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Nickel Oxide Catalysts for Partial Oxidation of Methane to Synthesis Gas

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Abstract

Nickel catalysts supported on different carriers (θ-Al_2O_3, γ-Al_2O_3, HZSM-5 with γ-Al_2O_3, HZSM-5, and NaX) have been investigated for the partial oxidation of methane. All the supported nickel catalysts showed a high activity for the formation of synthesis gas, and γ-Al_2O_3 was the most effective among all the tested carriers. The effect of the heat-treatment temperature of the 3 wt.% Ni/γ-Al_2O_3 catalyst on its catalytic activity was studied, and a considerable decrease in its activity was observed by the heat-treatment of the catalyst at 1000 °C compared with the catalysts prepared by the 300–800 °C – calcination. The XRD analysis suggested the formation of $NiAl_2O_4$ that is a non-reducible compound at the high calcination temperature. The addition of a modifier (Co, Ce, or La) to the 3 wt.% Ni/γ-Al_2O_3 catalyst increased the selectivity to H_2 and CO with the decreasing selectivity to CO_2, and the highest selectivity to H_2 was obtained by the 5 wt.% NiLa/γ-Al_2O_3. The developed 5 wt.% NiLa/γ-Al_2O_3 catalyst showed a high stability for 30 h for the partial oxidation of methane at 750 °C. The methane conversion reached 95%, selectivity to hydrogen 83% and 52% to carbon monoxide.

1. Introduction

According to the International Energy Agency (IEA), the demand of natural gas for energy production will increase until 2020. Methane is the main component of natural gas, and due to its economic feasibility, it has become the main source of synthesis gas and hydrogen produced by the reforming process [1].

The partial oxidation of methane into synthesis gas has created significant interest for researchers in the field of petrochemistry, because we will be able to use natural gas for at least 100–150 years as one of basic resources of the petrochemical industry [2–4]. Synthesis gas is also known to be an important material connecting methane with petrochemistry and can be directly converted to methanol which is a useful raw material for various chemicals; i.e., ethanol, formaldehyde, acetic acid, and methyl esters [5]. Additionally, the production of automobile fuel (MTG process) and alkenes (MTO process) from methanol have been actively investigated in order to achieve the practical use.

In the industrial production, although synthesis gas is produced by the steam-reforming of natural gas, the most promising one of all the known processes for synthesis–gas production is the oxidative conversion of methane. The composition of synthesis gas obtained in the process is more preferable for the production of methanol and liquid products by the Fischer-Tropsch reaction, because the cost of synthesis-gas produced by the partial oxidation of methane is estimated to be almost 1.5 times lower than that produced by steam reforming [6, 7]. In order to achieve a practical application of the oxidative conversion of methane, the development of highly active, stable, selective, and cost-effective catalysts are desired [8, 9].

The most effective and economic catalysts for the methane reforming are known to be the Ni-based catalysts, such as the Ni/γ-Al_2O_3 catalyst, due to its relatively low cost compared to other catalysts [10–12]. However, the main drawback of the Ni-based catalyst is the rapid deactivation of the catalyst caused by coke formation and/or sintering of the nickel under severe reaction conditions [13].

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Various nickel-based catalysts, such as Ni-γ-Al_2O_3 [14, 15], Ni-M-γ-Al_2O_3 (M = La [16], Co [17], Rh [18] and Cu [19]), and Ni supported on La_2O_3, $CeLaO_x$, and CeO_2 [20], were investigated for the oxidative conversion of methane. In these reactions, most of the catalysts showed a high activity, and the methane conversion value were in the range of 67–95%. However, the drawback of the catalyst is a low selectivity to the hydrogen formation.

It is well known that the introduction of cerium oxide to Ni-based catalysts as a promoter led to a significant improvement in their catalytic properties such as an increase in the activity and reduction of coke formation [21]. For example, the suppression of the coke formation can be achieved by the introduction of CeO_2, because having the high ability for oxygen storage allows regulating the oxygen concentration on the surface of the catalysis.

