

Methane Steam Reforming on Supported Nickel, Effect of Nickel Content for Product Hydrogen

Akila Belhadi^{1*}, Souhila Boumaza¹, Amar Djadoun², Mohamed Trari³, Ouiza Cherifi¹

¹Laboratory of Chemistry of Natural Gas, Faculty of Chemistry, USTHB, Algiers, Algeria

²Department of Géologie FSTGAT, USTHB, Algiers, Algeria

³Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry (USTHB), Algiers, Algeria
Email: ^{*}sarakila@yahoo.fr

Received 6 March 2016; accepted 2 May 2016; published 5 May 2016

Copyright © 2016 by authors and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

The steam reforming of methane over NiO/ZnO mixed oxides with different nickel contents was studied. Solids to x% Ni/ZnO (x = 4 and 10%) were deposited on ZnO by impregnation from nickel nitrate solution; after vaporization the solid is calcined at 500°C for 6 h. The catalysts were characterized by X-ray diffraction (XRD) and BET method, scanning electron microscopy (SEM) and temperature programmed reduction (TPR). The XRD patterns revealed the NiO phase for all calcined catalysts. The chemical analysis confirmed the theoretical values of nickel. The catalysts were pre-treated under hydrogen at 500°C *in situ*, overnight before testing for the steam reforming of methane reaction (CH₄/H₂O/Ar = 10/10/80) in the temperature range (475°C - 650°C) under atmospheric pressure. The activities of both catalysts were investigated in a fixed-bed reactor for the Methane Steam Reforming (MSR) reaction. Globally, it was shown that the catalyst 10% nickel content has an important effect on the catalytic performances of solids *i.e.* the better results of hydrogen production were obtained with 10% wt. Ni/ZnO (28 × 10⁻³ mol/g catalyst).

Keywords

Nickel Catalysts, ZnO, Methane Steam Reforming, Hydrogen

1. Introduction

For many years, the methane steam reforming (MSR) has been a leading technology for the generation of hydrogen in the refining and petrochemical complexes. MSR reaction is currently the dominant way used to obtain

^{*}Corresponding author.

syngas ($\text{H}_2 + \text{CO}$). The natural gas is the cleanest of all fossil fuels and MSR is a well-established process for the production of syngas and hydrogen [1]. In this respect, numerous supported catalysts have been tested, especially nickel and noble metal based catalysts, which have been found to exhibit promising catalytic performance [2]. Studies were carried out on the methane conversion, which focus on mainly two processes: direct and indirect conversion of methane. Furthermore, methane reforming at high temperatures results in the formation of carbon deposition via the decomposition of products with consequently a decrease of the energy efficiency [3] [4]. Hydrogen will have an important role in the future world economy scenario as a clean, renewable, and efficient fuel. It has been widely used in the petro-chemical processes like hydro-desulfurization, hydro-cracking, hydro-refining and so on. Nowadays, hydrogen becomes more and more involved as the feedstock in the synthesis of methanol/dimethyl ether (DME), and particularly, in the Fischer-Tropsch reaction to make liquid fuels from coal or natural gas. Besides, hydrogen is ideal for fuel cells, e.g., for proton exchange membrane (PEM) fuel cell [5] [6]. Therefore, it is not only an important chemical feedstock, but also a clean energy carrier. Accordingly, the demand for low-cost hydrogen would be always predominant either for the mass production or for distributed applications. However, hydrogen is known as an energy carrier, which must be produced from other primary energy sources. Its production from hydrocarbons, especially methane, *i.e.*, the principal constituent of natural gas, can be performed by mainly three ways: steam reforming, partial oxidation and auto thermal reforming [7]. It is acknowledged that the MSR is the most economical method for hydrogen production among the current commercial processes.

