3rd RUSSIAN CONGRESS ON CATALYSIS (MAY 22–26, 2017, NIZHNY NOVGOROD)

Supported Ru-Ni Catalysts for Biogas and Biohydrogen Conversion into Syngas

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Received September 14, 2017

Abstract—Catalytic properties of monometallic Ni and bimetallic Ru–Ni supported on Al_2O_3 , CaO– Al_2O_3 , and MgO– Al_2O_3 have been studied in mixed reforming of methane. Physicochemical properties of the catalytic systems have been studied by X-ray diffraction, scanning electron microscopy with energy dispersive spectroscope and temperature-programmed reduction by hydrogen. It has been shown that, of all the studied samples, the highest conversion of methane and carbon dioxide is achieved in the presence of the Ru–Ni/MgO– Al_2O_3 bimetallic catalyst. Temperature-programmed reduction has confirmed the effect of hydrogen spillower from ruthenium to NiO. The formation of Ru–Ni alloy has also been found.

Keywords: ruthenium–nickel catalysts, biogas, methane reforming, hydrogen spillower **DOI:** 10.1134/S0023158418040080

INTRODUCTION

The final products of anaerobic fermentation of molasses, which is very important for the cycling of matter and energy in ecosystems, are methane and carbon dioxide. The anaerobic fermentation of biomass, which often takes place in waste treatment facilities, is widely used in biogas synthesis [1, 2]. This complex process carried out by microorganisms and includes four main stages [3–6]:

(1) hydrolysis of organic compounds to monomers;

(2) acidogenesis, which results in the formation of hydrogen and carbon dioxide;

(3) acetogenesis, which is related to the oxidation of nongaseous products into hydrogen, carbon dioxide, and acetate (syntrophic degradation); and

(4) methanogenesis.

The two last stages can produce hydrogen in substantial amounts if appropriate conditions of fermentation are provided. Nevertheless, its commercial implementation is prevented by the low efficiency of the process and by detrimental compounds in the products [7, 8]. However, recent studies of this process confirm, that hydrogen production from biomass by fermentation will soon become technologically efficient [8–10].

Biochemical conversion of molasses makes it possible to obtain a gaseous mixture with a $CH_4/CO_2/H_2$ ratio of 2/2/1 [10].

Biogas can be used in syngas production with its further conversion into fuel components using the Fischer–Tropsch process. The conversion of methane into syngas occurs via two reactions:

Steam conversion of methane:

 $CH_4 + H_2O = CO + 3H_2$, $\Delta H = 206$ kJ/mol Carbon dioxide conversion of methane:

 $CH_4 + CO_2 = 2CO + 2H_2, \Delta H = 247 \text{ kJ/mol}$

These reactions are carried out on nickel catalysts promoted by noble metals. Crisafulli et al. [11] studied monometallic Ni/SiO₂ and bimetallic Ru-Ni/SiO₂ and Pd-Ni/SiO₂ catalysts in reforming of methane process. They found that promoting the catalyst by ruthenium or palladium considerably affects the catalytic activity of a nickel catalyst. The maximum activity was achieved in the case of a Ru–Ni/SiO₂ catalyst. This was explained by the high dispersion of nickel on the catalyst surface due to the formation of Ru-Ni clusters with a surface covered mostly by nickel. Luisetto et al. [12] also found positive effect of ruthenium on the activity of a Ni/ γ -Al₂O₃ catalyst in reforming of methane with carbon dioxide process. Authors reported, that the role of ruthenium is to facilitate the reduction of NiO. Ruthenium did not improve the dispersion of nickel. Takehira et al. [13] came to similar conclusion. They confirmed the alloy Ru-Ni formation and limitation of oxidizing process of Ni due to spillover effect. For these reasons, a bimetallic $Ru-Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst was much more stable in steam conversion of methane than a monometallic $Ni_{0.5}/Mg_{2.5}(Al)O$ catalyst.