In this study, we investigated the performance of the nickel catalyst supported on various carriers, i.e., γ-Al_2O_3, θ-Al_2O_3, ZSM-5 with γ-Al_2O_3, ZSM-5, and NaX for the oxidative conversion of methane to synthesis gas. Moreover, the effects of promoting additives (Co_2O_3, CeO_2, La_2O_3) on the performance and the physicochemical characteristics of the nickel catalysts were also investigated.

2. Experimental

Experiments to test the efficiency of the catalysts were carried out using an automated flow catalytic device (FCI-1 LLC "Modern laboratory equipment" Novosibirsk, Russia). The device consists of three main parts; the preparation of the initial gas mixture, a quartz flow-type reactor, and a gas chromatograph for the product analysis. The reactor was a quartz tube of 25 cm in length, and its internal diameter was 9–9.5 mm. During the experiments, the reactor was vertically placed in an electric furnace, and the reactant mixture was supplied to the reactor from the top. After the reactant was passed through the catalyst bed, the converted gas left the reactor through a hole in the lower part of the reactor. The reaction was performed at atmospheric pressure and the temperature was studied in the range of 600–900 °C. The amounts of the reaction products were determined by an absolute calibration method using a gas chromatograph equipped with a thermal conductivity detector (GC-1000 LLC "Chromos" Russia). The separation of each component in a product was carried out by two columns of molecular sieves 13X and Porapak T, using argon as the carrier gas.

The catalysts were prepared by the impregnation of γ-Al_2O_3 (S_{BET} = 190 m^2/g, 1.2 mm-φ; Shanghai Jiuzhou Chemicals Co., Ltd.) with a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Altei Company), drying at 350 °C (for 2 h), and then calcination at 500 °C for 3 h.

The physicochemical characteristics of the nickel catalysts were investigated by the following methods. The crystal phase and chemical composition of the catalysts were determined by an X-ray diffraction analysis (XRD) using a D2 Phaser with a LYNXEYE high speed detector (Bruker AXS) and an X-ray fluorescent analysis using PW2400 (Spectris Co., Ltd.), respectively. The specific surface area, pore volume, and pore-size distribution were measured by low-temperature nitrogen adsorption at 77 K using BELSORP-mini II (BEL Japan, Inc.). Morphology of the catalysts was observed by a scanning electron microscope (SEM) using S-4100 (Hitachi High-Technologies Corporation) and a transmission electron microscope (TEM) using Technai G220 (FEI Company). The investigation of the surface composition and the electronic state of the nickel atoms were carried out by XPS (Shimadzu Corp., AXIS-Nova).

3. Results and Discussion

Carriers (θ-Al_2O_3, γ-Al_2O_3, HZSM-5 with Al_2O_3, HZSM-5, and NaX) with different properties have been investigated for the partial oxidation of methane. The evaluation of the catalytic activity was performed using a conventional flow reactor at GHSV = 4500 h^{-1} and the ratio of the reactants was CH_4: O_2: Ar = 2:1:3.6 in the temperature range of 600–900 °C. Figure 1 represents the data obtained at the optimal reaction temperature being equal to 750 °C using only a support. The mixture of CO, CO_2, and H_2 was obtained during the reaction as products of the methane oxidation.

In this study, the partial oxidation of methane with oxygen was carried out with the reactants consisting of the stoichiometric oxygen/methane ratio for the formation of hydrogen and carbon monoxide:

$$CH_4 + \frac{1}{2} O_2 = CO + 2H_2$$

No significant effects of the specific surface area of the carrier on the catalytic activity were observed for the reaction. The highest activity was obtained by γ-Al_2O_3 with the specific surface area being equal to 170 m^2/g, and the ratio of hydrogen to carbon monoxide was H_2/CO = 1.5. Although the NaX had the highest surface area (663 m^2/g) among the tested carriers, its catalytic activity was lower than that of γ-Al_2O_3, due to the decomposition of the crystal structure during the reaction.

