Methane dissociation to CO_x-free hydrogen and carbon nanofiber over Ni-Cu/Al₂O₃ catalysts

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Abstract

The catalytic performance of copper promoted nickel/alumina catalysts was studied in thermocatalytic dissociation of methane for production of CO_x-free hydrogen and carbon nanofibers. Copper addition to nickel catalysts improved the catalytic performance due to increase in methane adsorption, higher reducibility and nickel dispersion on the catalyst surface. In addition, high affinity of copper with graphite structure prevents the generation of encapsulation carbon on the nickel surface and hinders the catalyst deactivation. The catalytic results confirmed that the increase in reaction temperature enhanced the CH₄ conversion. However the excessive increase in reaction temperature decreased the reactant (CH₄) conversion and catalyst lifetime.

Keywords

Methane dissociation; Hydrogen; Carbon nanofibers; Nickel; Copper; Gamma alumina

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1.Introduction

Hydrogen is the most promising clean fuel because of its successful demonstration in environmental aspects and fuel cells technologies. Moreover, pure hydrogen as a raw material has many applications in petroleum and petrochemical industries [1-4].

Hydrogen can be utilized to replace existing fuels but it is not a primary energy source, and should be manufactured from other resources. The most conventional processes for H₂ production are steam reforming, partial oxidation and autothermal reforming of methane. But these methods generate large amounts of carbon oxides as by-product. The hydrogen produced by the mentioned processes after purification (removing the CO_x) can be used in fuel cell applications. The removal of CO_x into ppm range needs expensive and complicated purification methods, which leads to the exploration of other alternative routes [5-7].

In recent years, thermocatalytic decomposition (TCD) of methane (CH₄→C+H₂O, ΔH°₂₉₈=74.8 kJ.mol⁻¹), has been recognized as an attractive alternative route to the traditional CO_x-free hydrogen production methods [3, 8-13]. Furthermore, TCD process produces carbon based materials with high added-value. The produced carbon based materials have received much attention due to the special properties, such as high stability in strong acids and bases solutions, high specific surface area and mechanical strength, which make them useful as catalyst support and H₂ storage materials [5,14].

Due to the partially filled 3d orbitals of the transition metals such as Ni, Co and Fe, they can improve the dissociation of CH₄ molecules through partially accepting electrons [15, 16]. Direct comparison demonstrates that the catalytic activity of the iron group metals for methane cracking is Ni>Co>Fe [17, 18]. Therefore, Ni-based catalysts have been widely investigated because of their high activity in methane thermocatalytic decomposition reaction.

TCD of methane is an endothermic reaction and the CH₄ conversion increases with the increase of the reaction temperature. Therefore to obtain high concentration of hydrogen operating at high temperature is necessary [19, 20]. However, operating at high temperatures deactivate the nickel based catalysts. Therefore, the addition of other metals as promoter can cause the increase in carbon yield and catalyst lifetime at higher temperatures in TCD of methane [5, 19]. The presence of Cu as a Ni promoter enhances the catalyst stability at high temperature. Moreover, copper addition improves the reducibility of nickel based catalysts [5, 6, 8, 21].

The objective of the present work is to develop Ni-Cu/Al₂O₃ catalysts with high catalytic stability for thermal decomposition of methane.

2.Experimental

2.1. Catalyst preparation

In the present work the sol–gel method was employed for preparation of alumina. In this method aluminum tri-isopropylate (98% purity, Merck) was initially hydrolyzed in distilled water by stirring at 80–85 °C for 1 h. Afterwards, for sol creation, nitric acid (65% purity, Merck) with a HNO₃/Al molar ratio of 1:1 was added to the prepared solution the produced sol was aged at 98 °C for 12 h. Then, the sol was maintained at 98 °C for 2 h in air and dried at 80°C and calcined at 450 °C for 4 h [22, 23]. The nickel based catalysts were prepared via wet impregnation method. Nickel nitrate (Ni(NO₃)₂·6H₂O, Merck) and copper nitrate (Cu(NO₃)₂·3H₂O, Merck) were employed as Ni and Cu precursors, respectively. For preparation of catalysts, the dehydrated catalyst support was impregnated with an aqueous solution containing the nickel and copper nitrates with suitable concentrations to obtain 50 wt.% Ni and various contents of copper. After this step, the prepared catalysts were dried at 80 °C and calcined at 450°C for 5 h.

