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Effect of Ce promotion on catalytic activity of Ni-Al catalysts in dry reforming of methane

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ABSTRACT

The Ni-Al, Ni-Ce, and Ni-Ce-Al catalysts tested in the dry methane reforming (DRM) were studied. Catalysts were synthesized by solution combustion synthesis and characterized by BET, XRD, and TEM. Catalytic activity was studied at 600–900 ºC with a 33%CH_4:33%CO_2:34%Ar (vol.%) fed with a total flow rate of 100 ml/min (3000 h^{-1}). The CH_4 and CO_2 conversion increased with the increase of Ce up to 15 wt.%, however, with further increase in Ce content conversion of gases decreased. Carbon was formed as filaments when catalysts worked at high temperatures. $CeAlO_3$ species could prevent the formation of filamentous carbon during DRM. Solution combustion synthesis is an attractive method of preparation of catalysts, due to the high dispersion of Ni particles, thus, the surface area is small, diminishing the coke deposition and enhancing the stability.

Keywords: synthesis gas, dry reforming of methane, solution combustion synthesis, Ni-Ce-Al catalysts

1. Introduction

The CO_2 conversion of methane or dry reforming of methane stands as a pivotal process in the realm of sustainable and environmentally conscious energy production. In a world increasingly grappling with the challenges of climate change and the need for efficient energy utilization, DRM emerges as a promising solution at the intersection of chemistry and energy technology. This chemical reaction involves the conversion of CH_4 with CO_2 to obtain synthesis gas with the H_2/CO ratio equal to unity, a valuable precursor in the synthesis of various chemicals and fuels [1]. The reaction of DRM is highly endothermic (ΔH_{298} = +247 kJ/mol).

Methane cracking, Boudouard reaction, and reverse water-gas shift reaction can cause substantial potential for coke deposition on surfaces. Another significant challenge is the tendency for active metal particles to sinter [2].

Several catalysts have been investigated in DRM to decrease carbon deposition on catalyst surfaces and metal sintering. The use of transition metal catalysts, such as supported Ni is abundant and cost-effective. Since supported nickel catalysts tend to deactivate, rare earth elements i.e. Ce and La can partially prevent this problem. For instance, Ni supported on a halloysite clay promoted with Co, Ce or La enhanced stability by suppressing metal sintering during DRM [3].

5 wt.% Ni incorporated into CeO_2-Al_2O_3 has been stable during 40 h with CH_4 conversion of 60% and CO_2 conversion of 79% [4]. It was reported that 3 wt.% Ce added to Ni/Al_2O_3 and $Ce_{1-x}Ni_xO_2$ enhanced the activity of the catalyst and resistance to carbon formation in DRM [5, 6], while Ni incorporated to Al_2O_3 and Ni/CeO_2 catalysts deactivated rapidly due to metal sintering and coke formation [7, 8]. In [9] 10 wt.% Ni/Al_2O_3 catalyst contained $NiAl_2O_4$ phase, while an enhanced activity in DRM was obtained for the catalyst with the addition of 5 wt.% CeO_2 due to formation of $CeAlO_3$, which enhanced carbon resistance of catalyst. In addition, dry reforming at low temperatures is also investigated [10]. The more

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active catalyst was Ni-Ce/SiO_2 than Ni-Ce/γ-Al_2O_3. The CH_4 conversion reached an equilibrium (60%), while for Ni-Ce/γ-Al_2O_3 CO_2 conversion was higher.

Catalyst synthesis

The catalysts were prepared by solution combustion synthesis. To synthesize 15Ni-35Ce 3 g of $Ni(NO_3)_2 \cdot 6H_2O$, 7 g of $Ce(NO_3)_3 \cdot 9H_2O$ and 10 g of urea were weighted on analytical balance. Deionized water preheated to 80 ºC (30 ml) was put into the beaker with salts. The solution was mixed well in the beaker. Then, the beaker containing the solution was placed in the preheated furnace at 500 ºC. After a few minutes gas release occurred, and then the solution was burnt with flame. Thereafter, the sample was cooled and powder was obtained. 15Ni-35Al and 15Ni-15Ce-20Al catalysts were prepared using the same procedure.

Catalytic experiments

Ni-Ce-Al catalysts were studied in DRM at the temperature range of 600-900 ºC. The gas mixture $CH_4/CO_2/Ar$ was fed at a ratio of 1:1:1 with GHSV of 3000 h^{-1}.

