

## Activity and Stability of Fe-V<sub>2</sub>O<sub>5</sub>/γ-Al<sub>2</sub>O<sub>3</sub> Nanocatalyst in the Reverse Water Gas Shift (RWGS) Reaction

A. Gharibi Kharaji<sup>1</sup>, M.A. Takassi<sup>2, +</sup> and A. Shariati<sup>1</sup>

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

<sup>2</sup>Science Department, Petroleum University of Technology, Ahwaz, Iran 6198144471

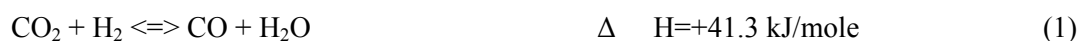
**Abstract.** Reverse Water Gas Shift (RWGS) reaction is one of the reactions in which CO<sub>2</sub> is transformed to other useful chemicals. The RWGS reaction was studied using nano γ-Al<sub>2</sub>O<sub>3</sub> catalyst and its promoted form catalyst (Fe-V<sub>2</sub>O<sub>5</sub>-Al<sub>2</sub>O<sub>3</sub>). The reaction was carried out with 10 bar total pressure and temperature 573-973 K in a batch reactor. Both catalysts were activated with hydrogen at 20 bars of total pressure and 873 K temperature in a batch reactor. The structure of Fe-V<sub>2</sub>O<sub>5</sub> species on the samples was determined by X-ray diffraction (XRD) and also X-ray fluorescence (XRF). In this paper the effect of Fe-V<sub>2</sub>O<sub>5</sub> on the activity and stability of nano γ-Al<sub>2</sub>O<sub>3</sub> based catalyst in the reverse water gas shift reaction was investigated. The results indicate that the promoted Fe-V<sub>2</sub>O<sub>5</sub>- γ-Al<sub>2</sub>O<sub>3</sub> exhibits a better catalytic activity that reaches to equilibrium conversion almost in 100 seconds at 773 K. However, it deactivated more than nano alumina.

**Keywords:** nanocatalyst, γ-Al<sub>2</sub>O<sub>3</sub> based catalyst, batch reactor, reverse water gas shift reaction, global warming.

### 1. Introduction

Carbon dioxide is one of the most important greenhouse gases that caused global warming. Carbon dioxide reduction is very important and urgent when global warming problems are becoming more and more serious. The increase of carbon dioxide concentration will seriously affect the equilibrium condition of weather and of the environment on earth. Consumption of greenhouse gases to produce useful chemicals could be a suitable solution to this problem [1-3].

The conversion of CO<sub>2</sub> to chemical resources has been studied by several methods; such conversion would reduce the greenhouse effects [4-6]. Considerably, the catalytic hydrogenation of CO<sub>2</sub> to form methanol is one of the efficient processes to treat a large quantity of CO<sub>2</sub>, minimizing the hydrogen loss contrasted with that of hydrocarbon production. Carbon dioxide hydrogenation to form methanol via a reverse water gas shift reaction convert CO<sub>2</sub> into methanol. In this process, carbon dioxide and hydrogen were converted to CO and H<sub>2</sub>O by the RWGS Reaction, and then the mixture gas of CO/CO<sub>2</sub>/H<sub>2</sub> was fed into the methanol reactor after removing the water. The higher conversion of CO<sub>2</sub> to CO in the RWGS reaction causes the larger yield of methanol in the process [7]. The RWGS reaction is given by the following equation,



For conventional industrial applications two types of RWGS catalysts are used. Fe-based high-temperature-shift (HTS) catalysts typically operate around 350–550 C. Because these catalysts are less susceptible to poisons, it is preferable to convert the bulk of the CO<sub>2</sub> at higher temperatures for many commercial applications. A more active Cu-based catalyst is typically used as a low-temperature shift (LTS) catalyst at 200–350 C [8-10].