2.2. Characterization

The N₂ adsorption/desorption analysis was performed at boiling temperature of nitrogen (-196°C) utilizing an automated gas adsorption analyzer (Tristar 3020, Micromeritics). Prior to analysis the samples were degassed under nitrogen atmosphere at 250°C for 2h. X-ray diffractometer (PANalytical X'Pert-Pro) with a Cu K α monochromatized radiation source and a Ni filter in the range $2\theta = 10-80^\circ$ was used for X-ray diffraction (XRD) analysis. Micromeritics chemisorb 2750 instrument was employed for temperature programmed reduction (TPR) analysis of the prepared catalysts. In this analysis, the specific weight of catalyst (100 mg) was heat treated (10°C/min) in a gaseous mixture (30 ml/min) of H₂: Ar (10:90). Before the analysis, the catalysts were degassed under an inert atmosphere (Ar) at 200°C for 2h. The similar instrument as described for TPR analysis was used for evaluating the carbon deposition over the spent catalysts by the temperature-programmed oxidation (TPO) method. In this analysis an oxidizing gas stream (30 ml/min, O₂: He (5:95)) was passed over the catalyst and the temperature increased to 800°C with a ramp rate of 10°C/min. The morphology of the prepared samples and spent catalysts was studied by the scanning electron microscopy (SEM) analysis with a VEGA TESCAN operated at 30 kV.

2.3. Catalyst evaluation

A fixed bed quartz micro-reactor with an internal diameter of 10 mm and a length 70 cm was used for evaluating the catalytic performance under ambient pressure. 50 mg of the catalyst particles (0.25-0.5 mm) was loaded into the reactor. The gaseous feedstock (30 vol.% CH₄ and 70 vol.% N₂) at gas hourly space velocities (GHSV) of 12000 and 24000 (ml.g⁻¹.h⁻¹) was introduced to reactor and the flow rates were controlled by

Bronkhorst High-Tech mass flow meter/controllers EL-FLOW[®] Select Series. Prior to analysis, the catalysts were reduced in-situ by a pure flow of H₂(25 ml/min) at 700 °C for 3 h. A Varian 3400 gas chromatograph with a TCD detector and a packed column (Carboxen 1000) was employed to analyze the effluent gases from the reactor.

3.Results and discussion

3.1.Structural characteristics

The structural characteristics determined by the BET and XRD analyses are presented in Table1. The prepared alumina possessed a high BET area and pore volume. Furthermore, the prepared Al₂O₃ (catalyst support) exhibited small pore and crystallite sizes that the results showed that the pore volume and BET area of catalyst support decreased after impregnation of nickel and copper. The textural properties revealed that the increasing in copper content decreased the BET area and porosity (pore volume) due to partial coverage and blockage of alumina pores by metal oxides, the collapse of mesoporous structure and particle agglomeration. The average crystallite size of the samples reported in Table 1. The results revealed that increasing in copper content decreased the average NiO crystallite size. This can be attributed to the participation of copper in particle dispersion as well as the formation of nickel-copper mixed oxides [24].

Fig. 1 shows the N₂ adsorption/desorption isotherms and also the pore size distribution of the catalyst support and calcined catalysts at 450°C. Based on the IUPAC classification, the prepared Al₂O₃ showed the IV type isotherm with H2 shaped hysteresis loop. This type of hysteresis loop confirmed that the prepared Al₂O₃ contains nonuniform mesopores with channels in cylindrical-shape [25, 26].

Also N₂ adsorption/desorption isotherms of the prepared catalysts can be considered as type V, which is related to the materials with mesoporous structure. Moreover, the

isotherms show type H3 hysteresis loop, which is related to materials with aggregated or agglomerated particles, which form pores with slit shape with nonuniform size and/or shape [25]. By comparing the N₂ adsorption/desorption isotherms shown in Fig. 1, it can be concluded that increasing the copper loading moved the formation point of hysteresis loop to higher relative pressure, confirming the broader pore size distribution [14,20]. This is in agreement with the results presented in Table 1.

According to Fig. 1b, the distribution of the pores of the catalysts are in the range of 3-18 nm, which shifts toward lower values with increasing the amount of copper up to 15 wt.%.

