

Dry Reforming of Methane on Carriers and Oxide Catalysts to Synthesis-Gas

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Abstract

The catalytic activity of carriers: θ -Al₂O₃, γ -Al₂O₃, 5A, 4A, 3A and 13X and the oxides of metals of variable valency – NiO, La₂O₃, CuO, MoO₃, MgO, V₂O₅, WO₃, CoO, Cr₂O₃, ZnO, ZrO₂, CeO₂, Fe₂O₃, supported on the effective carrier γ -Al₂O₃ by the method of capillary impregnation of the support with solutions of nitric salts of metals were investigated in the process of carbon dioxide conversion of methane (DRM). The optimal technological regimes for the process were: the reaction temperature -800 °C, the space velocity of the initial reactants – 1500 h⁻¹ with a methane to carbon dioxide ratio equal to 1. It was found that among the studied catalysts the highest activity is shown by the NiO/ γ -Al₂O₃ catalyst, where the yields of hydrogen and carbon monoxide reaches 45.4 and 42.4% by volume, respectively, when methane conversion is 89%. The XRF method showed that the content of alumina and nickel oxide after the reaction remained unchanged at 96.7 and 3.0%, respectively. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), small angle X-ray scattering (XRS) determined that nickel-containing NiO/ γ -Al₂O₃ catalyst form nickel nanoparticles (6.4–10 and 50–150 nm) and a uniform their distribution on the surface of the carrier takes place. These physical chemical characteristics have a positive effect on the activity of NiO/ γ -Al₂O₃ catalyst in the process of carbon dioxide conversion of methane to synthesis gas.

1. Introduction

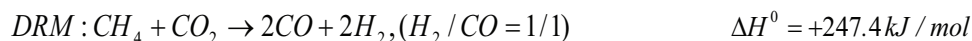
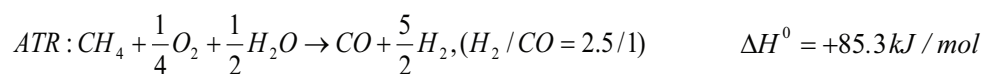
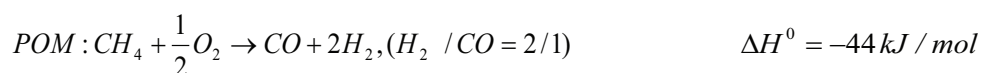
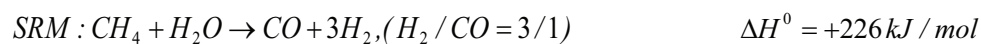
Currently, one of the acute environmental problems is the global warming of the Earth's climate due to the emission of greenhouse gases into the atmosphere. Among them, the most common are carbon dioxide (CO₂), which is largely produced by the fuel and energy industries and methane (CH₄), which is the main component of natural and associated petroleum gases [1]. Therefore, the utilization of methane and carbon dioxide into valuable products will make it possible to remove a wide range of economic, environmental and social problems for Kazakhstan as well [2].

This work is aimed at recycling greenhouse gases (methane and carbon dioxide) by catalytic method to an industrially important product – syn-

thesis-gas. Synthesis-gas, consisting of a mixture of CO and H₂ in various ratios, is an alternative source of raw materials for the petrochemical industry. The main areas of use of synthesis-gas [3–8] are the production of hydrogen, the production of methanol, Fischer-Tropsch synthesis, oxo-synthesis and the reduction of iron ore in metallurgy. Synthesis-gas can be effectively used in power engineering for the production of heat and electricity at gas turbine and combined-cycle plants and others.

There are several catalytic technologies for producing synthesis-gas of different composition, such as steam reforming of methane (SRM), partial oxidation of methane (POM), autothermal reforming (ATR) and carbon dioxide conversion of methane (DRM).