Supported nickel catalysts as heterogeneous catalysts have attracted a great attention because of their potential applications in the petrochemical industry such as hydrogenation, deoxygenation, methanation, reforming and hydrocracking. Besides good nickel particle dispersion in the catalyst support, the pore size is a crucial variable affecting the catalyst performance since the activity usually relies on the presence of accessible active centres located in the internal pore of the catalysts [8] [9]. Larger-pore sizes of the catalyst provide a better diffusion of reactants and products during the course of reaction [10]. Therefore, high dispersion of small particles of nickel and the large porosity of the catalyst are desirable. The catalyst support may play a more active role by increasing the dispersion and stability of metal particles.

During the reaction between methane and NiO-based oxides, the syngas yield depends on the oxidation degree of the oxygen carriers: highly oxidized oxide particles resulted in the formation of CO_2 and H_2O , while reduced particles favour the production of CO and H_2 [10]. The MSR reaction takes place through the dissociation of methane adsorbed onto the metallic Ni-sites and the dissociation of water adsorbed at the metal—support interface to produce CO and H_2 [11] [12].

A major challenge is that Ni catalysts possess a great thermodynamic potential for coke formation during reforming reactions, and several methods are discussed to synthesize coke resistant Ni catalysts [10] [13].

In this work we have studied the reactivity of catalysts NiO/ZnO at two Ni percentages $x\%$ Ni/ZnO ($x = 4$ and 10%) in the reaction ($\text{CH}_4 + \text{H}_2\text{O}$). The catalysts were characterized in the calcined state by atomic absorption BET method, X-ray diffraction (XRD), scanning electron microscopy (SEM) and temperature programmed reduction (TPR).

2. Experimental

2.1. Sample Preparation

The solids NiO/ZnO (ZnO (Kadox) were prepared by impregnation of ZnO support with $x\%$ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 M) (Merck) ($x = 4$ and 10%) [14]. The solution was stirred during 2 h, and evaporated at 80°C under agitation. The solid was dried overnight, calcined at 300°C (2 h) and 500°C (6 h) at a heating rate of $4^\circ\text{C}/\text{mn}$ in air flow ($1.2 \text{ L}\cdot\text{h}^{-1}$). The catalysts were sieved to have a particle diameter less than 0.16 mm .

2.2. Catalysts Characterization

The solids were analyzed by atomic absorption with a Perkin-Elmer 1100 B spectrometer. The specific surface areas were determined by the BET method using an analyzer of surface type (Coultronics 2100E). The crystalline structures were identified by X-ray diffraction (XRD) using a diffractometer ($\theta/2\theta$ CGF) provided with a proportional detector and using $K\alpha$ molybdenum anticathode ($\lambda = 0.70930 \text{ \AA}$). The patterns were obtained for 2θ

values ranging from 20° to 70° with a step size of 0.02°. The average crystallite size of the particles was calculated from the formula ($L = 0.9 \lambda / \beta \cos \theta$), where β is the width of the full width at half-height. The morphology of composite particles was observed by SEM (JEOL JSM-118 6360-LV). TPR was conducted on a U-shaped quartz tube embedded in a programmable furnace. 100 mg of the catalyst was pre-treated under pure He flow at 500°C for 1 h. The reducibility of the catalyst 4% Ni/ZnO at (TPR) was realized under hydrogen diluted in argon (5%) with a heating rate of 5°C/min in the range (25°C - 600°C), the TPR patterns were obtained by using a recorder connected to a GC equipped with TCD, the H₂ consumption is recorded during the test and quantified after calibration. and then reduced under a gas mixture flow (5% H₂, 95% Ar, 50 mL/min)

2.3. Catalytic Reaction Test

The catalyst was introduced in a fixed-bed quartz reactor placed within a tubular furnace, equipped with a programmed controller under atmospheric pressure. The bed temperature was monitored by a chromel-alumel thermocouple. 100 mg of catalyst were activated in situ under H₂ atmosphere at 500°C/12h and tested between 450°C and 600°C. The reactant gas mixture (H₂O/CH₄ = 3.3) was achieved by flowing CH₄ (10%)/Ar through a water saturator working at 65°C and then introduced in the reactor at a flow rate of 1.2 L/h. Before each run, the effluent passed through a water-trap at 0°C to remove water. The gas composition was analyzed by TCD chromatograph (Hewlett-Packard 5730) containing two 2 m carbosieve B columns (1/8 inch, 100 - 200 mesh). The conversion rates and the selectivity of CO₂ and CO were calculated from the following formulas:

Total rate of transformation:

$$TTG(\%) = \frac{n_{\text{CH}_4}(\text{transformé})}{n_{\text{CH}_4}(\text{total})} \times 100$$

Rate of transformation in compound “i”:

$$TTi(\%) = \frac{n_i}{n_{\text{CH}_4}} \times 100$$

Selectivity in compound “i”:

$$S_i(\%) = \frac{n_i}{n_{\text{CH}_4}(\text{transformé})} \times 100 = \frac{TTi}{TTG} \times 100$$

with:

i: CO, CO₂.

n_i: number of moles of compound “i”.

n_{CH₄}: number of moles of methane.

3. Results and Discussion

3.1. Catalytic Systems Characterization

The studied catalytic systems are summarized in **Table 1** whereas the XRD patterns after calcination are illustrated in **Figure 1**.

The results show that the nominal composition of the metal is very close to the theoretical one for the catalyst 4%. On the contrary, the nickel percentage remains weak compared to the nominal values (7% instead 10%).

Before reaction, the presence of NiO and the support are observed for all the catalysts. The results of XRD (**Table 1** and **Figure 1**), before reaction, show ZnO zincite in all catalysts as well as NiO. This result means that for the three catalysts, NiO is dispersed uniformly on the surface.

Even though the processes are related to extrinsic factors, a detailed understanding of the physical properties is needed for a high-quality catalyst. As expected, the XRD patterns of the preparation is mixed phase (**Figure 1**), the powder exhibits a good crystallinity with strong peaks corresponding to cubic NiO (JCPDS card N° 47 - 1049) and hexagonal Wurtzite ZnO (JCPDS card N° 36 - 1451) structures. NiO crystallizes in the rocksalt structure and the crystallite size of NiO, estimated from the full width at half maximum, average 30 nm. Nanoplates with smooth surface and high crystallinity can be observed from **Figure 2**.

Table 1. Characterization of the various nickel-based catalysts (before and after reaction) of 4% Ni/ZnO and 10% Ni/ZnO.

Samples	Ni (% Real weight) %Ni	BET area (m ² /g)	XRD results			
			d ^a (nm) NiO	d ^a (nm) Ni	before reaction	after reaction
ZnO	-	5	-	-	ZnO zincite	ZnO zincite
4% Ni/ZnO	4	2	30.4	20.5	NiO ZnO zincite	Ni ²⁺ ZnO zincite
10% Ni/ZnO	7	11	21.3	20.9	NiO ZnO zincite	Ni ²⁺ ZnO zincite

^a: Evaluated from the relation ($L = 0.9 \lambda / \beta \cos \theta$) of the most intense XRD peak.