The diffraction patterns of Al₂O₃ support and calcined nickel based catalysts at 450 °C are shown in Fig. 2a. The diffraction peaks at 37.4°, 43.4°, 63.2° and 75.3° are related to the nickel oxide phase (JCPDS. 73-1519) and the diffraction peaks observed at 37.4°, 46.1° and 66.9° are related to the alumina phase (JCPDS. 01-1308). In XRD patterns of the promoted catalysts no diffraction peaks related to CuO were seen. This implies that the copper in these samples was in the mixed oxide form (Ni_xCu_(x-1)O) [27]. Diffraction peaks at 37.4°, 43.4°, 63.1° and 75.3° can be assigned to NiO and Ni_xCu_(x-1)O phases, which have overlapped together. It is known that the nickel and copper can form a wide range of alloys at temperatures higher than 354 °C. At this temperature, partial substitution of copper in lattice sites of nickel occurs, which is in agreement with obtained results by XRD analysis [21, 28].

The mean crystallite size presented in Table 1 shows that the crystalline structure of nickel-based catalysts promoted with copper is affected by the amount of copper content. As can be observed the crystallite size decreased with grow thin copper content, which can be due to the role of copper in improvement of the particle dispersion. It is notable

that higher Cu content created smaller crystallite size while increasing in Ni content leads to the bigger crystallites size [22].

The XRD patterns of the reduced catalysts are shown in Fig. 3. In the XRD pattern of 50%Ni-10%Cu/Al₂O₃ catalyst, the peaks related to metallic Ni and Ni-Cu phase were observed at $2\theta = 44.6^\circ$, 52.2° and 76.5° . Other researchers confirmed that nickel and copper generate stable alloy up to 750°C [29- 31]. Also the diffraction peaks at $2\theta = 37.5^\circ$ and 67.1° were related to alumina (JCPDS. 01-1308). XRD analysis demonstrated that the NiO and Ni_xCu_yO phases were completely converted to Ni metal and Ni-Cu alloy during the reduction process. Also the crystallite sizes calculated by Debye-Scherrer equation were equal to 26.53 for 50%Ni-10%Cu/Al₂O₃ reduced catalyst.

3.2. Temperature programmed reduction analysis (TPR)

Fig. 2b shows the TPR analysis of the prepared catalysts. In TPR profile of the unpromoted catalyst (50%Ni/Al₂O₃) the small peak observed at 350 °C is related to the reduction of bulk NiO, which has a weak interaction with alumina. The peak observed in TPR profile in the range of 400-600 °C is attributed to the strong interaction between nickel oxide and alumina support (octahedrally coordinated Ni²⁺). In addition, the observed reduction peak at 710 °C is due to reduction of nickel aluminate (tetrahedrally coordinated Ni²⁺) [32].

It is seen that the copper addition to the nickel catalyst shifted the TPR profile to lower temperatures. Some researchers have reported that the presence of copper improves nickel reducibility, which is confirmed by the results of TPR analysis [6, 33, 34]. TPR profile of 50%Ni-5%Cu/Al₂O₃ catalyst displays three recognizable peaks. The peak at 235 °C is due to the transformation of Cu⁺² to Cu and its intensity increases with increasing the copper content. The peak at 450 °C is related to the reduction of Ni⁺² to Ni

and the reduction peak observed at 655 °C is related to reduction of NiAl_2O_4 . It is observed that the intensity of reduction peak related to nickel aluminate decreases with increasing the copper content. This shows that the increase in copper content leads to a decrease in formation of nickel aluminate [30].

3.3. SEM analysis

Fig. 4a depicts the SEM analyses of the catalyst support (Al_2O_3). This image confirmed that the prepared Al_2O_3 possessed a nanostructure. SEM images of fresh 50%Ni/ Al_2O_3 and 50%Ni-10%Cu/ Al_2O_3 catalysts in Fig. 4b and c depicted nonuniform agglomerated cubic particles with different sizes. In addition, the porosity of the prepared catalysts decreased because of incorporation of metal oxides into the Al_2O_3 support. It is noteworthy that particles of promoted catalysts are more uniform compared to unpromoted sample.

3.2. Catalytic performance

In order to investigate the effect of copper content and reaction temperature on the methane conversion, the thermocatalytic decomposition reaction was carried out at various temperatures over the prepared samples. Fig. 5 depicts the methane conversion in the temperature range of 575-800 °C.