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At present, SRM is the main way of obtaining synthesis-gas from natural gas [9–11]. Steam reforming – commercially-mastered process has the disadvantage associated with increased process temperature and a high ratio of $\text{H}_2/\text{CO} = 3$, unsuitable for Fischer-Tropsch synthesis [12]. Into SRM often adds oxygen to maintain high temperatures and promote oxidation of methane. This combined methane reforming route is known as autothermal methane reforming [13–15]. SRM and ATR, although they give a good H_2/CO ratio, requires special precautions and they are at the stage of laboratory testing [16–18]. Carbon dioxide conversion of methane, also called “dry” reforming of methane, is of particular interest, since it allows for utilization at one time two greenhouse gases – methane and carbon dioxide.

The main problems of DRM are low activity of reacting components ($\text{CH}_4 + \text{CO}_2$), i.e. high reaction endothermicity ($\Delta H = +247.4 \text{ kJ/mol}$) and catalyst instability to carbonization [19–20], as a result of which they lose their effectivity. Nickel catalysts are the most widely studied for these reactions, their main advantage over other transition metals is higher activity in the DRM reaction and low cost [21–28].

In the present work for the investigation of catalytic activity in the reaction of carbon dioxide conversion of methane various carriers ($\theta\text{-Al}_2\text{O}_3$, $\gamma\text{-Al}_2\text{O}_3$, 5A, 4A, 3A and 13X) and catalysts based on metal oxides of variable valence (NiO , La_2O_3 , CuO , MoO_3 , MgO , V_2O_5 , WO_3 , CoO , Cr_2O_3 , ZnO , ZrO_2 , CeO_2 , Fe_2O_3) supported on the effective carrier $\gamma\text{-Al}_2\text{O}_3$ were used.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by capillary impregnation of the support with solutions of nitric acid salts of metals of variable valence and subsequent drying at $300 \text{ }^\circ\text{C}$ (2 h) and calcination at $500 \text{ }^\circ\text{C}$ for three hours. Features of this method of preparation

of catalytic systems is that the carrier is impregnated by its moisture capacity with solutions of transition metal salts, and the active phase is concentrated on the surface in the form of a “crust”.

2.2. Catalytic tests

The catalytic activity of the samples was studied in a reactor made of quartz glass with a diameter of 9.5 mm, in an automated flow-through unit - FCI-1 LLC. The mixed gas ($\text{CH}_4 + \text{CO}_2 = 1:1$) was fed at a rate of $50 \text{ cm}^3/\text{min}$ to the catalytic reactor from above, and after passage of the reactor to the chromatograph to analyze the reaction products. The temperature of the reactor was set by a thermoregulator and monitored with an XA thermocouple, enclosed in quartz and located inside the catalyst bed. The reaction was carried out at atmospheric pressure, and the temperature was raised from 600 to $850 \text{ }^\circ\text{C}$ in step by step every $50 \text{ }^\circ\text{C}$. Control of the composition and flow rate of the initial reactive mixtures, regulation of the temperature of the reactor and evaporator, the start of the analyzes are carried out via software. The initial gases and reaction products were analyzed on-line on a chromatograph of the brand “Chromos GC-1000” with thermal conductivity and flame ionization detectors. To analyze the reaction products, two chromatographic columns were used, filled with a molecular sieve 13X and a Porapak-T sorbent. The length of the columns was 3 m, the inner diameter was 2 mm. Argon was used as the carrier gas. Qualitative and quantitative analysis was carried out using the absolute calibration method.

2.3. Catalyst characterization

A study of the physical chemical properties of nickel catalysts (the distribution of the active phase on the surface of the catalyst and the presence of nanoscale particles) was performed at the University of Saitama, Japan using the following methods: scanning electron microscopy (SEM) on a Hitachi

High-Technologies Corporation, S-4100 device and a transmission electron microscopy (TEM) on the FEI Company, Technai G220 device. The elemental composition of 3% NiO/ γ -Al₂O₃ was investigated by X-ray fluorescence spectrometry (X-Ray Fluorescence Spectrometer) method XRF on the Spectris Co., Ltd., PW2400. The presence of nanoscale particles in the catalyst composition was also determined by the method of small-angle X-ray scattering using the Hecus S3-MICRO (Cu-radiation with a W-filter) at the National Nanotechnology Laboratory of open type of the al-Farabi KazNU (Almaty, Kazakhstan).

