Catalytic decomposition of methane on Ni-containing catalysts prepared by heterophase sol-gel method

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Abstract. The most promising catalysts for the catalytic decomposition of methane are nickel-containing systems, since nickel has high activity, thermal stability, thermal conductivity, and relatively low cost. In this work, catalysts were prepared by the heterophase sol-gel method and investigated using catalytic equipment. The catalysts showed high stability and lifetime during the catalytic decomposition of methane at temperatures ranging from 535 to 675°C.

1 Introduction

In June 2018, Japan adopted the fifth Strategic Energy Plan, which envisages building a "hydrogen" society. To 2021, hydrogen strategies have been accepted in following countries such as Germany, France, Australia, South Korea, the United Kingdom, the Netherlands, the United States and Russia. Traditional methods for producing hydrogen, for example, such as electrolysis of water or steam reforming of methane, have a number of significant disadvantages. Electrolysis of water is a very energy-intensive process, and it only can be successfully implemented in the countries with cheap electricity. As a result of steam reforming of methane, a large amount of CO_2 is formed, which is difficult to utilize. Therefore, it is necessary to develop alternative methods for hydrogen producing, for example, catalytic decomposition of methane [1]

$$CH_4 \rightarrow C_{(solid)} + 2H_2 \qquad \Delta H^\circ = 75{,}6 \text{ kJ/mol.}$$

This method is free-from emissions, like carbon oxides (CO_x-free), and can be operate with low process temperatures and production of a valuable by-product, carbon nanofibers, which can be used in various applications [2, 3].

To carry out this process, a catalyst that can fit the requirements such as sufficiently developed specific surface area, high catalytic activity, long lifetime and low cost is needed.

Ni-containing catalysts have already demonstrated their efficiency in this process [4]. Most of the studies in this field firstly pay attention to the composition of catalysts, and did not pay attention to the texture characteristics [5, 6]. In this study, we obtained the experimental results regarding the influence of textural characteristics on the activity in

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catalytic decomposition of methane over nickel-containing catalysts at temperature range 535–675°C.

2 Experimental

2.1 Preparation of the catalyst

The catalysts were prepared using the following reagents: $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $C_8H_{20}O_4Si$ (Ethylsilicate-40, TEOS), ethanol, HCl и HNO_3.

The catalysts were prepared via heterophase sol-gel method [7]. A typical preparation procedure is described below. A pre-prepared solution containing ethanol, distilled water, and hydrochloric acid was added in TEOS (40 wt.% SiO_2) at room temperature and stirred strongly. The solution was kept at room temperature for 72 h.

The required portions of the crystalline hydrates of the nickel salt were calculated referred to pure nickel. The nickel nitrate complex was dissolved in a 25% aqueous ammonia solution. This solution was added to distilled water at room temperature under vigorous stirring:

$$Ni(NO_3)_2 + 2NH_4OH \rightarrow 2NH_4NO_3 + Ni(OH)_2\downarrow$$

The mixture was kept for 10 min, and then the flaky-like precipitate was filtered off and washed with deionised water to remove ammonium nitrate. To obtain highly dispersed nickel oxide, the resulting precipitate was dried in air at 110°C for 1 h and calcined in air at 250°C for 4 h :

$$Ni(OH)_2 \rightarrow NiO + H_2O$$

Then the obtained highly dispersed NiO was mixed with the hydralizate. The mixture was adjusted to the consistency of a homogeneous paste and dried in air at 150°C for 1 h. After that, the mixture was reduced with hydrogen at 255°C:

$$NiO + H_2 \rightarrow Ni + H_2O,$$

$$Si(OC_2H_5)_4 + H_2 \rightarrow SiO_2 + C_2H_5OH$$

Table 1 shows the composition of the synthesized catalysts.

Table 1. Composition of catalysts.

Designation	**Composition, wt.%**
Cat.1	$10Ni/90SiO_2$
Cat.2	$50Ni/50SiO_2$
Cat.3	$90Ni/10SiO_2$

2.2 Physico-chemical methods of catalyst research

Catalysts were studied using the low-temperature nitrogen adsorption method using Quantachrome NOVA 1000e instrument. Prior to analysis, the samples were degassed in vacuum at 300°C for 6 h to remove physically adsorbed gases and water.

The analysis of texture characteristics was carried out at a temperature of 77 K and relative pressures P/Po of the adsorptive gas (nitrogen) in the range from 0.005 to 0.995 to obtain complete adsorption and desorption isotherms. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. To obtain the size distribution of mesopores, the Barrett-Joyner-Halenda method was used.