In the course of methane reforming process, undesirable processes may also occur and they lead to the formation of carbon deposits resulting in catalyst deactivation. It is known that the carbon deposit formation depends on the composition of the reaction mixture used in reforming reaction. For instance, the low concentration of CO_2 or steam in the reaction mixture favors carbon deposit formation. There are several types of carbon deposits (carbon fibers, carbon tubes, graphitic carbon) some of which are capable of mechanically destructing a catalyst [14, 15]. This undesirable phenomenon can be excluded by choosing appropriate components of the catalytic system [12–19].

In this work, we show how to use of biogas obtained from biomass for syngas production. Mixed methane reforming process was carried out over both monoand bimetallic supported catalysts at 700 and 900°C, respectively. We studied physicochemical properties of the catalytic systems by XRD, scanning electron microscopy (SEM) and temperature-programmed reduction by hydrogen (TPR-H₂) methods.

EXPERIMENTAL

Preparation of Supports and Supported Catalysts

Alumina was obtained by precipitation from an aqueous solution of aluminum nitrate using ammonia as a precipitation agent (up to pH 9–10). The mixture thus prepared was left to stay for 24 h and then filtered and washed by distilled water to pH 7. The resulting $Al(OH)_3$ gel was dried in air at 100°C for 12 h and calcined in an atmosphere of air at 500°C for 4 h.

The modification of Al_2O_3 was carried out by the method of wet impregnation of prepared support by the corresponding amounts of the aqueous solutions of magnesium or calcium nitrates. Impregnated support was left to stay for 24 h, and then the solvent was evaporated. The resulting samples (5% CaO-Al_2O_3 and 5% MgO-Al_2O_3) were dried in air at 100°C for 12 h and calcined in air at 500°C for 4 h.

Monometallic nickel catalysts were obtained by wet impregnation. The nickel phase was supported on the support surface from an aqueous solution of nickel(II) nitrate. Upon impregnation and evaporation of the solvent, the samples were calcined in air at 500°C for 4 h.

Bimetallic (1% Ru–20% Ni) catalysts were obtained by the subsequent wet impregnation of monometallic nickel catalysts by an aqueous solution of ruthenium(III) chloride according to the procedure described above. Samples were calcined at 400°C for 4 h.

Methods of Catalyst Study

TPR-H₂ was carried out using automated TPR system AMI-1 (Altamira Instruments, USA) in a range of temperatures of $25-900^{\circ}$ C with a heating ramp of

about 10°C/min. The resulting catalytic systems were reduced in a mixture of hydrogen and argon (5% H_2 -95% Ar).

The phase composition of the catalytic systems was studied using an X'Pert PRO MPD analyzer (PANalytical, Netherlands) with CuK_{α} radiation ($\lambda = 154.05 \,\mu$ m) in the 2 θ range from 20° to 90°.

The morphology and composition of the catalyst was studied using a scanning electron microscope S-4700 (HITACHI, Japan), equipped by the energydispersive spectrometer ThermoNoran (Thermo Fisher Scientific, USA).

Methane conversion was carried out in a flow-type quartz microreactor with an inner diameter of 6 mm at an atmospheric pressure and temperatures of 700 and 900°C. The volume composition of the reaction mixture was $CH_4/CO_2/H_2/H_2O/Ar = 2/2/1/0.9/1.25$. The catalytic activity was measured after preliminary stabilization for 0.5 h. The catalyst sample weight in each run was 0.1 g. The overall gas flow was 100 cm³/min. The composition of gases before and after the reaction was measured using gas chromatographs Varian 3300 (Agilent Technologies, USA) and Chrom 4 (Laboratorní přístroje, Czech Republic) equipped with thermal conductivity detectors.

Methane and carbon dioxide conversions were calculated using the following formulas:

$$X_{\rm CH_4} = \left(1 - \frac{W_i(\rm CH_4) \cdot W_0(\rm Ar)}{W_0(\rm CH_4) \cdot W_i(\rm Ar)}\right) \times 100\%, \qquad (1)$$

$$X_{\rm CO_2} = \left(1 - \frac{W_i(\rm CO_2) \cdot W_0(\rm Ar)}{W_0(\rm CO_2) \cdot W_i(\rm Ar)}\right) \times 100\%, \qquad (2)$$

where W_0 and W_i are the volume concentration of the component in the reaction mixture before and after reaction.