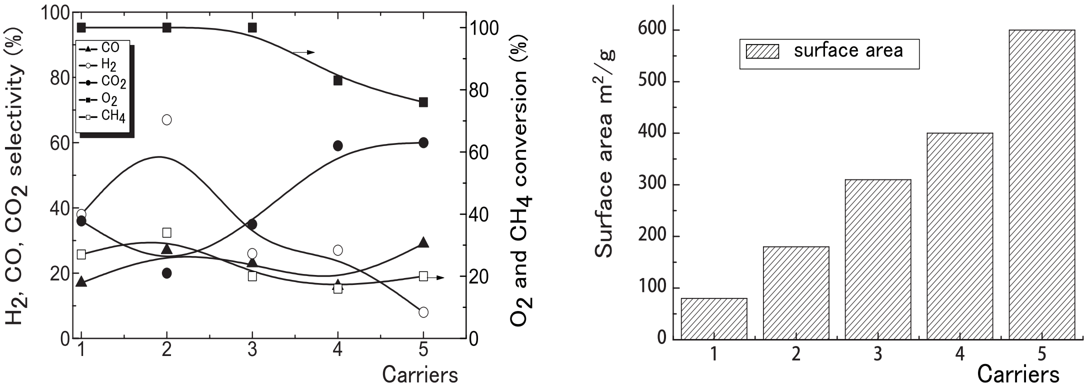

Fig. 1. Results of methane oxidation using various carriers at 750 °C: 1 – θ-Al_2O_3; 2 – γ-Al_2O_3; 3 – HZSM-5 with Al_2O_3; 4 – HZSM-5; 5 – NaX.

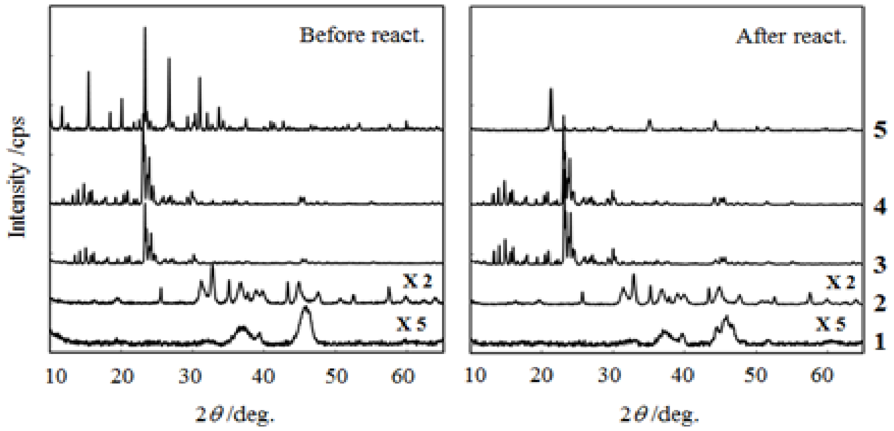

Fig. 2. XRD patterns of Ni/carrier catalysts before and after reaction at 750 °C (Ni loading = 3.0 wt.%): 1 – Ni/ θ – Al_2O_3, 2 – Ni/ γ – Al_2O_3, 3 – Ni/(H-ZSM5 + Al_2O_3), 4 – Ni/H-ZSM5, 5 – Ni/NaX.

Nickel catalysts supported on the carriers were also tested for the partial oxidation of methane. The results are shown in Fig. 3. The conversion and the concentration of H_2 and CO increased by adding Ni on the carrier, and the ratios of H_2/CO were close to the stoichiometric one based on the equation (1). The concentration of CO_2 was also reduced using supported Ni catalysts. The conversions of all catalysts except for Ni/NaX were not less than 90%, and the highest conversion of 95.3% was obtained using the Ni/γ-Al_2O_3 catalyst, whereas the Ni/NaX catalyst showed the lowest conversion of 81.3%. The XRD patterns of all the tested catalysts are summarized in Fig. 2. After the reaction, the XRD pattern of Ni/NaX dramatically changed, because of the decomposition of the zeolite framework of NaX. In contrast, no significant changes were observed in XRD patterns of the other catalysts.