The thermocatalytic decomposition reaction of methane is endothermic and consequently the methane conversion increases with increasing the temperature. However, nickel based catalysts are sensitive to the reaction temperature and rapidly become inactive at high temperature [35]. This sudden loss of activity is due to the coverage of active sites by carbon and therefore unavailability of them.

The reason for the formation of encapsulating carbon is the imbalance between produced carbon at metal-gas interface and diffusion of carbon into nickel particles and its nucleation and deposition on the nickel-graphite side [16, 17].

According to Fig. 5, copper addition leads to a decrease in catalysts activity at low temperature and this decrease becomes more significant by increasing the amount of loading. This is because of the passivity of copper in thermocatalytic decomposition reaction of methane even at temperatures higher than 900 °C. Moreover, the presence of copper improves the catalyst performance at high temperatures [6, 21, 36]. Although copper is inactive in the thermocatalytic decomposition reaction of methane, but the high affinity of copper with graphite structure, prevents the creation of graphite layer on the surface of nickel, which and hinders the deactivation of catalyst [5, 14]. Furthermore, copper increases the adsorption of methane on the catalyst surface and also affects the methane decomposition via particle dispersing and improving the reducibility of nickel through the formation of mixed oxides [5, 6, 21].

Fig. 6a demonstrates the stability profiles of copper promoted samples at 750 °C. As can be seen, addition of copper to nickel based catalysts leads to a drastic increment in catalyst stability, which is due to the role of copper in keeping the surfaces and active sites clean and available. By increasing the amount of copper from 5 to 10 wt.%, a significant increase in catalytic stability was observed.

However, by increasing the copper content to 15 wt.%, a considerable drop in activity was seen after 400 min. Excessive amounts of copper results in the development of quasi liquid state in the particles and therefore the active particles at the top of the fibers are easily cut to smaller particles and are encapsulated with carbon layers [35]. This phenomenon is the reason for unavailability of active components, which also decreases the lifetime of the catalyst [14, 35].

Fig. 6b depicts the effect of reaction temperature on the stability of 50%Ni-10%Cu/Al₂O₃ catalyst in the thermocatalytic dissociation reaction of methane. According to this figure, due to the endothermic nature of this reaction, the initial CH₄ conversion increases with increasing the temperature and the catalytic stability decreases significantly. Development of quasi liquid state and surface coverage of active components by encapsulating carbon are the main reasons for major decrease in catalyst lifetime with temperature [35].

3.5. Characterization of the spent catalysts

Fig. 3 depicts the XRD patterns of the spent 50%Ni-10%Cu/Al₂O₃ catalysts. In this pattern, diffraction peaks at $2\theta=44.6^\circ$, 51.9° and 76.2° can be attributed to Ni and Ni-Cu alloy with an average crystallite size of 19.93 nm [37]. The formation of quasi -liquid state and fragmentation of particles decreased the crystallite size decreased during the reaction.

In addition, the diffraction peaks at $2\theta=26.5^\circ$, 42.9° , 44.6° , 54.5° and 78° are assigned to graphitic carbon. However, the diffraction peak observed at 42.9° confirms the formation of nanocarbons with quasi-amorphous form [38]. The carbon with graphitic structure was the dominant phase on the spent catalysts. Fig. 7 demonstrates the TPO profile of the spent 50%Ni-10%Cu/Al₂O₃ catalyst. As can be seen, two peaks were detected in the TPO profile. The first peak at low temperature was belonged to carbon with encapsulated form. The encapsulating carbon can accumulate on the catalysts and cover the active sites and causes the deactivation of catalyst. High temperature peak can be attributed to carbon whiskers (nanofibers) with crystalline structure. TPO analysis confirmed the formation of graphitic carbon during the methane thermocatalytic decomposition [39].

Fig. 8 shows the SEM micrographs of the generated at the end of methane catalytic decomposition process over 50Ni-10%Cu/Al₂O₃ catalysts at different temperatures. SEM analyses confirm that the carbon has filamentous form. The diameter and the length of these filaments are in nano and micro scales, respectively. The interwoven nature of carbon, makes it impossible to determine the correct length of the produced nanofibers. The metallic Ni particles (Bright points) observed on the top of carbon filaments confirm the existence of the tip growth mechanism for creation of carbon filaments [40].