X-ray studies of the phase composition of the catalyst samples were carried out on a *DRON-4-07 diffractometer* using CuKα radiation (wavelength $\lambda = 1.54$ Å). The 2θ angle range was 20 to 70°.

To study the internal structure of the catalysts, particularly, the surface morphology, the transmission electron microscope *JEOL JEM-2200 FS* was used. The microscope was equipped with a 200-kV gun with the Schottky-type cathode and built into the column, fully integrated energy filter which also allows for elemental and chemical analysis of samples.

2.3 Studies of catalytic activity

The catalytic activity in the course of thermocatalytic decomposition of methane was studied in a catalytic unit with flow tube reactor with fixed bed (volume was 65 mL) at atmospheric pressure. The process temperature was ranged from 535 to 675°C.

A catalyst with weight 0.026 g was placed on a fixed bed inside the reactor. Methane with a 99.99 vol.% purity was fed with 39 mL/min flow rate. The gaseous products were analyzed using gas chromatography.

3 Results and discussion

The results of textural characteristic analysis of the catalysts are shown in Table 2.

Table 2. Texture characteristics of the catalyst.

Sample	**Specific surface area, m^2/g**	**Specific pore volume, cm^3/g**	**Average pore diameter, nm**
Cat.1	11.9	0.033	11.2
Cat.2	93.7	0.368	15.7
Cat.3	44.3	0.199	18.0

Since the pore size influences on the catalyst activity, so with the pore radius decreasing the rate of the process increases as long as diffusion resistance begins to have an effect on. While the decreasing in the surface utilization somewhat compensates the effect of its increase with a decrease in the pore radius.

The catalytic activity depends on the high specific surface area of the catalyst, i.e. due to the large number of pores and free access of methane to active sites on the inner surface of the pores throughout the entire volume of the catalyst.

From the data shown in Table 2, it can be seen that the catalyst with the highest specific surface area is Cat.2 catalyst with an average pore diameter of 15.7 nm, which is closest to the mesopore range. This catalyst has a larger total pore volume compared to Cat.1 and Cat.3 samples. With this one would expect high catalytic activity of the Cat.2 sample. Diffraction patterns of samples Cat.1, Cat.2 and Cat.3 are shown in Figure 3.

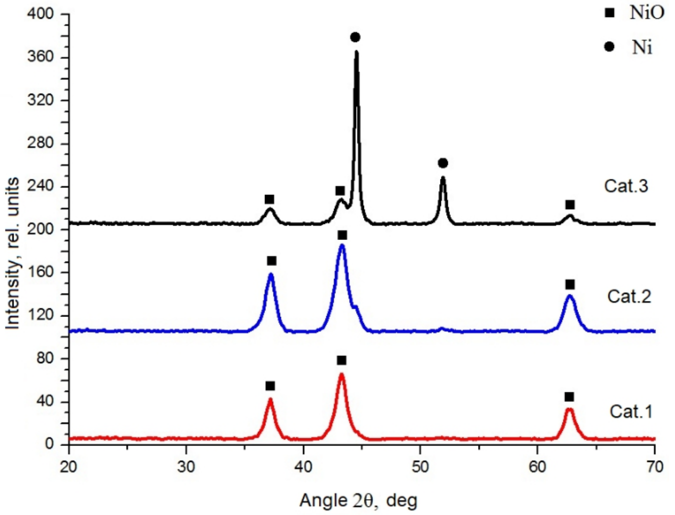

Fig. 1. Diffraction patterns of Ni-containing catalysts.

According to the X-ray diffraction data (Fig. 1), the presence of diffraction peaks corresponding to the crystalline phases of Ni and NiO was established in the composition of the catalysts. Silicon oxide was not shown because it is X-ray amorphous.

The average crystallite size was also determined (Table 3).

Table 3. Average crystallite size according to XRD data.

Sample	Average crystallite size, nm
Cat.1	10.57
Cat.2	9.73
Cat.3	14.10

According to XRD data, the samples Cat.1 and Cat.2 contain a rhombohedral phase of nickel oxide, while the sample Cat.3 also contains a face-centered cubic phase of metallic nickel. TEM images of the sample with the highest surface area Cat.2 are shown in Fig. 2.