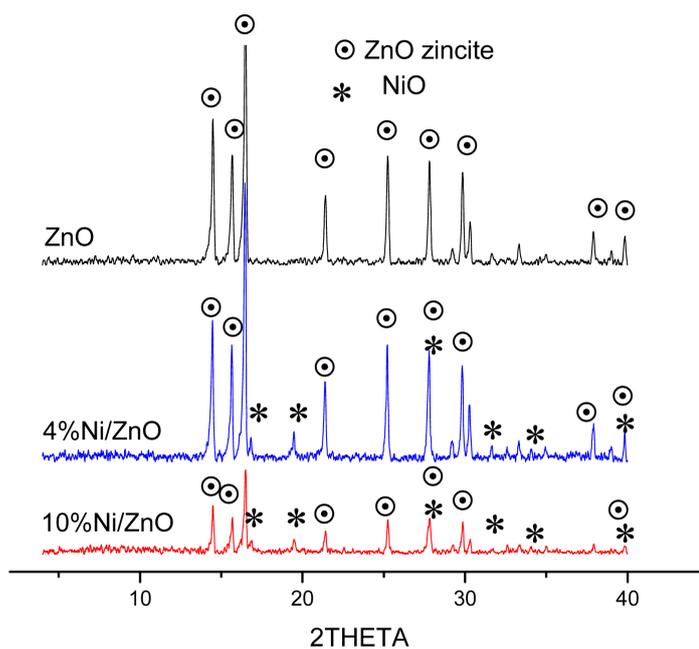
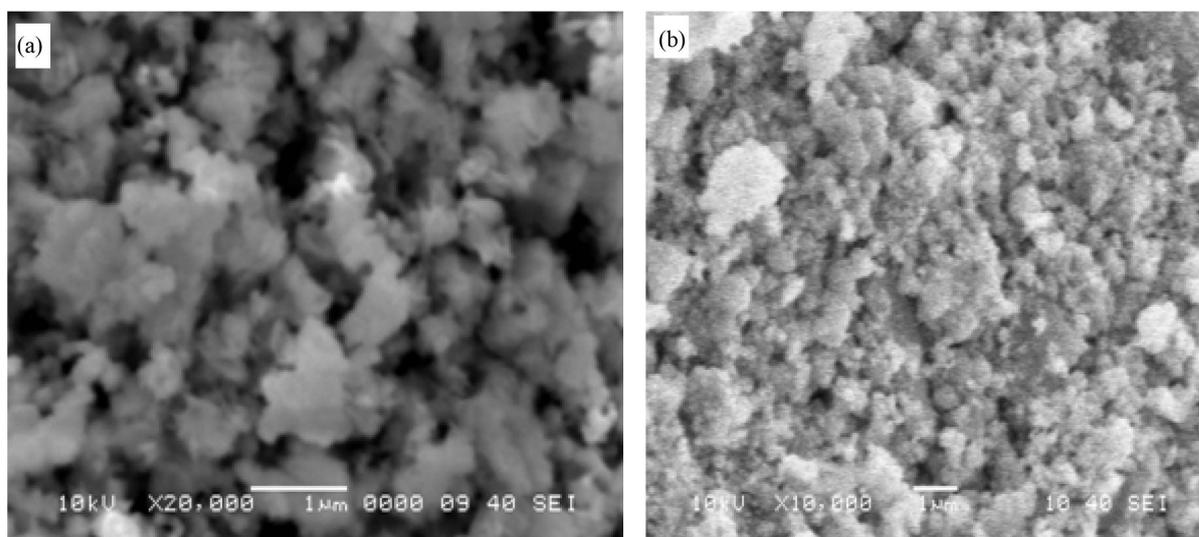
**Figure 1.** The patterns of support ZnO and catalysts, 4(%) Ni/OZnO and 10(%) NiO/ZnO. ⊙: ZnO zincite, *: NiO.**Figure 2.** SEM micrograph of (a) 4% NiO/ZnO and (b) 10% NiO/ZnO elaborated by impregnation after calcinations at 500°C.

Figure 2 shows the NiO/ZnO hetero-system prepared by impregnation method; one observes that NiO nanoparticles are well-mixed with ZnO distributed uniformly.

The TPR profiles of the bulk nickel and NiO/ZnO (**Figure 3**) are totally different. The reduction of NiO starts below 300°C and is completed rapidly while temperature above 460°C is required to reduce NiO/ZnO. The hetero-system presents one reduction peak at high temperature (460°C), probably due to the reduction of NiO with more or less strong interaction with the support ZnO. The reduction of NiO interacts weakly with the support occurs at 450°C [14] [15] and the calculated reduction rate reach 99.7%. Ni/ZnO is well dispersed onto the support ZnO with no chemical bond. In addition, NiO exists with small crystallites uniformly spread onto the ZnO surface, thus leading to their facile reduction under H₂/Ar flow.

The TPR profiles for the catalyst Ni/ZnO, exhibit one narrow peak with strong intensity at 460°C (**Figure 3**), in agreement with the literature. According to Jasik *et al.* [16], the narrow peak indicates that that the solid has a better dispersion with a good homogeneity of the active phase NiO over the ZnO support. However, the high reduction temperature implies a difficult reducibility. The temperature peak in the range (300°C - 500°C) has been assigned to NiO reduction [17]; the NiO reduction peak around 350°C agrees with the literature [18].