The comparison of the SEM images related to carbon filaments formed at different temperatures illustrate the effect of reaction temperature on the morphology of carbon filaments.. The presented results in literatures show that, at low temperatures perfect (solid) CNFs was formed and at high temperatures the formation of carbon nanotubes (CNTs) was observed [41-42].The length and diameter of carbon filaments decreased with increasing in operating temperature, Fig. 8.The decrease in diameter is related to formation of quasi-liquid state and fragmentation of the metal particles and the faster deactivation of catalyst is due to reducing the filament length [2]. Some researchers believed the change in diameters of carbon via reaction temperature because of various rate of nanocarbon nucleation [43].

3.6.Calcination temperature effect

The textural characteristics of the 50%Ni-10%Cu/Al₂O₃ catalysts after calcination at various temperatures are reported in Table 2. The results indicate that with increasing the calcination temperature the BET area decreased, which is accompanied by an growth in crystallite size of particles. The decrease in specific surface area happens due to the collapse of porous structure and agglomeration of particles by increasing the

temperature. Furthermore, the obtained results show a decrease in the volume and an increase in the diameter of the particles with increasing the calcination temperature.

The nitrogen adsorption/desorption isotherms and pore size distributions of the 50%Ni-10%Cu-Al₂O₃ catalyst calcined at various temperatures are depicted in Fig. 9. According to the IUPAC classifications the N₂adsorption/desorption isotherms are type V with H3 hysteresis loop. By comparing the isotherms shown in Fig. 9, it can be concluded that by rising the calcination temperature the hysteresis loop is started at higher relative partial pressures, indicating a broader pore size distribution and also decrease in the surface area, which are in agreement with the presented results in Table 2.

XRD patterns of the 50%Ni-10%Cu/Al₂O₃catalyst calcined at various temperatures are indicated in Fig. 10a. This Figure confirms the formation of NiAl₂O₄ by increasing the calcination temperature. Furthermore, increasing in calcination temperature increased the mean crystallite size, Table 2.

Fig. 10b depicts the TPR profile of the 50%Ni-10%Cu/Al₂O₃ catalysts calcined at various temperatures. It is seen that the TPR profile shifts slightly toward higher temperatures with increasing the calcination temperature. Also, reduction of the samples becomes more difficult, which is due to the stronger interaction of components with the support. The most important change in the pattern of the calcined sample at 750 °C is the observation of a reduction peak at 810 °C, which can be attributed to the reduction of nickel aluminate phase. This is in agreement with the XRD results, which confirmed the presence of nickel aluminate at elevated calcination temperatures.

The CH₄conversion of the 50%Ni-10%Cu/Al₂O₃ catalysts calcined at various temperatures is depicted in Fig. 11. The catalyst activity increases with temperature up to

750 °C. However, the conversion of methane decreases at higher temperatures, which is because of the creation of encapsulating carbon.

In addition, the catalyst performance improved by increasing the calcination temperature, which may be related to the more formation of nickel-copper oxide at high calcination temperatures. However, further increase in calcination temperature to 750 °C decreased the catalytic activity because of the decrease in specific surface area and agglomeration of particles as well as the formation of nickel aluminate phase.

3.7. Effect of GHSV and feed ratio

The effects of GHSV and CH₄/N₂ ratio on the activity of the 50%Ni-10%Cu/Al₂O₃ catalyst at 675 °C were studied and the results are shown in Fig. 12. It is seen that, the methane conversion decreases with increasing the GHSV, which is due to the decline in contact time between molecules of methane and catalyst surface. In addition, Fig. 12 shows that an increase in CH₄/N₂ molar ratio decreased the methane conversion, which is because of the increased ratio of entering molecules of methane to the number of available active sites. On the other hand, increasing the GHSV and CH₄/N₂ molar ratio leads to an increase in the amount of produced carbon, which enhances the possibility of active sites coverage which in turn reduces the catalyst activity.

4. Conclusions

Ni/Al₂O₃ and Ni-Cu/Al₂O₃ catalysts were synthesized by the wet impregnation technique and their catalytic performances were investigated in the methane thermocatalytic decomposition reaction for production of CO_x-free hydrogen and filamentous carbons. This study revealed that the nickel based catalysts are sensitive to the reaction temperature and become inactive at high temperature. Addition of copper

improved the catalytic performance by increasing the adsorption of methane on the catalyst surface and also affects methane decomposition via particle dispersing and improving the reducibility of nickel. In other hands, although copper is inactive in the thermocatalytic decomposition reaction of methane, high affinity of copper with graphite structure prevents the generation of encapsulation carbon on the nickel surface and hinders the catalyst deactivation.