We investigated the influence of the content of nickel oxide on γ-Al_2O_3 by changing the content from 0.05 to 10 wt.%. The data are shown in Fig. 4.

Figure 4 indicates that the increase in the nickel amount on γ-Al_2O_3 improved the catalytic activity. The reaction using only γ-Al_2O_3 afforded a 33.7% methane conversion. With the increasing nickel content from 0.05 to 5 wt.%, the methane conversion increased from 24 to 96%. When the reaction was performed using the catalysts having a Ni content over 3 wt.%, the methane conversion became 95–96%. Additionally, it is worth noting that the undesirable CO_2 significantly decreased from 27 to 5% when the amount of nickel increased from 0.05 to 7 wt.%.

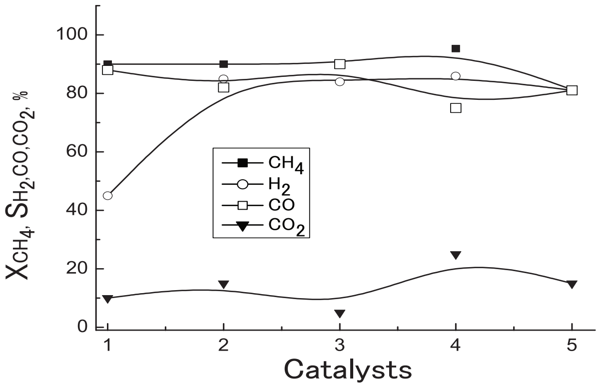

Fig. 3 CH_4 partial oxidation using Ni/carrier catalysts at 750 °C (Ni loading = 3.0 wt.%): 1 – θ-Al_2O_3; 2 – γ-Al_2O_3; 3 – HZSM-5 with Al_2O_3; 4 – HZSM-5; 5 – NaX.

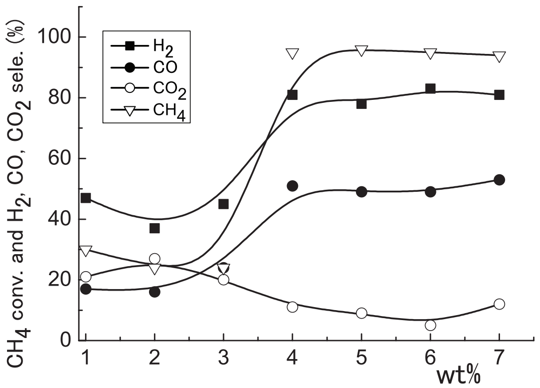

Fig. 4 Results of methane oxidation using Ni/γ-Al_2O_3 catalysts having different nickel contents at 750 °C: 1 – 0.05%Ni; 2 – 0.5%Ni; 3 – 1%Ni; 4 – 3%Ni; 5 – 5%Ni; 6 – 7%Ni; 7 – 10%Ni / γ – Al_2O_3.

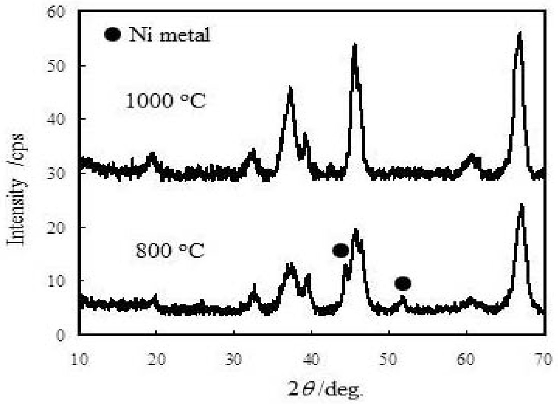

Fig. 5 XRD patterns of Ni/γ-Al_2O_3 catalysts calcined at 800 and 1000 °C.