---

<sup>+</sup> Tel: 98 9125788430

E-mail address: takassi@put.ac.ir; abolfazl.gharibi@yahoo.com

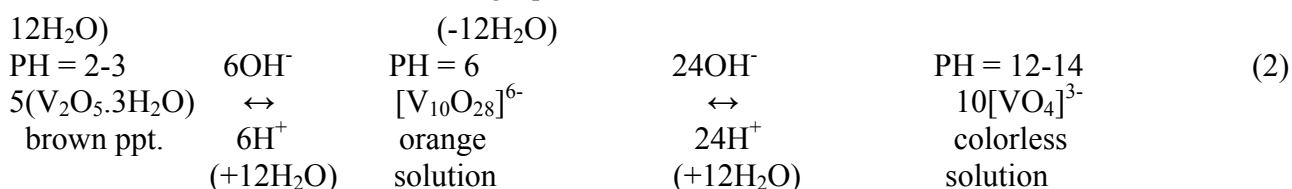
In literature, RWGS were carried out in low temperature (below 350 C) over Pd, Pt, Au, Ag, Cu, Cu-ZnO, Pt-K and Pt-Na based catalysts [11-15] and it was carried out in HTS over Fe, Fe<sub>3</sub>O<sub>4</sub>, ZnO, MgO and ZnFe<sub>2</sub>O<sub>4</sub> catalysts[16-18]. Fe-based HTS catalysts are far too inactive and pose serious volume and weight restraints. Cu-based LTS catalysts are very active at lower temperatures, but they become unstable at higher temperatures and their pyrophoric nature makes them undesirable for safe and efficient operation [9, 10].

The endothermic reverse water gas shift reaction can be used to produce CO from CO<sub>2</sub> at high temperatures over Fe, FeSi, Fe<sub>3</sub>O<sub>4</sub>, Fe-Cu, ZnO, Pt, Pt-Ca and Pt-Mg based catalysts [7, 19-22] and this reaction was used at low temperatures over Cu, Cu-ZnO and Pd based catalysts [16, 23, 24]. Moreover fuel cells operate efficiently on H<sub>2</sub>, but there are still some serious problems related to hydrogen accessibility and acceptability. Consequently, in order to promote fuel cells' commercialization, research must be aimed to the development of fuel cells able to operate with fuels other than hydrogen, such as commercial (e.g. natural gas, LPG, gasoline and diesel) or green fuels [25]. Biomass gasification produces gas mixtures of bio-fuels, that consist of H<sub>2</sub> (20–25%), CO (25–30%) and CO<sub>2</sub> (10–15%) [26]. Therefore, via RWGS reaction, it is possible to adapt the CO/H<sub>2</sub> ratio by converting the passive CO<sub>2</sub> to fuel CO and decreasing at the same time, the H<sub>2</sub> content in the gas mixture[27]. Herein, we report the activity and the characterization of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nano particles and Fe-V<sub>2</sub>O<sub>5</sub> supported  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nano particles as catalysts for the RWGS reaction.

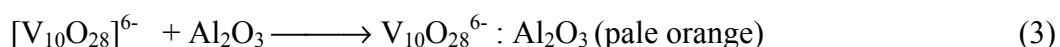
## 2. Experimental

### 2.1. Catalyst Preparation

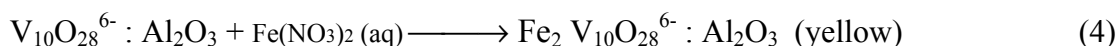
Nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles were purchased from East Nano Material Co. Inc. and used as a base catalyst for RWGS reaction. Fe-V<sub>2</sub>O<sub>5</sub> supported on nano particles (Fe-V<sub>2</sub>O<sub>5</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was prepared using a two-step co-impregnation method. Specifically, 0.05 mole of 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 to the V<sup>+5</sup> state. The Na<sub>3</sub>VO<sub>4</sub> was formed and the solution was filtered. Then the solution was acidified slowly with 6molar nitric acid down to PH equal to 6. These reactions are summarized in the following equilibrium.



In the first step, decavanadate anion was deposited on the nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder. Specifically for every 1 gram of complex, 4 grams of nano (10-20 nm)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was added to the decavanadate solution. The solution was stirred for 20 hours. After this time all decavanadate anion was chemisorbed evenly on the surface of nano powders. The deposition process is shown below:



0.01 mole of Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O (Merck) was dissolved in sufficient distilled water. Then the ferric complex was added drop wise to the chemisorbed decavanadate/nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> slurry, while the solution was stirred. Stirring was continued for 15 hours. The following reaction took place on the surface of nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>:



In the second step, slurry solution was filtered and washed with distilled water to remove the ionic co-products, and then was dried at air condition. The catalyst was reduced partially in a batch reactor at 873 K and 25 bars for 5 hours.

The structures of the prepared nano catalyst and support were determined from their X-ray diffraction (XRD) patterns with a PW1840 X-ray powder diffract meter using Cu tube anode operated at 40 kV and 30 mA with step size 0.02 from 5° to 90°.