RESULTS AND DISCUSSION

Figure 1 shows the results of TPR-H₂ experiments for monometallic nickel and bimetallic Ru-Ni catalysts supported on nonpromoted and promoted CaO-Al₂O₃ or MgO–Al₂O₃ supports. The curve recorded for Ni/Al₂O₃ catalyst show three hydrogen consumption peaks (Fig. 1a). The first two have maximums at 260 and 380°C related to the reduction of surface NiO compounds that are bound and not bound to the support [21]. The third reduction peak located in the temperature range 500–900°C is related with the Ni–O– Al (like in spinel $NiAl_2O_4$) linkage reduction. On the TPR-H₂ profile of the Ni/CaO–Al₂O₃ catalyst, one can see the same reduction stages as in the above case (Fig. 1a). However, the proportions between individual effects have changed. At ~450°C, there is an intensity peak assigned to the reduction of NiO interacting with the support. The lower intensity of the high temperature reduction peak can be explained by the fact that calcium oxide covering the catalyst surface which prevents the Ni-O-Al species formation. The TPR-H₂



Fig. 1. TPR-H₂ profiles for (a) the monometallic 20% Ni/Al_2O_3 catalyst after calcination in air for 4 h at 500°C and (b) the bimetallic 1% Ru–20% Ni/Al_2O_3 catalyst after calcination in air for 4 h at 400°C.

recorded for 20% Ni/MgO $-Al_2O_3$ has a simial shape for the profile of Ni/Al₂O₃ catalyst (Fig. 1a). The TPR-H₂ curve of 20% Ni/MgO $-Al_2O_3$ reduction shows three stages analogous to other catalytic systems which are described aboy. It is also worth to note that all observed reduction stages are shifted towards higher temperature range compared to monometallic nickel catalyst supported on Al_2O_3 .

Figure 1b show the results of reduction studies for bimetallic systems. The reduction of the 1%Ru-20%Ni/Al₂O₃ shows similar reduction behavior recorded for monometallic Ni catalyst. The only difference is the appearance of an additional effect related to the reduction of RuO₂ situated at temperature below 200°C. This has also been noted in our earlier studies [21, 22]. It is well known that promotion of nickel catalyst by ruthenium facilitates its reduction what is confirmed by the shift of the reduction effect towards lower temperature range. This is explained by the spillover effect between ruthenium and nickel (II) oxide.

XRD of reduced monometallic and bimetallic catalysts are shown in Fig. 2. The diffraction pattern of the Ni/Al₂O₃ sample has peaks at 2 θ of 35°, 46°, and 67° related to the γ -Al₂O₃ phase. The same pattern has additional reflexes related to NiO and Ni phases. Results described in [22] for nickel catalysts were analogous. The presence of both Ni and NiO phases confirmed the partial reduction of the active phase of the supported catalyst at 500°C. Taking into account ionic of Al³⁺, Mg²⁺, and Ca²⁺, we suggest that spinel structure is formed only in the case of Mg²⁺ and Al³⁺ compounds. On the diffraction patterns, there are reflexes at $2\theta = 35^{\circ}$ and 67° , which can be due to the γ -Al₂O₃ phase or MgAl₂O₄ spinel structure. The formation of the spinel phase can be indicated by a small shift and broadening of the corresponding reflexes. There is also a noticeable shift of the characteristic nickel reflex (at $2\theta = 45^{\circ}$) toward lower reflection angles, which



Fig. 2. XRD patterns for mono and bimetallic catalysts reduced at 500° C for 2 h in the 5% H₂-95% Ar mixture.