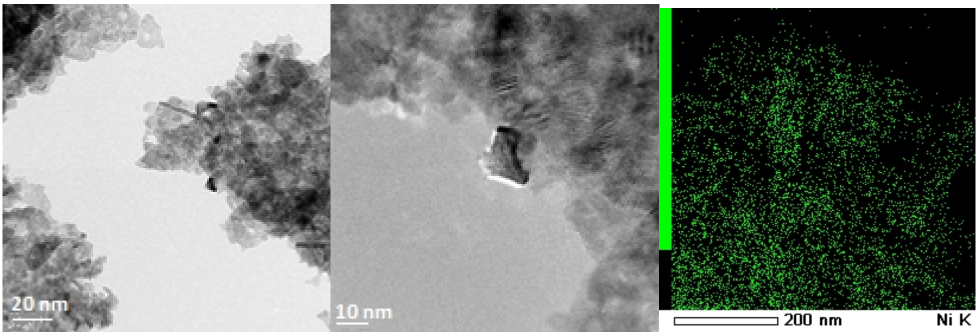

Fig. 2. Transmission electronmicrograph of catalyst Cat.2.

As seen from the figure, the average size of nickel metal particles is 11 nm, and the distribution of nickel particles on the support is uniform.

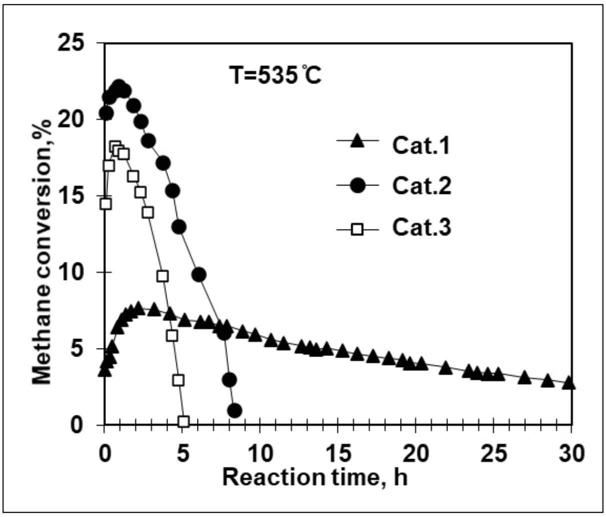

Fig. 3. Dependence of methane conversion on reaction time.

Studies of the catalytic activity of these samples (see Fig. 3) at 535°C have shown that the texture characteristics of the nickel catalyst have a greater effect on the conversion of methane than the content of nickel itself in the catalyst. Cat.2, which had the highest surface area and total pore volume compared to Cat.1 and Cat.3, had a maximum methane conversion at 23%. However, Cat.1, with the smallest specific surface area and the smallest total pore volume, exhibited a long-life on flow with more than 30 h without the catalyst being deactivated yet.

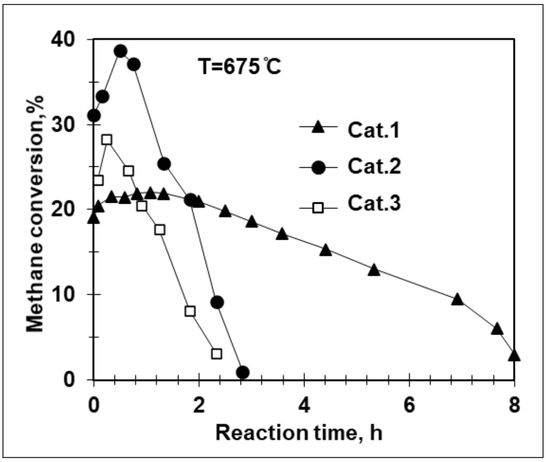

Fig. 4. Dependence of methane conversion on reaction time.

Increasing the reaction temperature to 675°C resulted in methane conversion increase , however, the lifetime of the catalysts significantly decreased compared to 535°C (see Fig. 4). Cat.2 showed a maximum conversion at 38%, while Cat.1 showed a maximum catalyst life of about 8 h.

4 Conclusions

It has been shown that the heterophase sol-gel method can be used for synthesis of catalyst with an average particle size of 11 nm, and it was found that the conversion of methane during methane thermocatalytic decomposition is more influenced by the texture characteristics of the catalyst than by the amount of nickel in the catalyst. It was found that the conversion of methane increases when increasing the temperature to 675°C, independently on the textural characteristics and composition of the catalyst. While the maximum catalyst lifetime depends on specific surface area and much stronger, on the lower specific surface area and total pore volume of the catalyst.

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