### 2.2. Reaction apparatus and procedures

The activities of the catalysts were studied for the RWGS reaction at the temperature range of 573-973 K at 10 bars pressure with the H<sub>2</sub>/CO<sub>2</sub> ratio of 1 in the reactant gas. RWGS activity experiments were

conducted in a batch reactor at 10 bar pressure. K-type thermocouples were installed in the reactor for the measurement of reaction temperature. Catalyst (5 g) was placed in the reactor. The catalyst was reduced using  $H_2$  at 873 K for 5 hours prior to the experiment. Gas mixture containing 50%  $CO_2$ , 50%  $H_2$  was fed to the reactor. A condenser was used to dry the product stream before GC analysis. The gaseous effluent was analyzed using a GC (Young Lin) equipped with MS and Q columns and a HID detector.

### 3. Results and Discussions

Fig.1 shows the structure of the prepared nano supported catalyst which is taken from the XRD patterns. The patterns showed the slightly change in  $Al_2O_3$  peaks, and  $V_2O_5$  with impregnation method affected only slightly the textural properties of  $\gamma-Al_2O_3$ . The same result is also seen in the work of Wang et al [28]. The lines corresponding to Fe are not observed either, probably because it is found in very low proportion. The XRF results indicated the presence of Fe, V, and Al ions in the prepared  $Fe-V_2O_5/\gamma-Al_2O_3$  nanocatalyst.

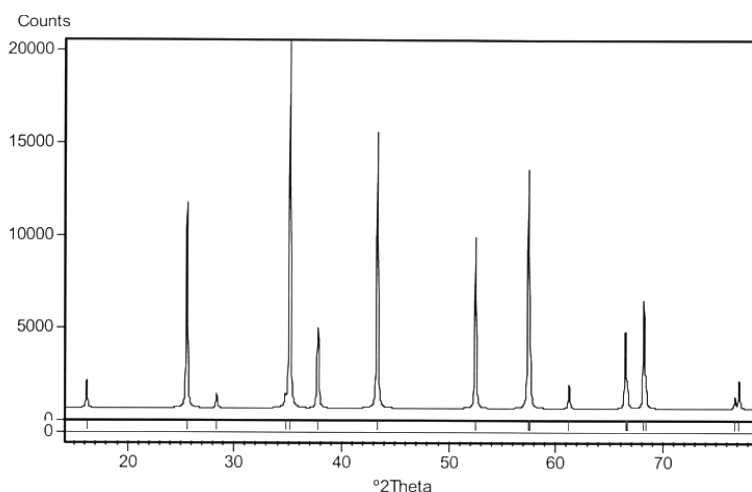


Fig. 1: X-ray diffraction of  $Fe-V_2O_5/\gamma-Al_2O_3$  catalyst.

The catalyst activity based on  $CO_2$  conversion for  $\gamma-Al_2O_3$  and promoted  $\gamma-Al_2O_3$  catalysts are shown in Fig. 2. Addition of promoter enhanced the catalyst activity. The RWGS reaction with promoted catalyst reaches to the equilibrium conversion in 100 seconds.

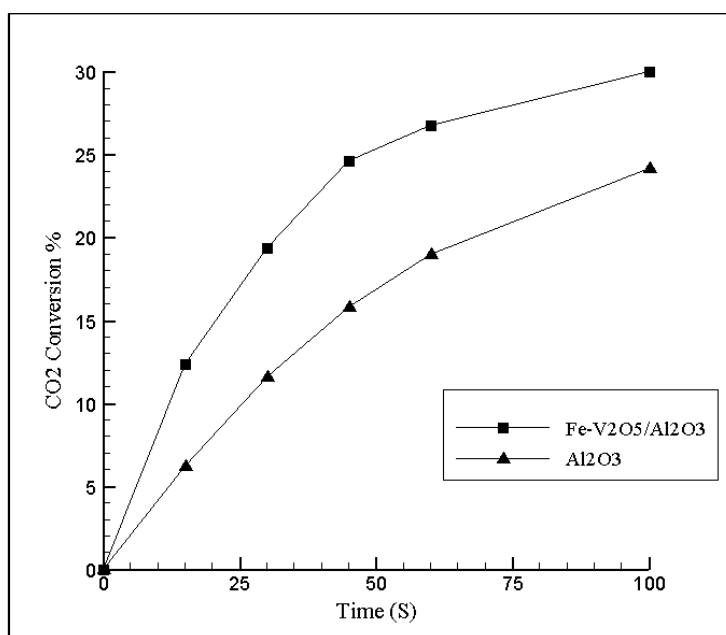


Fig. 2: Catalytic Activity based on  $CO_2$  Conversion of two catalytic systems vs. time

Fig.3 shows that as temperature increases the CO<sub>2</sub> conversion of both catalyst systems reaches to the equilibrium conversion. However, the CO<sub>2</sub> conversion of promoted nano catalyst is closer to the equilibrium conversion. The difference between activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and promoted catalyst is more sensed at the lower temperature.