3. Results and discussion

Carbon dioxide conversion of methane was used to study carriers (θ -Al₂O₃, γ -Al₂O₃, 5A, 4A, 3A and 13X). The carriers were examined at a reaction space rate of 1500 h⁻¹, the ratio of methane to carbon dioxide CH₄:CO₂ = 1:1 in the temperature range 600–900 °C. The Table 1 shows the data obtained at the optimum reaction temperature of 800 °C.

The results showed that among the tested carriers the most effective is aluminum oxide of gamma modification. On γ -Al₂O₃ methane conversion is 20%, the concentration of hydrogen and carbon monoxide reaches up to 0.6 and 2.9 vol.%, respectively. Among the zeolites, the most active are 13X and HY, where methane conversion is 17 and 20%, respectively.

According to the activity of conversion of methane to synthesis-gas, the studied carriers are arranged in the following sequence: γ -Al₂O₃ (20%) > HY (20%) > θ -Al₂O₃ (18%) > 13X (17%) > 3A (15%) > HZSM-5 (13%) > 5A (10%) > 4A (9%).

Table 1
Influence of the nature of the carrier
on the yield of synthesis-gas

#	Carriers	Conversion CH ₄ and CO ₂ , %		Reaction products, vol %	
		X _{CH4}	X _{CO2}	C _{H2}	C _{CO}
1	γ -Al ₂ O ₃	20	20	0.6	2.9
2	zeolite 5A	10	9	0.1	2.8
3	zeolite 3A	15	15	0.3	2.5
4	θ -Al ₂ O ₃	18	18	0.5	3.1
5	zeolite 4A	9	8	0.1	2.5
6	zeolite 13X	17	17	0.4	3.6
7	HY	20	13	0.6	2.7
8	HZSM-5	13	17	0.3	3.0

Table 2

The effect of the concentration of phosphorus oxide supported on γ -Al₂O₃ on the yield of synthesis-gas

#	Sample	Conversion CH ₄ and CO ₂ , %		Reaction products, vol %	
		X _{CH4}	X _{CO2}	C _{H2}	C _{CO}
1	γ -Al ₂ O ₃	20	20	0.6	2.9
2	0.5% P ₂ O ₅ - γ -Al ₂ O ₃	21	23	0.8	4.7
3	1% P ₂ O ₅ - γ -Al ₂ O ₃	10	12	0.3	4.2
4	3% P ₂ O ₅ - γ -Al ₂ O ₃	10	10	0.3	1.8

The activity of these carriers can be related to their acidity. It is known [29] that aluminum oxide, in comparison with synthetic zeolites, is a more acidic carrier. Among the carriers studied by us, γ -Al₂O₃, an acidic carrier, is most active. To confirm the dependence of the activity of Al₂O₃ on acidity, alumina was impregnated with a moisture content of a small amount of phosphoric acid, followed by drying at 300 °C (2 h) and calcination at 500 °C (3 h) to increase its acidity. The results of DRM on P₂O₅/ γ -Al₂O₃ are presented in Table 2.

As can be seen from Table 2, an increase in the P₂O₅ content from 0 to 0.5% leads to an increase in the activity of Al₂O₃ in the reaction of DRM. In this case, the hydrogen yield increases from 0.6 to 0.8, and carbon monoxide from 2.9 to 4.7% by volume. Further increase in the concentration of P₂O₅ to 3% is impractical, as leads to a decrease in the yield of synthesis-gas. This fact may indicate that the formed active centers of acidic nature in certain concentrations have a positive effect on the effectivity of the carrier.

Thus, the optimal carrier γ -Al₂O₃ was determined for the preparation of catalysts for the carbon dioxide conversion of methane. Among zeolites, 13X and HY can also be recommended as the catalyst support for dry methane reforming.