2 mL of catalyst powder was loaded into a stationary bed quartz reactor. The catalyst powder was poured onto a layer of quartz wool. The gas chromatograph “Chromos GC-1000” with Chromos software was used to analyze the composition of the reactants and gaseous products. X-ray diffraction was performed for analysis of the phase composition in DRON-4-0.7 diffractometer with CoKα tube using in the range 2θ = 5-100°. Metal particle size was studied using TEM analysis done with the Jeol JEM-1400Plus instrument. The surface area was evaluated using the Micromeritics 3Flex-3500 instrument and calculated by the BET method.

2. Results and discussion

2.1 Characterization of catalysts

XRD results. The XRD patterns of catalysts are shown in Fig. 1. Metallic Ni (Ni0) appears as peaks at 52.5°, 61.4°, and 92.4° in fresh and spent catalysts. The XRD pattern of bimetallic 15Ni-35Al [11] has only amorphous features (Fig. 1c), while the amorphous content in 15Ni-35Ce is also large (Fig. 1a). In the latter, CeO_2 has more crystalline phases in the fresh catalyst compared to other fresh catalysts. The crystallinity of the catalyst tested in a short-term experiment at 850 ºC is slightly higher and, crystalline Ni^0 is also clearly present in addition to CeO_2. The crystallinity of fresh 15Ni-15Ce-20Al catalyst is very low, as well as shows a high degree of amorphous content is high. The cubic $CeAlO_3$ is found with a

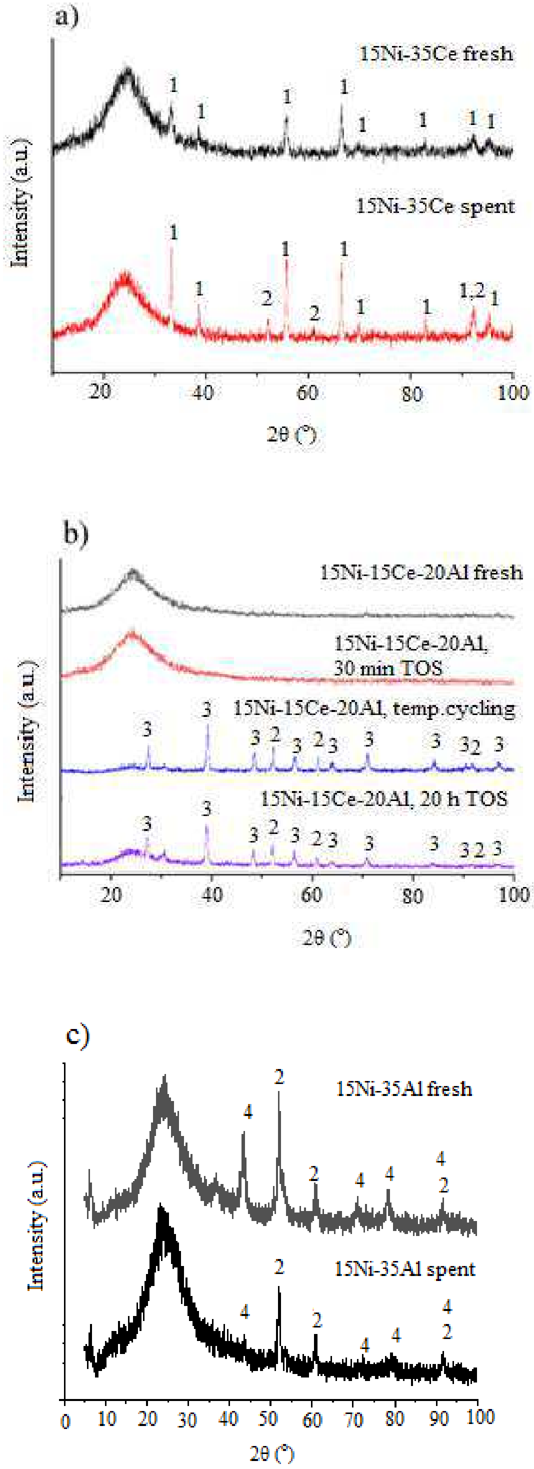

Fig. 1. XRD data of catalysts before and after reaction: a) 15Ni-35Ce (TOS = 30 min); b) 15Ni-15Ce-20Al (TOS = 30 min, at 600-900-600 ºC and 20 h TOS); c) 15Ni-35Al (TOS = 30 min). Notation: 1. CeO_2, 2. Ni^0, 3. $CeAlO_3$, 4. $NiAl_2O_4$.