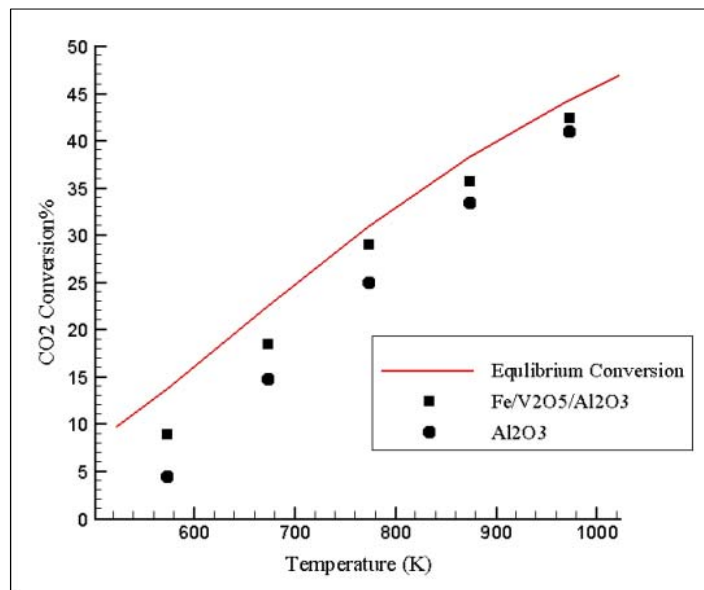


Fig. 3: The CO<sub>2</sub> conversion of both catalytic systems vs. temperature.

Fig. 4 shows the rate of CO<sub>2</sub> consumption vs. time. The rate of CO<sub>2</sub> conversion decreases during the reaction time. It could be due to the feed deficiency in reaction medium. When the promoted nano catalyst used, 80% of equilibrium condition occurs in 45 seconds of reaction time, while for nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, it started with a lower initial rate and the rate of CO<sub>2</sub> consumption decreased with a smaller slope. Both catalysts were tested for their activity. After 15 hours of operation they were deactivated slightly. The results of CO<sub>2</sub> conversion for fresh and aged catalysts at 873 K temperature and 45 seconds are reported in Table1. CO<sub>2</sub> conversion was much higher when the catalysts were fresh. Since the condition for feed compositions and reaction temperature are the same for both catalyst systems, the difference between the CO<sub>2</sub> conversions is due to the deactivation of the catalyst. As seen in Table1 the promoted nano catalyst deactivated more than the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst.

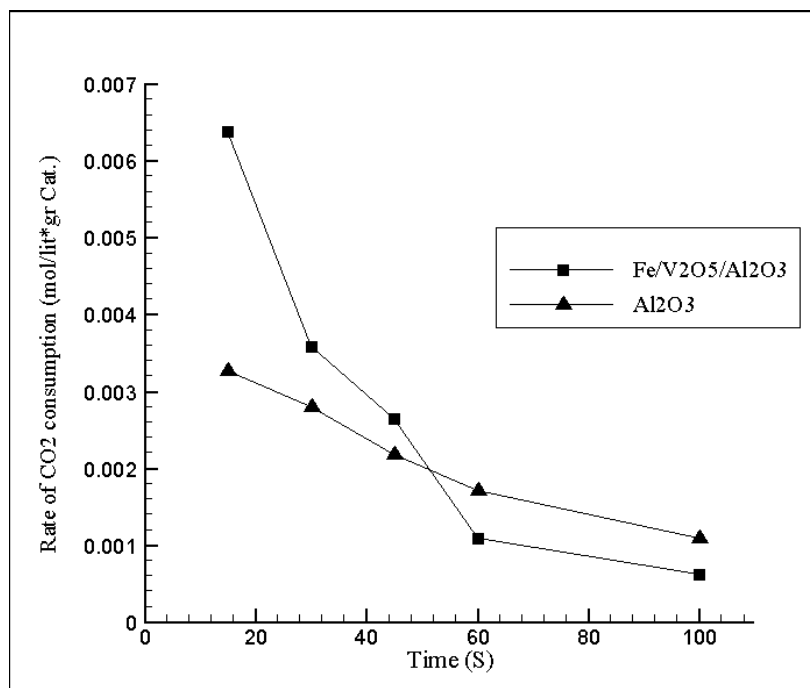


Fig. 4: The rate of consumption of CO<sub>2</sub> of two catalyst systems vs. time.