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Fig. 3. SEM images and energy-dispersive spectra for the catalysts (a) 20%Ni-1%Ru/Al₂O₃, (b) 20%Ni-1%Ru/5%CaO-Al₂O₃, and (c) 20%Ni-1%Ru/5%MgO-Al₂O₃ calcined in air at 500° C for 4 h.

confirms the formation of the ruthenium-nickel alloy formation.

The surface morphology and elemental composition of bimetallic Ru-Ni supported catalysts were determined by scanning electron microscope equipped with energy dispersive spectrometer. The analysis of the surface composition of bimetallic catalysts (Fig. 3) showed the presence of nickel, aluminum, chlorine, and oxygen. The results obtained for promoted catalysts confirmed also the presence of calcium and magnesium on the surface of the modified by MgO and CaO nickel catalysts. Based on the analysis of energy-dispersive spectra, one may conclude that the highest dispersion of nickel was observed in the case of 20%Ni-1%Ru/5%MgO-Al₂O₃.

It is also worth to notice, that the presence of chlorine on the surface of the all bimetallic supported catalysts was also detected. The presence of chlorine on the catalyst surface is explained by its introduction during impregnation step of the catalyst. The lowest

Table 1. The effect of reaction temperature on the catalytic activity in methane conversion for mono- and bimetallic catalysts supported on 5%Al₂O₃-95%MgO Al₂O₃ and 5%CaO-95%Al₂O₃

Catalyst	Conversion of CH ₄ , %	Conversion of CO ₂ , %	Conversion of CH_4 , %	Conversion of CO ₂ , %
	700 °C		900 °C	
20%Ni/Al ₂ O ₃	57	62	100	93
20%Ni/Al ₂ O ₃ -CaO	52	60	98	91
20%Ni/Al ₂ O ₃ -MgO	54	58	99	93
1%Ru $-20%$ Ni/Al ₂ O ₃	48	56	98	92
1%Ru $-20%$ Ni/Al ₂ O ₃ $-$ CaO	54	60	98	91
1%Ru-20%Ni/Al ₂ O ₃ -MgO	66	69	99	93

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dispersion of nickel was observed in the case of the $Ru-Ni/CaO-Al_2O$ catalyst.

Table 1 shows the results of the catalytic activity tests performed for the investigated catalysts in mixed reforming of methane process expressed as methane and carbon dioxide conversions. The catalytic activity studies show that the higher temperature of reaction leads to a higher conversion of methane and carbon dioxide. Monometallic catalysts have a similar catalytic activity at 700°C. The catalytic measurements showed also that only bimetallic Ru-Ni/MgO–Al₂O₃ supported catalysts exhibited high values of methane and carbon dioxide conversions.

The promotion effect of ruthenium on nickel catalyst reduction was proven by $TPR-H_2$ method. This can be due to the oxidation of the carbon deposits present on the catalyst surface:

$$C + CO_2 = 2CO.$$

On the other hand, when the mixed methane reforming process is carried out at 900°C, almost all studied catalysts, independently of their composition, show similar values of CO_2 and CH_4 conversions. These results are related to the limitation of the rate of deposit formation process at higher temperatures.

It is notable, that the promoting effect of ruthenium was confirmed only for a bimetallic catalyst supported on the MgO–Al₂O₃ support. This can be explained by the higher dispersion of nickel on MgO– Al₂O₃ compared to other supporting materials.

CONCLUSIONS

In this work we propose an efficient method for biomethane and biohydrogen conversion to syngas. The promotion effect of ruthenium on nickel catalyst reduction was proven by TPR-H₂ method. Catalytic activity tests showed that the highest methane and carbon dioxide conversion were obtained for the Ru– Ni/MgO–Al₂O₃ bimetallic catalysts. This is likely to be due to the uniform distribution on nickel of the support surface of the catalyst.

ACKNOWLEDGMENTS

This work was supported under the project BIO-STRATEG2/297310/13/NCBiR/2016.