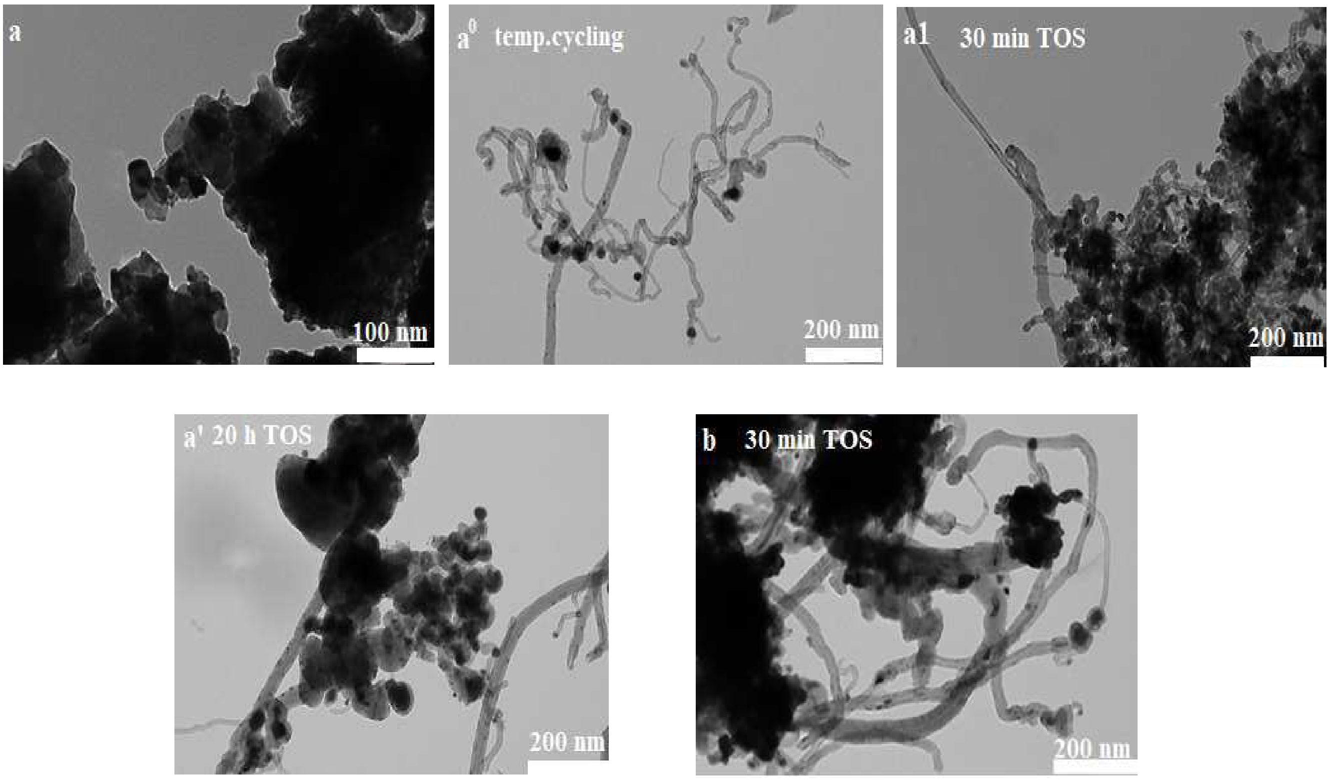

Fig 2. Transmission Electron Microscope of: a) fresh 15Ni-15Ce-20Al; a1) 15Ni-15Ce-20Al after 30 min TOS; a^{o}) 15Ni-15Ce-20Al after temperature cycling at 600-900-600 ºC; a') 15Ni-15Ce-20Al after 20 h TOS; b) 15Ni-35Ce spent.

few very weak peaks. The spent catalyst has also amorphous content, however, peaks of metallic Ni can be distinguishable from the background. No reflexes of CeO_2 phase were identified in 15Ni-15Ce-20Al.

When this catalyst was used in a long-term stability test (Figure 1b), increasing temperature, the $CeAlO_3$ phase, with a better fit to peaks with a tetragonal unit cell than cubic, was formed together with metallic Ni as confirmed with the main peaks at 25°, 39.2°, 48.5°, 56.6° and 70.9° of $CeAlO_3$.