3.2. Catalytic Activity

3.2.1. Variation of the Catalytic Activity over the Reaction Time

The methane conversion shows that a stationary regime is reached after ~3 h, whatever the employed catalyst and **Figure 4** illustrates this phenomenon for 4%Ni/ZnO. The setting in mode is accompanied by the CO₂ formation which strongly decreases as the stationary regime settles with the profit of the CO formation. This indicates an incomplete reduction of catalysts during the pre-treatment under H₂ atmosphere (500°C) and consequently the reaction mixture produces reduced species on the surface [19]. The carbon balance (%) at the output of the reactor, established in the temperature range (475°C - 650°C) for the MSR reaction is gathered in **Table 2**. We noticed that the catalyst containing zinc gave less coke.

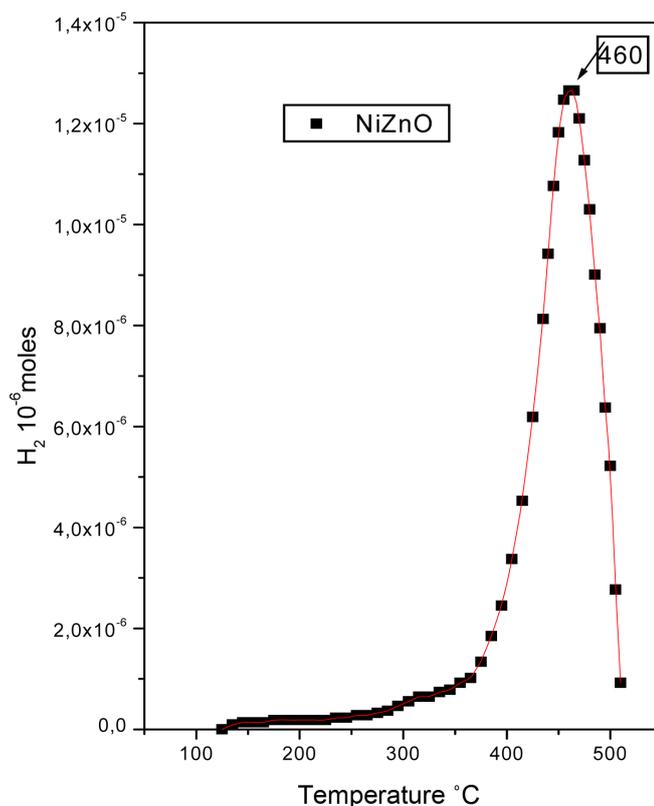


Figure 3. TPR profile of finely dispersed 4% NiO/ZnO powder elaborated by impregnation after calcinations at 500°C.

3.2.2. Effect of Nickel Percentage

Figure 5 shows the evolution of the methane conversion as a function of the reaction temperature; the results clearly indicate that the conversion increases with raising temperature. It appears that the best conversions are those obtained with the catalyst 4% Ni while the higher percentage of hydrogen is obtained on the catalyst catalyst 10% Ni (**Figure 6**). These results, which vary from one catalyst to another, appear to depend not only on the interaction between nickel and support, but also on the state of dispersion of the nickel on the area of different catalysts.

It is clear from **Table 2**, that the CO conversion is comparable for the two catalysts. The solid which produces less coke is the one that gives the best production of hydrogen (10% NiO/ZnO) [20].

Table 2. Catalytic performance of the NiO based catalysts at 650°C.