REFERENCES

 Boone, D.R., Whitman, W.B., and Rouvière, P., *Meth-anogenesis*, Chapman and Hall, ed. Ferry J.G., Ed., London, 1993, p. 35.

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- 2. Garcia, J.L., Patel, B.K.C., and Ollivier B., *Anaerobe*, 2000, vol. 6, p. 205.
- Thauer, R.K., Jungermann, K., and Decker, K., *Bacteriol. Rev.*, 1977, vol. 41, p. 100.
- 4. Sieber, J.R., McInerney, M.J., and Gunsalus, R.P., Annual Rev. Microbiol., 2012, vol. 66, p. 429.
- Chojnacka, A., Szczęsny, P., Błaszczyk, M.K., Zielenkiewicz, U., Detman, A., Salamon, A., and Sikora, A., *PLOS ONE*, 2015, vol. 10, no. 5, p. e0128008.
- Lee, S.-H., Park, J.-H., Kim, S.-H., Yu, B.J., Yoon, J.-J., and Park, H.-D., *Bioresour. Technol.*, 2015, vol. 190, p. 543.
- Kvesitadze, G., Sadunishvili, T., Dudauri, T., Zakariashvili, N., Partskhaladze, G., Ugrekhelidze, V., Tsiklauri, G., Metreveli, B., and Jobava, M., *Energy*, 2012, vol. 37, p. 94.
- Park, M.J., Jo, J.H., Park, D., Lee, D.S., and Park, J.M., *Int. J. Hydrogen Energy*, 2010, vol. 35, no. 12, p. 6194.
- 9. Guwy, A.J., Dinsdale, R.M., and Kim, J.R., *Bioresour. Technol.*, 2011, vol. 102, no. 18, p. 8534.
- Detman, A., Chojnacka, A., Błaszczyk, M., Kaźmierczak, W., Piotrowski, J., and Sikora, A., *Pol. J. Environ. Stud.*, 2017, vol. 26, no. 3, p. 1023.
- Crisafulli, C., Scirè, S., Maggiore, R., Minicò, S., and Galvagno, S., *Catal. Lett.*, 1999, vol. 59, p. 21
- Luisetto, I., Sarno, C., Felicisc, D., Basoli, F., Battocchio, C., Tuti, S., Licoccia, S., and Di Bartolomeo, E., *Fuel Proces. Technol.*, 2017, vol. 158, p. 130.
- 13. Takehira, K., Ohi, T., Miyata, T., Shiraga, M., and Sano, T., *Top. Catal.*, 2007, vol. 42–43, p. 471.
- 14. Rostrup-Nielsen, J.R., *Catal. Sci. Technol.*, 1984, vol. 5, p. 106.
- 15. Tracz, E., Scholz, R., and Borowiecki, T., *Appl. Catal.*, 1990, vol. 66, p. 133.
- Alstrup, I., Clausen, B., Olsen, C., Smits, R., and Rostrup-Nielsen, J.R., *Stud. Surf. Sci. Catal.*, 1998, vol. 119, p. 5.
- Hansen, J.B., and Nielsen, P.E.H., Methanol synthesis, in *Handbook of Heterogenous Catalysis*, 2nd ed., 2008, vol. 6, p. 2920.
- 18. Borowiecki, T. and Ryczkowski, J., Focus Catal. Res., 2006, ch. 5, p. 101.
- 19. Rostrup-Nielsen, J.R., J. Catal., 1984, vol. 85, p. 31.
- Mierczynski, P., Vasilev, K., Mierczynska, A., Maniukiewicz, W., Szynkowskaa, M.I., and Maniecki, T.P., *Appl. Catal.*, *B*, 2016, vol. 185, p. 281.
- 21. Mierczynski, P., Maniukiewicz, W., and Maniecki, T.P., *Cent. Eur. J. Chem.*, 2013, vol. 11, no. 6, p. 912.
- 22. Charisiou, N.D., Baklavaridis, A., Papadakis, V.G., and Goula, M.A., *Waste Biomass Valorization*, 2016, vol. 7, p. 725.