15Ni-15Ce-20Al tested in stability at 850 ºC for 10 h shows the appearance of a peak at 30.5°, which becomes more visible after 20 h TOS.

TEM results were shown for Ni-Ce-Al catalyst tested in DRM (Table 1).

In the TEM images of all spent catalysts, the carbon nanotubes can be easily detected. As it can be seen from Table 1, the average size of metal particles is 15 nm for both 15Ni-35Ce and 15Ni-15Ce-20Al, while for 15Ni-35Al [11] nickel particle size was the lowest. The average particle size of metal was not significantly affected by the temperature cycling exposure for 15Ni-15Ce-20Al. However, metal particles increased after stability. The type of carbon deposited on Ni-Ce-Al catalysts is filamentous, while Ni-Al has graphitic coke on its surface.

Table 1. TEM results of the fresh and spent catalysts.

Catalyst	Spent metal particle size (nm)
15Ni-15Ce-20Al	[a]15,[b]18,[c]23
15Ni-35Ce	[a]15
15Ni-35Al	[a]12

Ni particle size for [a]30 min TOS, temperature cycling experiment 600-900-600 ºC and [c]20 h TOS at 850 ºC.

The BET surface areas are demonstrated in Table 2. The specific surface areas of the catalysts prepared by solution combustion methods are very small and the catalysts contain more mesopores than micropores.

Table 2. BET surface areas of catalysts BR – before and AR – after reaction.

Catalyst	BR/AR	S_{BET}
		m^2/g
15Ni-35Al [11]	AR	8
15Ni-15Ce-20Al	BR	8
15Ni-15Ce-20Al	AR	5
15Ni-35Ce	BR	10
15Ni-35Ce	AR	5

2.2 Catalytic results

Effect of Ce loading. Evaluation of catalytic behaviour at short time-on-stream (TOS = 30 min) of Ni catalysts with different Ce loadings in DRM was done at 850 °C (Fig. 3). The conversions of CH_4 and CO_2 gradually increased, while Ce was loaded up to 15 % Ce, there after, decrease with higher Ce loading. H_2 and CO yields were slighlthly decrease with Ce content increasing. Ce loading very much. Higher Ce loading does not strengthen the metal-support interaction. Ni-Ce catalysts without Al can be reduced difficult, thus decrease the catalytic activity, for example, for 15Ni-35Ce.

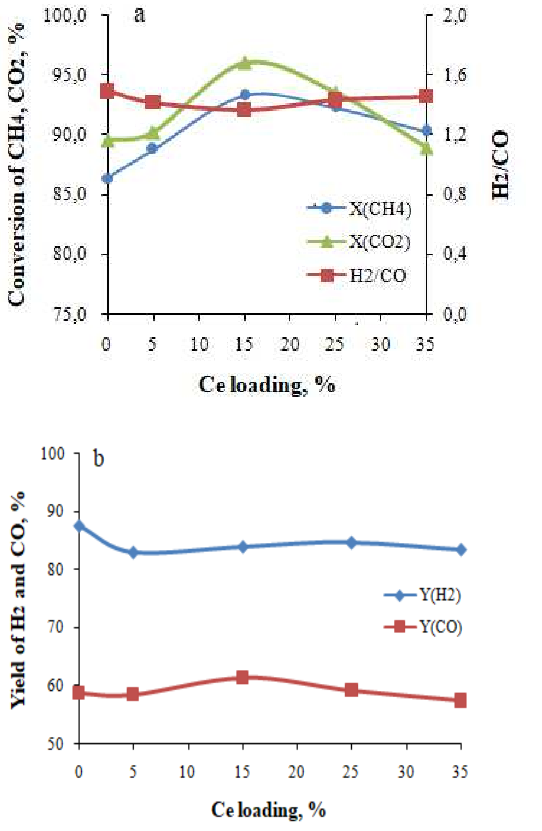

Fig. 3. Effect of Ce loading on a) conversion of gases, H_2/CO and b) yield of products.

2.3 Effect of temperature cycling in DRM over trimetallic Ni-Ce-Al catalyst

In order to investigate the stability of 15Ni-15Ce-20Al during the increase of temperature, a catalytic test was performed during 5 h using a 33% CH_4:33% CO_2:34% Ar at 600-900-600 °C as illustrated in Fig. 4. Catalytic activity did not decrease when turning back to 600 °C due to formation of $CeAlO_3$ phase, which helps with improving of activity.