The effects of the heat treatment temperature on the specific surface area, volume and size of the pores as well as the catalytic activity of the Ni/γ-Al_2O_3 catalyst were studied. The results are presented in Table 1. An increase of calcination temperature from 300 to 800 °C afforded a minor effect on the catalytic activity, whereas the increase in the temperature from 800 to 1000 °C caused a significant decrease in both the conversion (95 to 26%) and specific surface area (172 to 118 m^2/g). The specific pore volume also decreased from 0.084 to 0.059 cm^3/g, however, the average pore size only slightly changed. The observed effect is due to the formation of the spinel-like $NiAl_2O_4$, which is a thermodynamically favored compound at a higher temperature. The formation of $NiAl_2O_4$ prevented the reduction of NiO to Ni metal as the active species of the reforming. The XRD patterns of the Ni/γ-Al_2O_3 catalysts calcined at 800 and 1000 °C are shown in Fig. 5.

In the XRD pattern of the 800 °C – calcined Ni/γ-Al_2O_3 catalyst, diffraction peaks derived from Ni particles were clearly observed, whereas no significant peaks were detected in the pattern of the 1000 °C – calcined one. Based on the facts of the reforming and XRD analysis, we concluded that the low activity of the 1000 °C – calcined Ni/γ-Al_2O_3 catalyst is attributable to the formation of $NiAl_2O_4$ that is a non-reducible compound.

Figure 6 shows the TEM photographs of the Ni/γ-Al_2O_3 catalysts calcined at 800 and 1000 °C. The nickel particles having an approximate 10–20 nm diameter were clearly observed in the photograph (a). Meanwhile, we could not observe the nickel particles in the photograph (b) of the 1000 °C – calcined Ni/γ-Al_2O_3 catalyst.

The Ni/γ-Al_2O_3 catalyst was modified with oxides of cobalt, cerium, and lanthanum. The catalysts were evaluated during the reaction at the GHSV = 4500 h^{-1} and the ratio of the reaction mixture was CH_4: O_2: Ar = 2:1:3.6. These results are shown in Fig. 7.

The modification of the Ni/γ-Al_2O_3 catalyst reduced the yield of CO_2 in the reaction products with the increasing CO yield. Among the tested catalysts, the NiLa/γ-Al_2O_3 catalyst was the most effective one for the formation of synthesis gas because of the decreasing CO_2 content from 11 to 0.3%. For the reaction using the La-modified catalyst, the H_2 yield also increased from 81% to 83%.

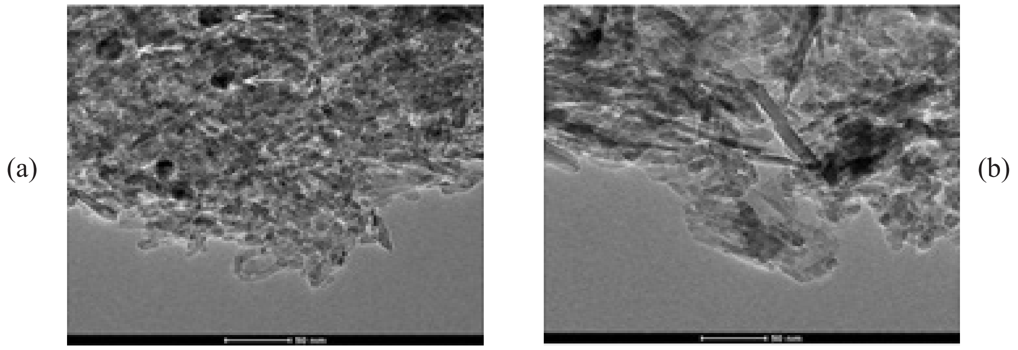

Fig. 6. TEM photographs of the Ni/γ-Al_2O_3 catalysts (after the reaction): (a) – 800 °C calcination and (b) – 1000 °C calcination.