Table 1: CO<sub>2</sub> conversion for fresh and aged catalysts

Catalyst	Conversion of Fresh Catalyst	Conversion of Aged Catalyst
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	15.8%	15%
Fe-V <sub>2</sub> O <sub>5</sub> supported on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	24.6%	21.7%

## 4. Conclusions

The promoted nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Fe-V<sub>2</sub>O<sub>5</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) showed a better catalytic activity than nano  $\gamma$ -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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and promoted catalyst is more at the lower temperature and at high temperature they have almost similar behaviour. It has also reached to the equilibrium conversion sooner than nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Promoted nano catalyst reaches 80% of equilibrium condition in 45 seconds of reaction time and has higher initial rate of CO<sub>2</sub> consumption than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. However, it deactivated more than nano alumina. Promoted catalyst reaches to equilibrium conversion almost in 100 seconds at 773 K.

The promoted nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (Fe-V<sub>2</sub>O<sub>5</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) showed a better catalytic activity than nano  $\gamma$ -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  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and promoted catalyst is more sensed at the lower temperature and at high temperature they have almost similar behaviour. It has also reached to the equilibrium conversion sooner than nano  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Promoted nano catalyst reaches 80% of equilibrium condition in 45 seconds of reaction time and has higher initial rate of CO<sub>2</sub> consumption than  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. However, it deactivated more than nano alumina. Promoted catalyst reaches to equilibrium conversion almost in 100 seconds at 773 K.

## 5. Acknowledgements

Authors gratefully acknowledge the Petroleum University of Technology and the Iranian Nano Technology Initiative Council for financial support.

## 6. References

- [1] J.H. Edwards. Potential sources of CO<sub>2</sub> and the options for its large-scale utilisation now and in the future. *Catal. Today*. 1995, 23: 59-61.
- [2] Y. Souma, H. Ando, H.M. Fujiwara, R. Kieffer. Catalytic hydrogenation of carbon dioxide to hydrocarbons, *Energy Conversion and Management. Energy Convers. Manage.* 1995, 36: 593.
- [3] S.-E. Park, S.-S. Nam, M.-J. Choi, K.-W. Lee. Catalytic reduction of carbon dioxide: The effects of catalysts and reductants. *Energy Convers. Manage.* 1995, 36: 573.
- [4] P.G. Jessop, T. Ikariya, R. Noyori. Homogeneous Hydrogenation of Carbon Dioxide, *Chemical Reviewers. Chem. Rev.* 1995, 95 (2): 259.
- [5] J.M. Lehn, R. Ziessel. Photochemical reduction of carbon dioxide to formate catalyzed by 2,2'-bipyridine- or 1,10-phenanthroline-ruthenium(II) complexes. *J. Organomet. Chem.* 1990, 382:157.
- [6] W. Leitner, *Angew. Carbon Dioxide as a Raw Material: The Synthesis of Formic Acid and Its Derivatives from CO<sub>2</sub>. Chem. Int. Engl.* 1995, 34: 2207.
- [7] S.-W. Park, O.-Sh. Joo, K.-D. Jung, H. Kim, S.-H. Han. Development of ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst for reverse-water-gas-shift reaction of CAMERE process. *Appl. Catal. A.* 2001, 211: 81-90.
- [8] C. Satterfield. *Heterogeneous Catalysis in Industrial Practice.* Krieger Publishing Company, 1996.