In the next series of experiments, catalysts containing metal oxides of variable valence metals such as NiO, La₂O₃, CuO, MoO₃, MgO, V₂O₅, WO₃, CoO, Cr₂O₃, ZnO, ZrO₂, CeO₂, Fe₂O₃ on an effective carrier γ -Al₂O₃ were prepared and investigated on their activity in the process of carbon dioxide conversion of methane. The DRM results obtained at the optimum temperature of 800 °C are shown in Fig. 1.

As can be seen from Fig. 1, the lowest yields of hydrogen and carbon monoxide are observed on catalysts containing lanthanum, magnesium, tungsten, zinc, zirconium and cerium oxides.

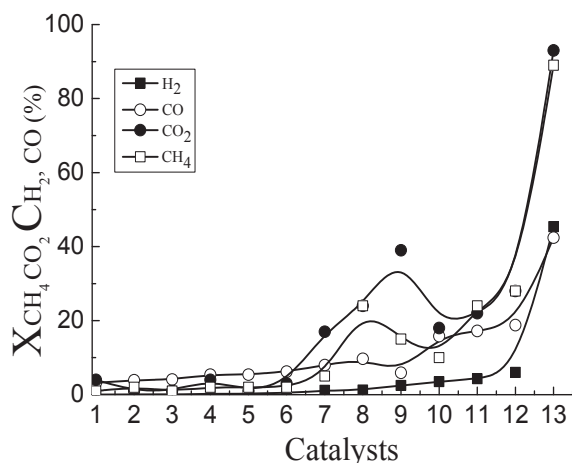


Fig. 1. Dependence of the synthesis-gas yield in the reaction of DRM on the nature of oxide catalysts supported on γ - Al_2O_3 : 1 – La_2O_3 ; 2 – MgO ; 3 – WO_3 ; 4 – ZnO ; 5 – ZrO_2 ; 6 – CeO_2 ; 7 – Fe_2O_3 ; 8 – Cr_2O_3 ; 9 – CoO ; 10 – V_2O_5 ; 11 – MoO_3 ; 12 – CuO ; 13 – NiO .

Methane conversion is about 1–2%. Beginning with $\text{Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ to $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$, the methane conversion increases from 4 to 28% and simultaneously the concentration of hydrogen and carbon monoxide in the reaction products increase.

Among the catalysts studied, the highest activity was shown by $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$. The yield of hydrogen and carbon monoxide reaches 45.4 and 42.4% by volume, respectively, with methane conversion of 89%.

Further, the physical chemical characteristics of the effective 3% $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst were investigated.

Figure 2 shows SEM micrographs of alumina gamma modification and $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst before and after the methane oxidation reaction. On the micrograph of alumina amorphous phases with a layered form are observed. With the deposition of nickel oxide on the carrier, it can be seen that medium and large particles of circular shape are formed. The main part of the particles has a size in the range of 50–150 nm. From the micrograph of the $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst tested during dry methane reforming, it can be seen that under the influence of the reaction medium, the formation of carbon filaments on the surface of the catalyst, as well as the uniform distribution of the particle on the surface of the carrier take place.