Table 1

Effect of heat-treatment temperature on catalytic activity of Ni/γ-Al_2O_3

Catalyst	T/°C	X_{CH_4}/%	S_{H_2}/%	SCO/%	Surface area/(m^2/g)	Pore volume/(cm^3/g)	Average pore size/nm
γ-Al_2O_3	-	34	67	57	171	0.084	1.98
Ni/γ-Al_2O_3	300	95	81	94	172	0.085	1.99
Ni/γ-Al_2O_3	500	94	83	90	163	0.081	1.99
Ni/γ-Al_2O_3	800	95	81	98	152	0.075	1.98
Ni/γ-Al_2O_3	1000	26	50	36	118	0.059	1.99

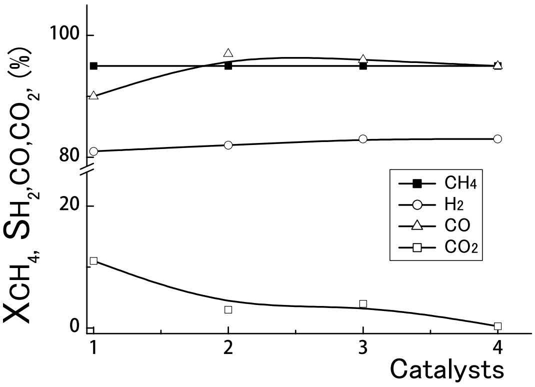

Fig. 7. Effects of second element addition to Ni/Al_2O_3 on activity and selectivity for partial oxidation of methane at 750 °C: 1 – Ni/Al_2O_3; 2 – NiCo/Al_2O_3; 3 – NiCe/Al_2O_3; 4 – NiLa/Al_2O_3.

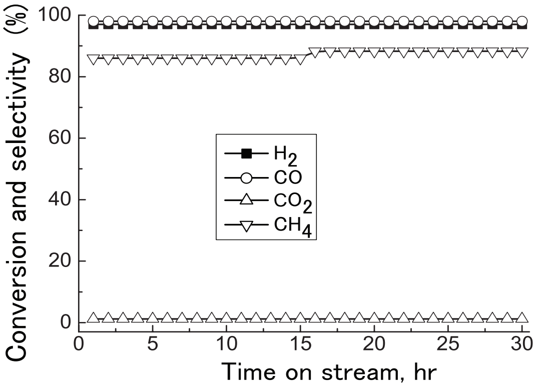

Fig. 8. Long-term test of NiLa/γ-Al_2O_3 catalyst for partial oxidation of CH_4 at 750 °C.

The stability of the NiLa/Al_2O_3 catalyst was investigated for the partial oxidation of methane under the following conditions: T = 750 °C, GHSV = 1000 h^{-1}, t = 30 h, and CH_4:O_2 = 66.7:33.3. The results are presented in Fig. 8. As shown in the Fig. 8, the NiLa/γ-Al_2O_3 catalysts did not lose its activity for 30 h, and the H_2/CO ratio also showed a constant value being equal to 1.9 during the reaction. After 30 h, the selectivities of CO and H_2 increased to 98.8 and 97.3%, respectively, at the 88.3% methane conversion with the 1.2% CO_2 selectivity.

The SEM photographs of the Ni-M/γ-Al_2O_3 (M = La, Ce, and Co) catalysts used for 30 h indicated a different situation for the coke formation (Fig. 9). The Ni/γ-Al_2O_3 and NiCo/γ-Al_2O_3 catalysts formed a significant amount of the tube- or yarn-like cokes, whereas no significant amount of coke was observed on the surface of the NiCe and NiLa/γ-Al_2O_3 catalysts. These results suggested that the addition of La and Ce improved the surface properties of the Ni/γ-Al_2O_3 catalyst. We tried to determine the amount of coke on the Ni/γ-Al_2O_3 (after the reaction for 30 h at 750 °C) by TG-DTA measurement, however, no significant amount of coke was detected.