Catalyst	Selectivity CO (%)	Selectivity CO ₂ (%)	% C	H ₂ 10 ⁻³ (mol/g·h)
4% Ni/ZnO	62	23.0	15.4	8.50
10% Ni/ZnO	60	40.0	0	25.00

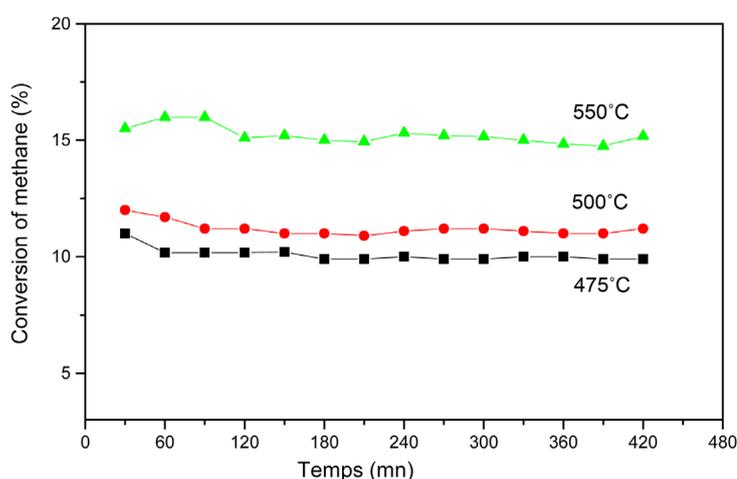


Figure 4. Methane conversion vs. reaction time for 4% Ni/ZnO catalyst at different temperatures; $m = 0.1$ g, $T_{red} = 500^\circ\text{C}$, $d = 1.2$ L/h, $\text{H}_2\text{O}/\text{CH}_4 = 3.3$.

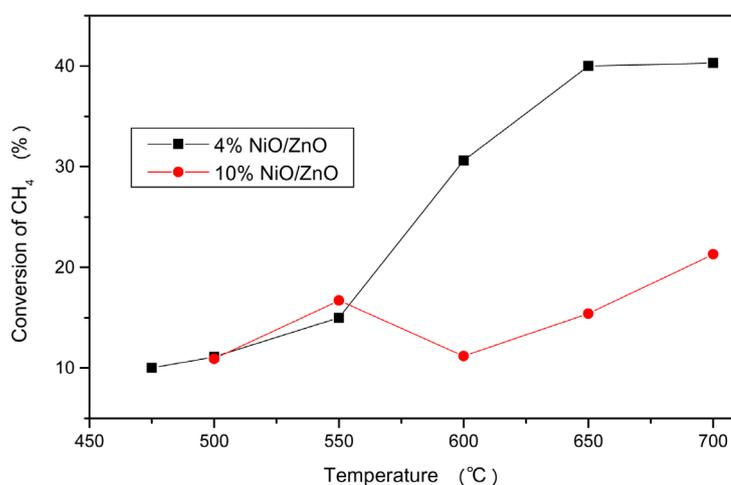


Figure 5. Methane conversion versus temperature for nickel-based catalysts 4% and 10% NiO/ZnO, $m = 0.1$ g, $T_{red} = 500^\circ\text{C}$, $d = 1.2$ L/h, $\text{H}_2\text{O}/\text{CH}_4 = 3.3$.