XRD results confirmed the existence of the $\text{Ni}_x\text{Cu}_{(1-x)}\text{O}_4$ species and Ni-Cu alloys in calcined and reduced catalysts, respectively. Temperature programmed reduction (TPR) profiles revealed that the copper addition improved the nickel oxide reducibility .

The catalytic performance was significantly related to the copper loading and operating temperature. The results demonstrated that the 50%Ni–10%Cu/ Al_2O_3 catalyst is an appropriate catalyst compared to other investigated catalysts. The catalytic results confirmed that increasing in reaction temperature, improved the initial methane conversion because of the endothermic nature of this reaction but excessive growth at reaction temperature decreases methane conversion and catalyst lifetime because of quasi liquid state and imbalance between carbon formation and migration rates.

The comparison of the SEM images of carbon fibers produced at various temperatures illustrate the significant effect of reaction temperature on the morphology of carbon nanofibers. The diameter of carbon nanofibers decreased with increasing in reaction temperatures. The SEM analysis of the used catalysts with various reaction temperatures showed that the produced carbon is in intertwined filaments form.

Acknowledgements

The authors appreciate the support from Iran National Science Foundation (INSF) and University of Kashan (Grant No. 158426/63).

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Fig. 1. N₂ adsorption/desorption isotherms and Pore size distributions (a): Gamma alumina [23], (b): the 50%Ni/Al₂O₃ [22] and 50%Ni-n%Cu/Al₂O₃ catalysts.

Fig. 2. (a):XRD patterns of the prepared samples (Al₂O₃ [23], 50%Ni/Al₂O₃ [22]) and (b):TPR profiles of (1):50%Ni/Al₂O₃ [22] and 50%Ni-Cu/Al₂O₃ catalysts with (2):5%Cu, (3): 10%Cu, (4): 15%Cu calcined at 450 °C.

Fig. 3. XRD patterns of the reduced catalyst at 700°C and spent catalyst (Reaction conditions: CH₄:N₂= 3:7,GHSV = 12,000 ml.h⁻¹g_{cat}⁻¹, T=750°C).

Fig. 4. SEM images of (a): prepared alumina, (b): 50%Ni/Al₂O₃ and (c): 50%Ni-10%Cu/Al₂O₃ (prepared catalysts calcined at 450 °C).

Fig. 5. CH₄ conversion (%) as function of Cu content and reaction temperature (Reaction conditions: CH₄:N₂=3:7, GHSV=24,000 ml.h⁻¹g_{cat}⁻¹) (50%Ni/Al₂O₃ [22]).

Fig. 6. (a): Stability of the 50%Ni/Al₂O₃ [22] and 50%Ni-Cu/Al₂O₃ catalysts with various Cu loadings at T=750°C, (b): Stability of the 50% Ni-10%Cu/Al₂O₃ catalyst at different reaction temperatures (CH₄:N₂=3:7, GHSV=12,000ml.h⁻¹g_{cat}⁻¹).

Fig. 7. TPO profile of the spent catalyst (T=750°C, CH₄:N₂=3:7, GHSV=12,000ml.h⁻¹g_{cat}⁻¹).

Fig. 8. SEM images of the spent 50%Ni-10%Cu/Al₂O₃ catalyst at(a): 675°C and (b): 750°C (CH₄:N₂=3:7, GHSV=12,000 ml.h⁻¹g_{cat}⁻¹).

Fig. 9.N₂ adsorption/desorption isotherms and pore size distributions of the 50%Ni-10%Cu/Al₂O₃ calcined at different temperatures.

Fig. 10. (a): XRD patterns of 50% Ni-10%Cu/Al₂O₃ catalysts calcined at (1): 450°C, (2): 600°C, (3): 50°C and (b): profiles of 50%Ni-10%Cu/Al₂O₃ catalysts calcined at different temperatures.

Fig. 11. CH₄ conversion as function of calcination and reaction temperatures (Reaction conditions: CH₄:N₂=3:7, GHSV=24,000 ml.h⁻¹g_{cat}⁻¹).

Fig. 12. Effect of GHSV and feed ratio on methane conversion of the 50%Ni-10%Cu/Al₂O₃ catalyst, T=675 °C.