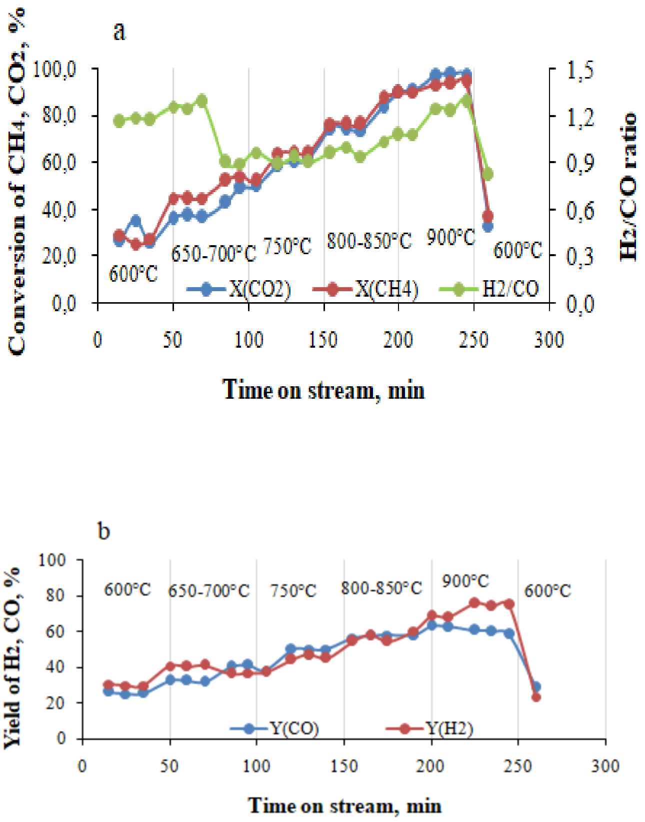

Fig. 4. Influence of temperature cycling on a) CH_4 and CO_2 conversion, and H_2/CO; b) yield of products.

2.4 Long time stability

Due to a relatively better performance of 15Ni-15Ce-20Al catalyst, its stability was further elucidated at 850 °C using GHSV 3000 h^{-1} for a longer time of 20 h. The conversion of CH_4 decreased linearly with time. After 10 h of catalytic reaction, a non-linear deactivation was considerable due to a small increase in CO_2 and CH_4 conversion. Many studies revealed that a filamentous type of coke is formed on Ce promoted catalysts.

In this work decrease in conversion can be attributed to the filamentous coke that leads to a blockage of the active surface. As carbon filaments continue to develop over time on the surface, they gradually encase the nickel particles within them. Additionally, there exists a crucial stage in the growth of carbon nanotubes where catalyst deactivation becomes significantly more noticeable.

3. Conclusions

Several Ni oxide catalysts were prepared via the solution combustion synthesis, studied by XRD,

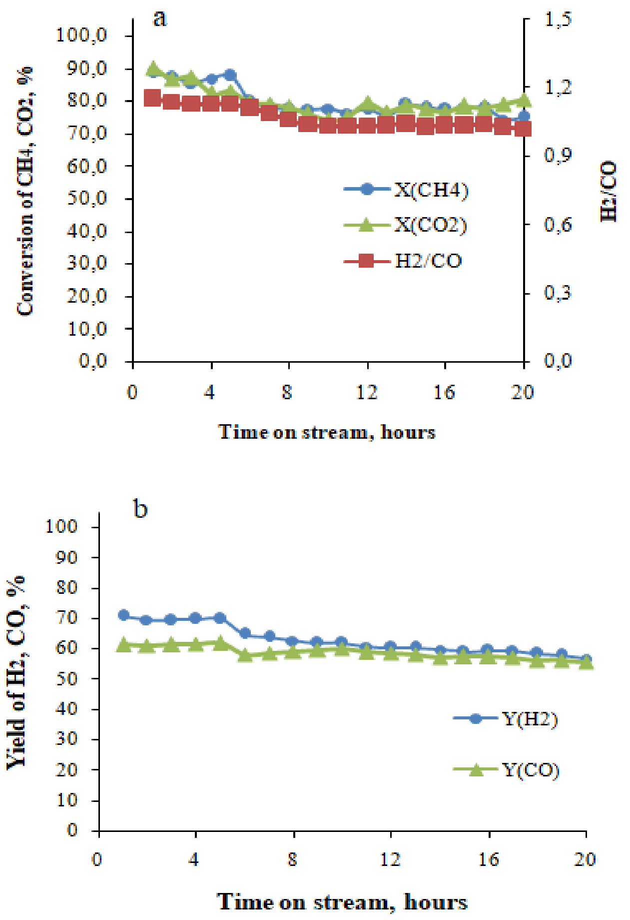

Fig. 5. Influence of time-on-stream on a) CH_4 and CO_2 conversion, and H_2/CO; b) yield of products.

