2O_3$  catalyst. The XRD pattern showed some peaks of  $V_2O_5$  at  $2\theta = 26.5, 31.8, 47.1, 67.5$  and other peaks of  $V_2O_5$  which appear in the same position as  $Al_2O_3$  that include peaks at  $2\theta = 25.6, 37.8, 52.6, 61.3, 66.5, 68.3, 76.9, 77.2$ . The lines corresponding to iron are not observed, because of its amorphous form over  $V_2O_5/\gamma-Al_2O_3$  and good dispersion. However, the XRF analysis confirms the presence of iron and vanadium in the Fe- $V_2O_5/\gamma-Al_2O_3$  catalyst. The surface areas of these catalysts were measured by the BET method. The surface areas of  $V_2O_5/\gamma-Al_2O_3$  and Fe- $V_2O_5/\gamma-Al_2O_3$  are  $158\text{ m}^2\text{ g}^{-1}$  and  $142\text{ m}^2\text{ g}^{-1}$  respectively.

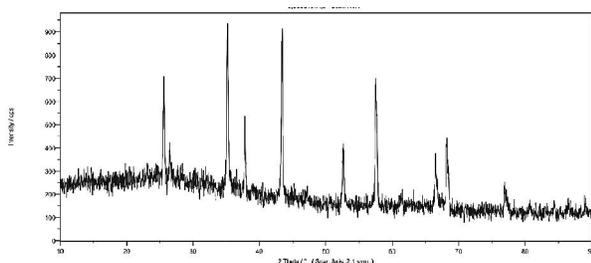


Figure 2: The XRD pattern for Fe- $V_2O_5/\gamma-Al_2O_3$  catalyst

The catalyst activity based on  $CO_2$  conversion for  $V_2O_5/\gamma-Al_2O_3$  and promoted  $V_2O_5/\gamma-Al_2O_3$  catalysts are demonstrated in Figure 3. Addition of promoter enhanced the catalyst activity. The RWGS reaction with promoted catalyst reached to the equilibrium conversion in 100 seconds.

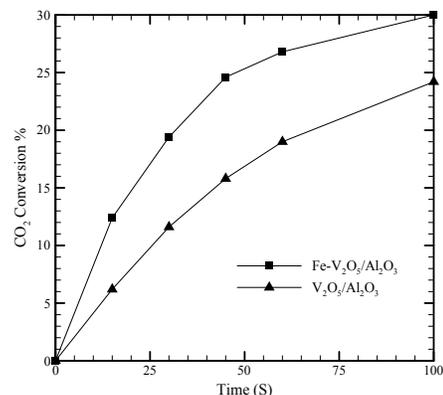


Figure 3:  $CO_2$  Conversion of two catalytic systems vs. time (temperature = 873 K,  $H_2/CO_2 = 1$ , total pressure = 1 MPa)

Figure 4 shows the effect of temperature on the reaction, when temperature increases the  $CO_2$  conversions of both catalyst systems reached to the equilibrium conversion. However, the  $CO_2$  conversion of promoted nano catalyst is closer to the equilibrium conversion. The difference between activities of  $V_2O_5/\gamma-Al_2O_3$  and its promoted catalyst becomes more obvious at the lower temperature.

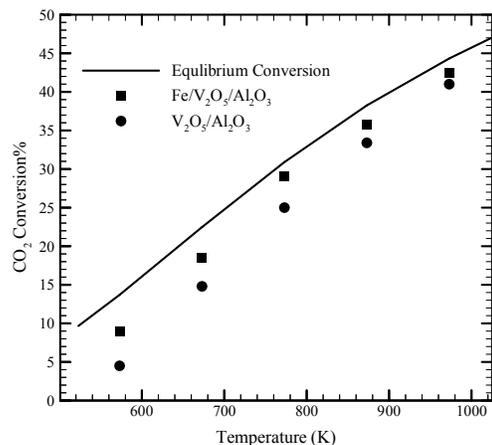


Figure 4: The  $CO_2$  conversion of both catalytic systems vs. temperature (time = 100 sec,  $H_2/CO_2 = 1$ , total pressure = 1 MPa)

Figure 5 demonstrates the rate of  $CO_2$  conversion with time. Increasing the reaction time, a decrease in  $CO_2$  conversion was observed. It could be due to the feed deficiency in reaction medium. When the promoted nano catalyst used, the reaction reaches to 80% of its equilibrium condition within 45 seconds of reaction time.

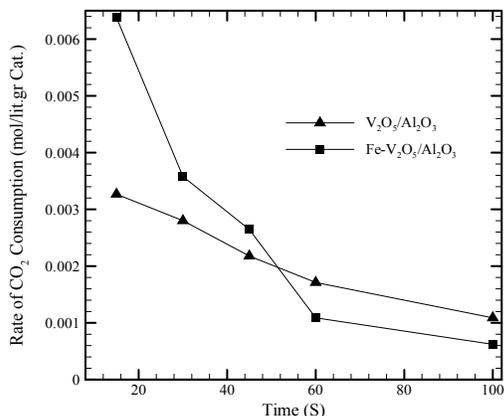


Figure 5: The rate of CO<sub>2</sub> consumption of two catalyst systems vs. time (temperature =873 K, H<sub>2</sub>/CO<sub>2</sub> =1, total pressure=1 MPa)

V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst started with a lower initial rate. When time of the reaction increases, the rate of CO<sub>2</sub> conversion decreases with a smaller slope. Both catalysts were tested for their activities. After 15 hours of operation time, they were deactivated slightly.