We attempted to clarify the properties of the nickel by XPS measurement, however, the $2p_{2/3}$ peaks derived from nickel were not detected for all the nickel catalysts after the reaction.

4. Conclusions

For the reaction of partial oxidation of methane using the Ni catalytsts supported on various carriers, such as θ-Al_2O_3, γ-Al_2O_3, HZSM-5 with Al_2O_3, HZSM-5, and NaX, γ-Al_2O_3 was the most effective one among the studied carriers. The heat-treatment temperature of Ni/γ-Al_2O_3 affected the catalytic activity, and its calcination at 1000 °C caused catalyst deactivation by the formation of the non-reducible $NiAl_2O_4$.

The addition of modifiers (Co, Ce, and La) to the Ni/γ-Al_2O_3 catalyst increased the yields of H_2 and CO with the decreasing CO_2 content in the reaction products. We successfully developed the most effective NiLa/γ-Al_2O_3 catalyst, which showed a high stability for 30 h with excellent selectivities such as 83% to hydrogen and 52% to carbon monoxide at the 95% methane conversion.

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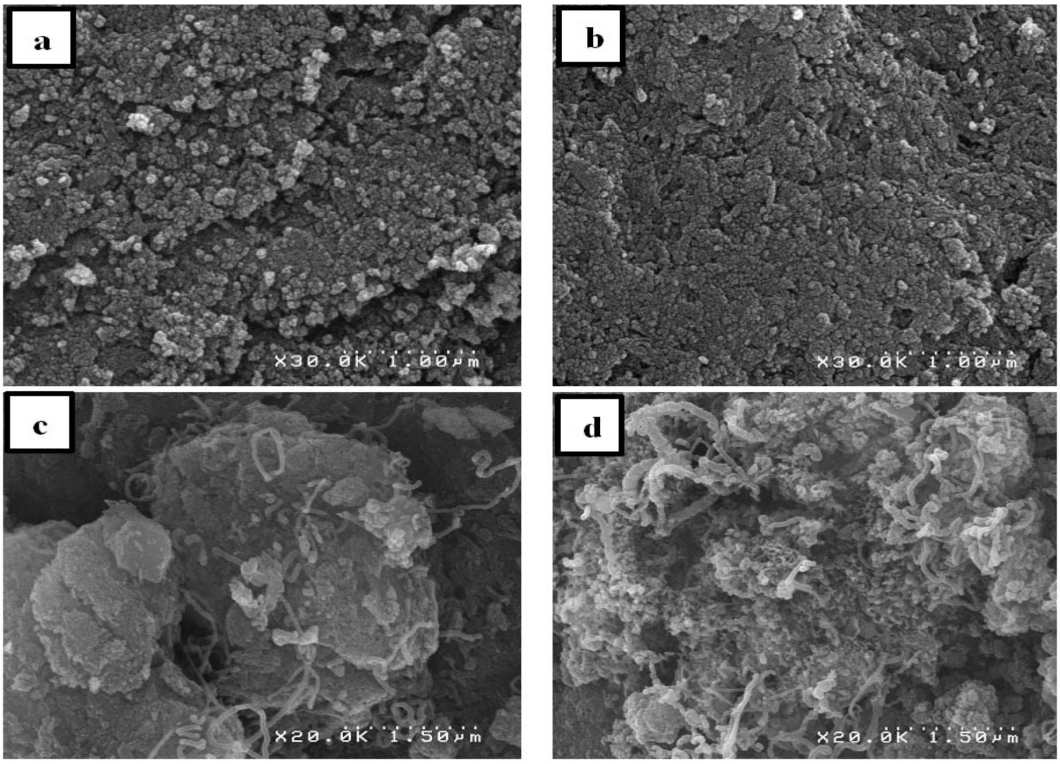

Fig. 9. SEM photographs of M-Ni/γ-Al_2O_3 catalysts after reaction at 750 °C for 30 h: (a) – NiLa/γ-Al_2O_3; (b) – NiCe/γ-Al_2O_3; (c) – NiCo/ γ-Al_2O_3; (d) – Ni/γ-Al_2O_3.