BET and TEM analyses, and tested in DRM. The surface areas of the prepared catalyst were in the range of 5–10 m^2/g, which is typical for this type of catalysts. The metal particle sizes varied between 12–23 nm. XRD results of the catalysts before and after reaction showed that the crystallinity was low for Ni-Al and Ni-Ce catalysts, as well as for Ni-Ce-Al before reaction. However, the intensity of peaks of the Ni-Ce-Al catalyst rose with during DRM, simultaneously Ni^0 was formed. $NiAl_2O_4$ and $CeAlO_3$ phases appeared in Ni-Al and Ni-Ce-Al, respectively, during reaction, which might facilitate better stability of the catalyst.

Based on the initial catalyst screening, temperature stability for trimetallic Ni-Ce-Al, was investigated via cycling the temperature during DRM from 600 to 900 back to 600 ºC. For this catalyst H_2/CO molar ratio was close to unity. 15Ni-15Ce-20Al did not lose the activity in second cycle.

Long-term stability tests for Ni-Ce-Al catalyst showed that the former catalyst exhibited relative small deactivation after 10 h.

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Влияние промотирования церием на каталитическую активность катализаторов Ni-Al в сухом риформинге метана

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АННОТАЦИЯ

Были изучены катализаторы Ni-Al, Ni-Ce и Ni-Ce-Al, разработанные в процессе сухого риформинга метана (СРМ). Катализаторы были приготовлены методом горения раствора и исследованы методами БЭТ, РФА и ПЭМ. Каталитическую активность исследовали при температурах 600-900 ºC при подаче $33\%CH_4:33\%CO_2:34\%Ar$ (об.%) с общей скоростью потока 100 мл/мин (3000 $ч^{-1}$). Конверсия CH_4 и CO_2 увеличивалась с увеличением церия до 15 мас. %, однако при дальнейшем увеличении содержания Ce конверсия газов снижалась. Углерод образовывался в виде нитей, когда катализаторы работали при высокой температуре. Частицы $CeAlO_3$ могут предотвращать образование нитевидного углерода во время СРМ. Синтез горения раствора является привлекательным методом получения катализаторов из-за высокой дисперсности частиц Ni, таким образом, площадь поверхности невелика, что уменьшает отложение кокса и повышает стабильность.

Ключевые слова: синтез-газ, сухой риформинг метана, синтез горения раствора, катализаторы Ni-Ce-Al

Церий промоторлығының метанның құрғақ риформингісінде Ni-Al катализаторларының каталитикалық активтілігіне әсері

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АҢДАТПА

Метанның құрғақ риформингісі (МҚР) үдерісінде Ni-Al, Ni-Ce және Ni-Ce-Al катализаторлары зерттелді. Катализаторлар ерітіндіде жану әдісі арқылы дайындалды және физико-химиялық БЭТ, РФТ және ТЭМ әдістерімен талдаулар жасалынды. Бастапқы рекциялық қоспа 33%CH_4:33%CO_2:34%Ar W=3000 сағ$^{-1}$ T=600-900 ^{o}C температураларда ағынды каталитикалық қондырғыда катализдік белсенділігі зерттелді. Катализатор құрамындағы Ce концентрациясын 15% көтергенде CH_4 және CO_2 конверсиясы артты, ал керісінше Ce концентрациясының артуы газдардың конверсиясының төмендеуіне алып келеді. Жоғары температурада катализаторлардың бетінде жіп тәрізді көміртек түзілді. МҚР үдерісінде $CeAlO_3$ қосылысы жіп тәрізді көміртектің пайда болуына жол бермейді. Меншікті бет ауданының төмендеуімен кокстың түзілуі азайып, тұрақтылығының артуы нәтижесінде ерітіндіде жану синтезі Ni бөлшектерінің жоғарғы дисперстілігіне байланысты катализаторларды әзірлеудің тиімді әдісі болып табылады.

Түйінді сөздер: синтез-газ, метанның құрғақ риформингісі, ерітіндіде жану синтезі, Ni-Ce-Al катализаторлары.