Table 1. Structural characteristics of the catalyst support and catalysts

Catalyst	BET surface ^a area (m ² /g)	Particle size ^b D _{BET} (nm)	Pore volume ^c (cm ³ /g)	Pore size ^d (nm)	Crystal size ^e D _{XRD} (nm)
Al ₂ O ₃ (support)	188.24	8.06	0.65	8.05	7.63
50%Ni/Al ₂ O ₃	89.28	12.27	0.20	7.93	24.27
50%Ni-5%Cu/Al ₂ O ₃	72.25	14.86	0.18	8.33	21.65
50%Ni-10%Cu /Al ₂ O ₃	70.34	15.00	0.17	8.59	21.22
50%Ni-15%Cu /Al ₂ O ₃	51.89	19.92	0.15	9.35	19.97

^a Calculated by the Brunauer–Emmett–Teller(BET) equation.

^b Calculated by $D=6000/\rho \cdot S_{\text{BET}}$

^c Barrett-Joyner-Halenda (BJH)desorption pore volume.

^d Barrett-Joyner-Halenda (BJH) desorption average pore diameter.

^e Average NiO crystalline diameter using Scherrer equation from XRD

Table 2. Structural characteristics of the 50%Ni-10% Cu/Al₂O₃ calcined at different temperatures

Calcination	BET surface	Particle size	Pore volume	Pore size	Crystal size
temperature (°C)	area (m²/g)	D_{BET} (nm)	(cm³/g)	(nm)	D_{XRD} (nm)
450	70.34	15.00	0.17	8.59	21.22
600	51.50	20.45	0.15	9.42	26.42
750	27.20	38.73	0.14	12.37	29.97

Fig. 1. N_2 adsorption/desorption isotherms and Pore size distributions (a): Gamma alumina [23], (b): the 50%Ni/ Al_2O_3 [22] and 50%Ni-n%Cu/ Al_2O_3 catalysts.

Fig. 2. (a): XRD patterns of the prepared samples (Al_2O_3 [23], 50%Ni/ Al_2O_3 [22]) and **(b):** TPR profiles of **(1):** 50%Ni/ Al_2O_3 [22] and 50%Ni-Cu/ Al_2O_3 catalysts with **(2):** 5%Cu, **(3):** 10%Cu, **(4):** 15%Cu calcined at 450 $^\circ\text{C}$.

Fig. 3. XRD patterns of the reduced catalyst at 700°C and spent catalyst (Reaction conditions: CH₄:N₂= 3:7, GHSV = 12,000 ml.h⁻¹g_{cat}⁻¹, T=750°C).

Fig. 4. SEM images of (a): prepared alumina, (b): 50%Ni/Al₂O₃ and (c): 50%Ni-10%Cu/Al₂O₃ (prepared catalysts calcined at 450 °C).

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Fig. 7. TPO profile of the spent catalyst ($T=750^{\circ}\text{C}$, $\text{CH}_4:\text{N}_2=3:7$, $\text{GHSV}=12,000\text{ml.h}^{-1}\text{g}_{\text{cat}}^{-1}$).

Fig. 8. SEM images of the spent 50%Ni-10%Cu/ Al_2O_3 catalyst at (a): 675°C and (b): 750°C ($\text{CH}_4:\text{N}_2=3:7$, GHSV=12,000 $\text{ml.h}^{-1}\text{g}_{\text{cat}}^{-1}$).

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Fig. 10. (a): XRD patterns of 50% Ni-10%Cu/ Al_2O_3 catalysts calcined at (1): 450 $^{\circ}\text{C}$, (2): 600 $^{\circ}\text{C}$, (3): 50 $^{\circ}\text{C}$ and (b): profiles of 50%Ni-10%Cu/ Al_2O_3 catalysts calcined at different temperatures.

Fig. 11. CH₄ conversion as function of calcination and reaction temperatures (Reaction conditions: CH₄:N₂=3:7, GHSV=24,000 ml.h⁻¹g_{cat}⁻¹).

Fig. 12. Effect of GHSV and feed ratio on methane conversion of the 50%Ni-10%Cu/Al₂O₃ catalyst, T=675 °C.

Addition of copper to nickel catalyst supported on mesoporous nanocrystalline gamma alumina improved the catalytic activity and stability in thermocatalytic decomposition of methane. SEM micrograph of the spent catalyst (50%Ni-10%Cu/Al₂O₃ at 675 °C) exhibited the formation of filamentous carbon.