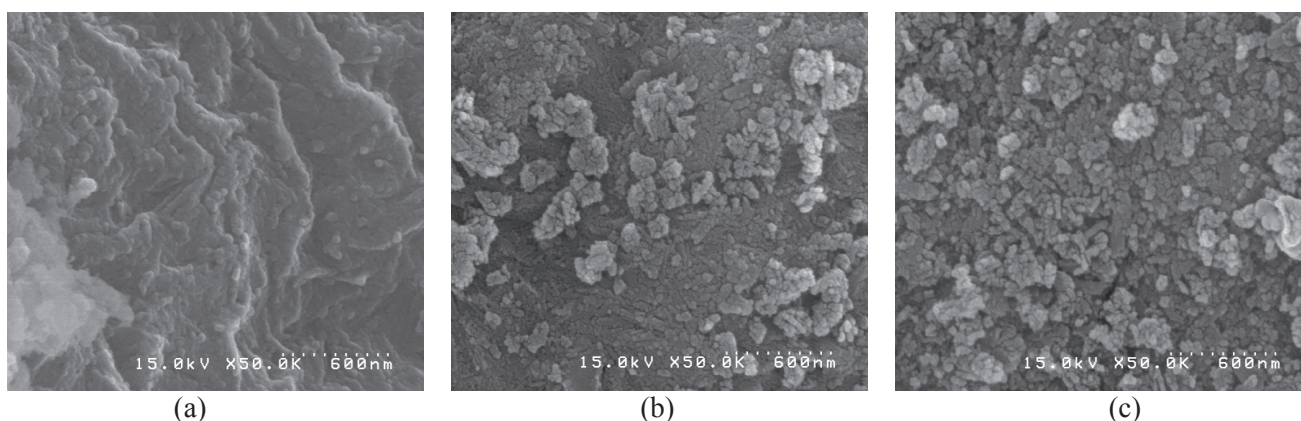


Fig. 2. SEM photomicrographs: $\gamma\text{-Al}_2\text{O}_3$ (a); $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ before the reaction (b); $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ after the reaction (c).

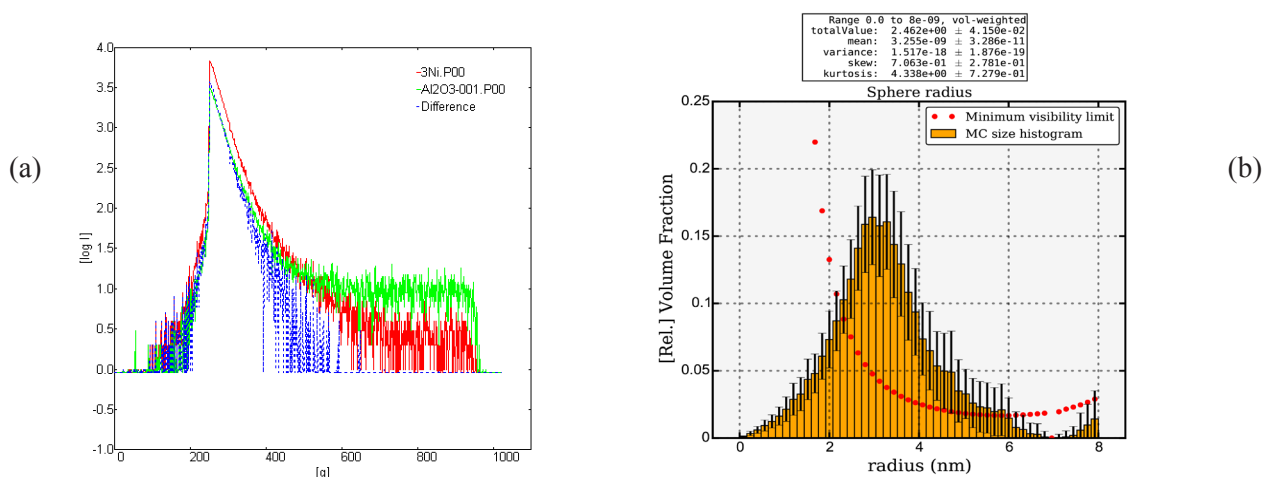


Fig. 3. Small Angle X-ray Scattering Spectra of catalysts.

The results of the study of a NiO/ γ -Al₂O₃ catalyst sample by the XRF method show that before and after its testing in the DRM reaction, the content of aluminum and nickel oxides remains unchanged and amounts to 96.7 and 3.0 wt.% respectively. The content of other impurities does not exceed 0.01–0.32%. Thus, a positive effect is that there is no ablation of the active phase of the tested catalyst during the reaction.

By the method of small-angle X-ray scattering (XRS), the spectra of the carrier (Al₂O₃) and the NiO/ γ -Al₂O₃ catalyst after the DRM reaction, shown in Fig. 3a, were taken. The difference between them (Fig. 3b) means the contribution of nanoparticles with average dimensions of 6.4 nm, which were formed in the NiO/Al₂O₃ catalyst composition.

Figure 4 shows photographs of the TEM of NiO/ γ -Al₂O₃ catalyst. It is seen from the photograph that nanocrystalline nickel particles with dimensions of 10 nm are formed on the catalyst.