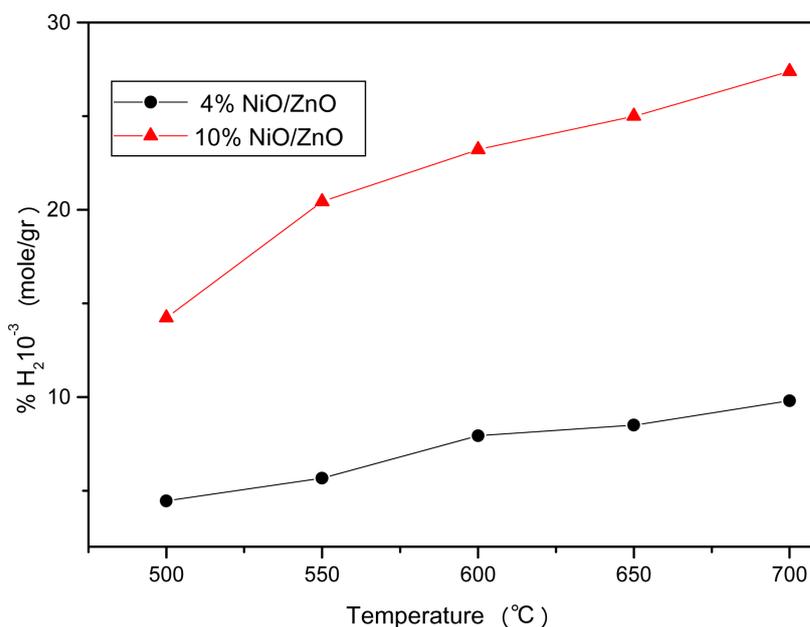


Figure 6. Production of hydrogen as a function of temperature on the nickel-based catalysts, $m = 0.1$ g, $T_{red} = 500^{\circ}\text{C}$, $D = 1.2$ L/h, $\text{H}_2\text{O}/\text{CH}_4 = 3.3$.

The Ni_x/ZnO catalytic system showed, during the MSR reaction, that the H₂ evolution was directly related to the activity, the latter decreases with decreasing the particle size and decreasing also with time on stream.

4. Conclusion

The tests of the steam reforming of methane were performed at 650°C under atmospheric pressure. The results have shown that the catalytic activity in the steam methane reforming is strongly dependent on the percentage of nickel. These results appear to depend not only on the interaction between the nickel and the support, but also on the state of dispersion of nickel on the surface. Good production of hydrogen is observed over the catalyst at 10% NiO/ZnO.

References

- [1] Collodi, G. and Wheeler, F. (2010) Hydrogen Production via Steam Reforming with CO₂ Capture. *Chemical Engineering Transactions*, **19**, 37-42.
- [2] Lemonidou, A.A. and Vasalos, I.A. (2002) Carbon Dioxide Reforming of Methane over 5 wt.% Ni/CaO-Al₂O₃ Catalyst. *Applied Catalysis A: General*, **228**, 227-235. [http://dx.doi.org/10.1016/S0926-860X\(01\)00974-7](http://dx.doi.org/10.1016/S0926-860X(01)00974-7)
- [3] Nagaoka, K., Takanabe, K. and Aika, K. (2002) Influence of the Phase Composition of Titania on Catalytic Behavior of Co/TiO₂ for the Dry Reforming of Methane. *Chemical Communications*, **2002**, 1006-1007. <http://dx.doi.org/10.1039/b201717m>
- [4] Wei, J. and Iglesia, E. (2004) Isotopic and Kinetic Assessment of the Mechanism of Methane Reforming and Decomposition Reactions on Supported Iridium Catalysts. *Physical Chemistry Chemical Physics*, **13**, 3754-3759. <http://dx.doi.org/10.1039/b400934g>
- [5] Rostrup-Nielsen. (2004) *JR. Catal. Rev.*, 247-270.
- [6] Zhai, X.L., Cheng, Y.H., Zhang, Z.T., Jin, Y. and Cheng, Y. (2011) Steam Reforming of Methane over Ni Catalyst in Micro-Channel Reactor. *International Journal of Hydrogen Energy*, **36**, 7105-7113. <http://dx.doi.org/10.1016/j.ijhydene.2011.03.065>
- [7] Ismagilov, Z.R., Pushkarev, V.V., Podyacheva, O.Y., Koryabkina, N.A. and Veringa, H.A. (2001) A Catalytic Heat-Exchanging Tubular Reactor for Combining of High Temperature Exothermic and Endothermic Reactions. *Chemical Engineering Journal*, **82**, 355-360. [http://dx.doi.org/10.1016/S1385-8947\(00\)00349-1](http://dx.doi.org/10.1016/S1385-8947(00)00349-1)
- [8] Maschmeyer, T. (1998) Derivatized Mesoporous Solids. *Current Opinion in Solid State and Materials Science*, **3**, 71-