References

[1]. N.M. Popova, K. Dossumov, Nauka, Almaty, Kazakhstan, 2007 (in Russian).

[2]. K. Dossumov, G.Y. Yergazyieva, L.K. Myltykbayeva, U. Suyunbaev, N.A. Asanov, A.M. Gyulmaliev, Coke and Chemistry 58 (5) (2015) 178–183.

[3]. K. Dossumov, L.K. Myltykbayeva, G.Y. Yergaziyeva, 12th European Congress on Catalysis – EuropaCat-XI, Kazan, Russia (2015) 1628–1629.

[4]. H. Nishimoto, K. Nakagawa, N. Ikenaga, M. Nishitani-G., T. Ando, T. Suziki, Appl. Catal. A: Gen. 264 (2004) 65–67.

[5]. A.P.E. York, T. Xiao, M.L.H. Green, Top. Catal. 22 (2003) 345–358.

[6]. B. Lemke, C. Roodhouse, N. Glumae, H. Krier, Int. J. Hydrogen Energy 30 (2005) 893–902.

[7]. P. Frontera, A. Aloise, A. Macario, F. Crea, P.L. Antonucci, G. Giordano, J.B. Nagy, Res. Chem. Intermediat. 37 (2011) 267–279.

[8]. L.D. Vella, J.A. Villoria, S. Specchia, N. Mota, J.L.G. Fierro, V. Specchai, Catal. Today 171 (2011) 84–96.

[9]. B. Valle, B. Aramburu, A. Remiro, J. Bilbao, A.G. Gayubo, Appl. Catal. B: Environ. 147 (2014) 402–410.

[10]. L. Pelletier, D.S.D. Liu, Appl. Catal. A: Gen. 317 (2007) 293–298.

[11]. J. Hu, C. Yu, Y. Bi, L. Wei, J. Chen, X. Chen, Chinese J. Catal. 35 (2014) 8–20.

[12]. R.M. Navarro, M.A. Pena, J.L.G. Fierro, Chem. Rev. 107 (2007) 3952–3991.

[13]. I.H. Son, S.J. Lee, A. Soon, H.-S. Roh, H. Lee, Appl. Catal. B: Environ. 134–135 (2013) 103–109.

[14]. Y. Wang, J. Peng, C. Zhou, Z.-Y. Lim, C. Wu, S. Ye, W.G. Wang, Int. J. Hydrogen Energ. 39 (2014): 778–787 (2014).

[15]. K. Tao, L. Shi, Q. Ma, D. Wang, C. Zeng, C. Kong, M. Wu, L. Chen, S. Zhou, Y. Hu, Chem. Eng. J., 221 (2013) 25–31.

[16]. J. Ye, Z. Li, H. Duan, Y. Liu, J. Rare Earth 24 (2006) 302–308.

[17]. R. Liu, M. Yang, C. Huang, W. Weng, H. Wan, Chinese J. Catal. 34 (2013) 146–151.

[18]. V.D. Cesar, M.A.S. Baldanza, C.A. Henriqes, F. Pompeo, G. Santori, J. Múnera, E. Lombardo, M. Schmal, L. Cornaglia, N. Nichio, Int. J. Hydrogen Energ. 38 (2013) 5616–5626.

[19]. L. De Rogatis, T. Montini, A. Cognigni, L. Olivi, P. Fornasiero, Catal. Today 145 (2009) 176–185.

[20]. A.M. Venezia, V. La Parola, G. Pantaleo, P. Calatozzo, R. Bal, Proc. of 7th Tokyo Conf. Adv. Catal. Sci. & Technol. O-E07: 48 (2014).

[21]. T.Y. Kim, S.M. Kim, W.S. Lee, S.I. Woo, Int. J. Hydrogen Energy 38 (14) (2013) 6027–6032.