The physical chemical characteristics of the NiO/ γ -Al₂O₃ catalyst allow us to assume that its activity is due to the formation of the nanophase and their uniform distribution on the carrier surface.

All the investigated catalysts were analyzed by X-ray diffraction and are shown in Fig. 5. XRD spectra show that, after the DRM reaction, nickel and spinel phase NiAl₂O₄ are observed on the surface of the nickel catalyst, in contrast to other studied metals of variable valency, which may determine its activity. These can be active nickel catalyst nanoparticles and a uniform distribution of the active phase on the carrier surface detected by TEM, SEM, XRF, and X-ray scattering (XRS), which apparently determines the activity of this catalyst during the DRM reaction.

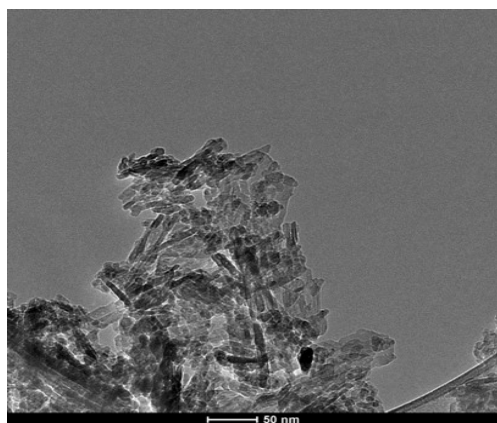


Fig. 4. Photographs of TEM NiO/ γ -Al₂O₃ catalyst after reaction of DRM.

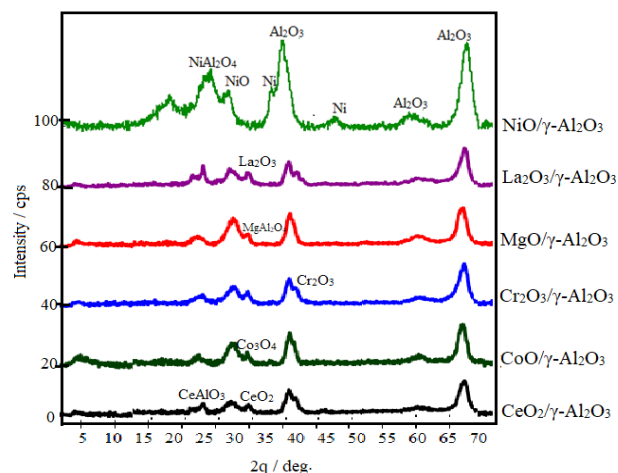


Fig. 5. XRD spectra of catalysts after the reaction of DRM.

4. Conclusions

Thus, an effective carrier of γ -Al₂O₃ for carbon dioxide reforming of methane is determined. Catalysts containing oxides of metals of variable valency – NiO, La₂O₃, CuO, MoO₃, MgO, V₂O₅, WO₃, CoO, Cr₂O₃, ZnO, ZrO₂, CeO₂, Fe₂O₃ on the effective carrier γ -Al₂O₃ were prepared and their activity was studied in the process of carbon dioxide conversion of methane. It was found that among the studied catalysts the highest activity is shown by the NiO/ γ -Al₂O₃ catalyst, where the yield of hydrogen and carbon monoxide reaches 45.4 and 42.4% by volume, respectively, when methane conversion is 89%. Investigation of the NiO/ γ -Al₂O₃ catalyst by the XRF method before and after the DRM reaction showed that the content of aluminum and nickel oxides remained unchanged at 96.7 and 3.0 wt.% respectively. Using TEM, XRS and SEM it was determined that nickel nanoparticles (6.4–10 and 50–150 nm) are formed on a nickel-containing NiO/ γ -Al₂O₃ catalyst and uniform distribution of the particles is observed on the carrier surface. These characteristics have a positive effect on the activity of NiO/ γ -Al₂O₃ catalyst in the process of carbon dioxide conversion of methane to synthesis gas.

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