78. [http://dx.doi.org/10.1016/S1359-0286\(98\)80068-5](http://dx.doi.org/10.1016/S1359-0286(98)80068-5)
- [9] Lancaster, T.M., Lee, S.S. and Ying, J.Y. (2005) Effect of Surface Modification on the Reactivity of MCF-Supported IndaBOX. *Chemical Communications*, **28**, 3577-3579. <http://dx.doi.org/10.1039/b506205e>
- [10] Ortiz, M., de Diego, L.F., Abad, A., Garcia-Labiano, F., Gayan, P. and Adanez, J. (2012) Catalytic Activity of Ni-Based Oxygen-Carriers for Steam Methane Reforming in Chemical-Looping Processes. *Energy & Fuels*, **26**, 791-800. <http://dx.doi.org/10.1021/ef2013612>
- [11] Dong, W.S., Roh, H.S., Jun, K.W., Park, S.E. and Oh, Y.S. (2002) Methane Reforming over Ni/Ce-ZrO₂ Catalysts: Effect of Nickel Content. *Applied Catalysis A: General*, **226**, 63-72. [http://dx.doi.org/10.1016/S0926-860X\(01\)00883-3](http://dx.doi.org/10.1016/S0926-860X(01)00883-3)
- [12] Pistonesi, C., Juan, A., Irigoyen, B. and Amadeo, N. (2007) Theoretical and Experimental Study of Methane Steam Reforming Reactions over Nickel Catalyst. *Applied Surface Science*, **253**, 4427-4437. <http://dx.doi.org/10.1016/j.apsusc.2006.09.054>
- [13] Liu, C.J., Ye, J.Y., Jiang, J.J. and Pan, Y.X. (2011) Progresses in the Preparation of Coke Resistant Ni-based Catalyst for Steam and CO₂ Reforming of Methane. *ChemCatChem*, **3**, 529-541. <http://dx.doi.org/10.1002/cctc.201000358>
- [14] Belhadi, A. and Cherifi, O. (2009) Effect of Ni Catalysts and Ni Promoted by Metals on Silica Toward the Reaction of Steam Reforming of Methane to Syngas. *Journal of the Algerian Chemical Society*, **19**, 49-61.
- [15] Maluf, S.S. and Assaf, E.M. (2009) Ni Catalysts with Mo Promoter for Methane Steam Reforming. *Fuel*, **88**, 1547-1553. <http://dx.doi.org/10.1016/j.fuel.2009.03.025>
- [16] Jasik, A., Wojcieszak, R., Monteverdi, S., Ziolek, M. and Bettahar, M.M. (2005) Study of Nickel Catalysts Supported on Al₂O₃, SiO₂ or Nb₂O₅ Oxides. *Journal of Molecular Catalysis A: Chemical*, **242**, 81-90. <http://dx.doi.org/10.1016/j.molcata.2005.07.013>
- [17] Joo, O.S. and Jung, K.D. (2002) CH₄ Dry Reforming on Alumina-Supported Nickel Catalyst. *Bulletin of the Korean Chemical Society*, **23**, 1149-1153. <http://dx.doi.org/10.5012/bkcs.2002.23.8.1149>
- [18] Shan, W., Luo, M., Ying, P., Shen, W. and Li, C. (2003) Reduction Property and Catalytic Activity of Ce_{1-x}Ni_xO₂ Mixed Oxide Catalysts for CH₄ Oxidation. *Applied Catalysis A: General*, **246**, 1-9. [http://dx.doi.org/10.1016/S0926-860X\(02\)00659-2](http://dx.doi.org/10.1016/S0926-860X(02)00659-2)
- [19] Wei, J. and Iglesia, E. (2004) Isotopic and Kinetic Assessment of the Mechanism of Reactions of CH₄ with CO₂ or H₂O to Form Synthesis Gas and Carbon on Nickel Catalysts. *Journal of Catalysis*, **224**, 370-383. <http://dx.doi.org/10.1016/j.jcat.2004.02.032>
- [20] Belhadi, A., Trari, M., Rabia, C. and Cherifi, O. (2013) Methane Steam Reforming on Supported Nickel Based Catalysts. Effect of Oxide ZrO₂, La₂O₃ and Nickel Composition. *Open Journal of Physical Chemistry*, **3**, 89-96.