- [9] A. Ghenciu. Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems. *Curr. Opin. Solid State Mater. Sci.* 2002, 6: 395.
- [10] R.A. Dagle, A. Platon, D.R. Palo, A.K. Datye, J.M. Vohs, Y. Wang. PdZnAl catalysts for the reactions of water-gas-shift, methanol steam reforming, and reverse-water-gas-shift. *Appl. Catal. A.* 2008, 342: 63–68.
- [11] N. L. Wieder, M. Cargnello, K. Bakhmutsky, T. Montini, P. Fornasiero, R. J. Gorte. A study of the water-gas-shift reaction over Pd@CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> core-shell catalysts. *J. Phys. Chem. C.* 2011, 115: 915–919.
- [12] Y. Zhai, D. Pierre, R. Si, W. Deng, P. Ferrin, A. U. Nilekar, G. Peng, J. A. Herron, D.-C. Bell, H. Saltsburg, M. Mavrikakis, M. F.-Stephanopoulos. Alkali-stabilized Pt-OH<sub>x</sub> species catalyze low-temperature water-gas-shift reactions. *Science.* 2010, 633: 329.
- [13] D.C. Grenoble, M.M. Estadt and D.F. Ollis. The chemistry and catalysis of the water gas shift reaction : 1. The kinetics over supported metal catalysts. *J. Catal.* 1981, 67: 90-102.
- [14] P. A. Deshpande, M.S. Hegde, G. Madras. Pd and Pt ions as highly active sites for the water–gas shift reaction over combustion synthesized zirconia and zirconia-modified ceria. *Appl. Catal. B.* 2010, 96: 83–93.
- [15] T. Tabakova, F. Boccuzzi, M. Manzoli, J.W. Sobczak, V. Idakiev, D. Andreeva. A comparative study of nanosized IB/ceria catalysts for low-temperature water-gas shift reaction. *Appl.Catal. A.* 2006, 298: 127–143.
- [16] G.C. Chinchén, R.H. Logan, M.S. Spencer. Reply to comments on the activity and state of the copper surface in methanol synthesis catalysts. *Appl. Catal.* 1984, 32: 371-372.
- [17] T. Salmi, L.-E. Lindfors, S. Bostrom. A dynamic study of the water-gas shift reaction over an industrial ferrochrome catalyst. *Journal of Catalysis.* 1988, 112: 345-356
- [18] D.G. Rethwisch and J.A. Dumesic. Adsorptive and catalytic properties of supported metal oxides : III. Water-gas shift over supported iron and zinc oxides. *Appl. Catal.* 1986, 101: 35-42.
- [19] M.C. R.-Martinez, D. C.-Amoros, A. L.-Solano, C. C.-M deLecea. Carbon dioxide hydrogenation catalyzed by alkaline earth- and platinum-based catalysts supported on carbon. *Appl. Catal. A.* 1994, 116: 187-204.
- [20] J. Kaspar, M. Graziani, A.H. Rahman, A. Trovarelli, E.J.S. Vichi, E.C. da Silva. Carbon dioxide hydrogenation over iron containing catalysts. *Appl. Catal. A.* 1994, 117: 125-137.
- [21] C.S. Chen, W.H. Cheng, S.S. Lin. Study of iron-promoted Cu/SiO<sub>2</sub> catalyst on high temperature reverse water gas shift reaction. *Applied Catalysis A.* 2004, 257: 97–106.
- [22] O.-Sh. Joo and K.-D. Jung. Stability of ZnAl<sub>2</sub>O<sub>4</sub> Catalyst for Reverse-Water-Gas-Shift Reaction (RWGSR). *Bull. Korean Chem. Soc.* 2003, 24: 86-90.
- [23] R.A. Koeppele, A. Baiker, A. Wokaun. 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.* 1992, 84: 77-79.
- [24] D.J. Pettigew, D.L. Trimm, N.W. Cant. The effects of rare earth oxides on the reverse water-gas-shift reaction on palladium/alumina. *Catal. Lett.* 1994, 28: 313-319.
- [25] J.T.S. Irvine, A. Sauvet. Improved oxidation of hydrocarbons with new electrodes in high temperature fuel cells. *Fuel Cells.* 2001, (3–4): 205–210.
- [26] P. McKendry. Energy production from biomass (Part 3): Gasification technologies. *Bioresource Technol.* 2002, 83: 55–63.
- [27] G. Pekridis, K. Kalimeri, N. Kaklidis, E. Vakouftsi, E.F. Iliopoulou, C. Athanasiou, G.E. Marnellos. Study of the reverse water gas shift (RWGS) reaction over Pt in a solid oxide fuel cell (SOFC) operating under open and closed-circuit conditions. *Catalysis Today.* 2007, 127: 337–346
- [28] C.M. Wang, T.C. Tsai, I. Wang. Deep Hydrodesulfurization over Co/Mo Catalysts Supported On Oxides Containing Vanadium. *J. Catal.* 2009, 262: 206–214.