Stoichiometry of RWGS reaction expresses that Conversion of CO<sub>2</sub> and H<sub>2</sub> must be equal but they were not the same for the understudy catalysts. The difference originated from side reactions such as Fischer Tropsch and Methanation (Pettigrew et al, 1994; Yan et al, 2000; Pérez-Alonso et al, 2008). CO selectivity was defined in equation 4. The CO selectivity of the Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst was decreased by raising temperature (Figure 6) and it had a sharp change at temperatures higher than 773K. According to figures 2 and 4, at a temperature of 773 K, Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst reaches to the equilibrium condition and has an acceptable CO activity and selectivity.

$$\text{CO selectivity} = \frac{\text{moles of produced CO} \times 100}{\text{moles of used CO}_2} \quad (4)$$

The results of CO selectivity of Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst versus time (not shown here) indicate that CO selectivity decreases with reaction time. A CO selectivity of 88% was observed after 100 seconds of reaction time, while this selectivity was 97% in earlier reaction time (45 seconds) at the same operation conditions (P = 20 bars, T = 773K). The reduction in selectivity could be due to the formation of co-products. Using Fe promoted V<sub>2</sub>O<sub>5</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalyst, 80% conversion of CO<sub>2</sub> to CO was obtained in 45 seconds of reaction time at a temperature of 773K and a pressure of 20 bars. Therefore, the optimum time for production of CO through RWGS to produce methanol is 45 seconds.

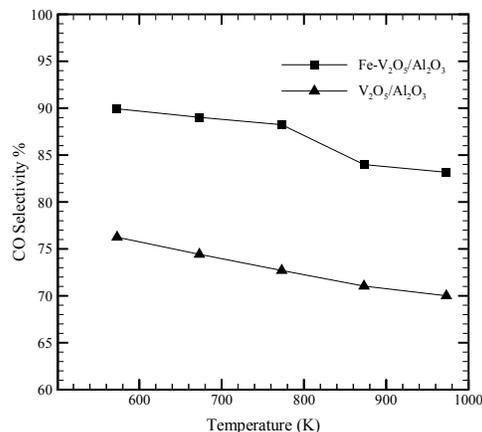


Figure 6: CO Selectivity for both catalyst systems vs. temperature (time=100 sec, H<sub>2</sub>/CO<sub>2</sub>=1, total pressure=1 MPa)

Stability test of the Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst is done at harsh operations condition. The stability of the catalyst was investigated under the reaction condition of 873 K and GHSV of 30,000 ml/h.gcat. The time-on-stream (TOS) analysis of the activity for the RWGS reaction was carried out for a continuous period of 60 h and the result is shown in Figure 7. This catalyst showed a high CO<sub>2</sub> conversion of 30%. It was evident that this catalyst exhibits good stability within a period of 60 h.

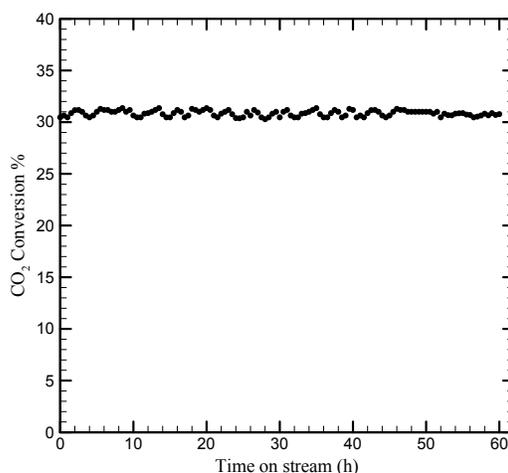


Figure 7: Stability of Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for RWGS reaction with respect to time on stream (873 K, CO<sub>2</sub>/H<sub>2</sub>=1:1, and GHSV= 30,000 ml/h.gcat)

### 3. Conclusion

The promoted nano γ-Al<sub>2</sub>O<sub>3</sub> catalyst (Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub>) showed a better catalytic activity than V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst for the reverse water gas shift reaction at the same operating conditions. The difference between activity of V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and

promoted catalyst is more obvious at lower temperatures and at higher temperatures they have almost similar behavior. The promoted nano catalyst has also reached sooner to the equilibrium conversion than unpromoted nano catalyst. Promoted nano catalyst reaches to 80% of equilibrium conditions after 45 seconds of reaction time and has higher initial rate of CO<sub>2</sub> conversion than V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. However, when the operation time increases, the prompted catalyst deactivated more than unpromoted nano γ-alumina catalyst, but it has demonstrated an acceptable stability.

The yield in methanol production is in accordance to CO conversion through RWGS reaction and its selectivity. Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst reaches the equilibrium conditions at 773K with an acceptable CO selectivity at this temperature. Yet the value of selectivity was 97% in the first 45 seconds of operation time and the reaction reached to 80% equilibrium conversion at the above mentioned time and temperature. Therefore, the optimum condition for the production of CO through RWGS to produce methanol is 45 seconds at reaction temperature of 773 K.

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#### Corresponding Author:

Dr. Mohammad Ali Takassi  
Department of science  
Petroleum University of Technology  
Email: [takassi@put.ac.ir](mailto:takassi@put.ac.ir)

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