



## Effect of the chemical composition of $(\text{MgO})_x(\text{Al}_2\text{O}_3)_y$ support on the catalytic performance of Ni and Ni–Au catalysts for the partial oxidation of methane

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### ABSTRACT

The 5%Ni and 5%Ni–2%Au catalysts were supported on mixed oxides  $(\text{MgO})_x(\text{Al}_2\text{O}_3)_y$ . The supports were co-precipitated with molar ratio  $\text{Mg}/\text{Al}=0.25\text{--}2$ . The catalysts were studied in the partial oxidation of methane (POM). The reducibility properties, X-ray characterization, activity, selectivity and carbon resistance depending on composition of support were investigated. The highest activity (100% of  $\text{CH}_4$  conversion and 98% of CO selectivity) and stability during 72 h were achieved for 5%Ni and 5%Ni–2%Au/ $(\text{MgO})_x(\text{Al}_2\text{O}_3)_y$ . The catalysts supported on  $(\text{MgO})_x(\text{Al}_2\text{O}_3)_y$  showed high resistance toward carbon deposition.

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### 1. Introduction

The partial oxidation of  $\text{CH}_4$  ( $\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$ ,  $\Delta H_{298\text{K}}^\circ = -36 \text{ kJ mol}^{-1}$ ) is a process of the synthesis gas production with molar ratio of  $\text{H}_2/\text{CO}=2$ , being suitable for Fischer–Tropsch synthesis process. The noble metals such as Ru, Rh, and Pt [1] and common–Ni [2] supported on  $\text{Al}_2\text{O}_3$  are applied for this reaction [3]. Alumina is widely used as a catalyst carrier for many processes, but its catalytic and physicochemical properties are not always satisfactory because of that, mixed oxides  $\text{Al}_2\text{O}_3\text{--Me}_x\text{O}_y$ , have emerged as a new class of support materials [4]. The various compositions of mixed oxides:  $\text{MgO--Al}_2\text{O}_3$ ,  $\text{CuO--Al}_2\text{O}_3$ ,  $\text{ZrO}_2\text{--Al}_2\text{O}_3$ ,  $\text{ZnO--Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3\text{--Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3\text{--Al}_2\text{O}_3$ ,  $\text{CeO}_2\text{--ZrO}_2$ , and  $\text{La}_{1-x}\text{Ce}_x\text{NiO}_3$  were investigated in  $\text{CH}_4$  reforming processes [5–7].

The enhancement of catalytic activity, selectivity and resistance to carbon deposition of Ni catalysts supported on  $\text{MgO--Al}_2\text{O}_3$  is attributed to better dispersion of Ni on binary support and increase of support basicity [8]. The formation of solid solution NiO–MgO protects against the  $\text{NiAl}_2\text{O}_4$  formation and provide to presence of small uniform Ni particles being very active in  $\text{CH}_4$  reforming [9,10]. The electron transfer from NiO to MgO in the lattice of NiO–MgO solid solution increasing the interactions between the oxides slowed down the reduction of NiO phase during the preparation step. The gradual reduction of NiO–MgO leads to the high dispersion of Ni particles on the catalyst what is the cause of resistance to carbon deactivation [11]. The Mg–Al mixed oxide seems to

be suitable support also for Ru, Rh, and Pt noble metals in steam and dry reforming of methane [12,13].

The catalysts containing various compositions of  $\text{MgO--Al}_2\text{O}_3$  support were studied earlier (Mg/Al ratios of 0.1–0.9) [14,15]. However, presented results do not explain the correlation between composition of binary supports and activity and stability of catalytic systems.

The bimetallic catalysts consist of two noble metals [16]: non-noble and noble [17,18] as well as two non-noble elements [19] are well known as better catalytic systems than monometallic one and can be promising catalytic material in many processes. The researchers have focused attention on application the noble metals like Ru, Rh, and Pt as a promoters of Ni catalysts, which improve activity as well as carbon resistance of nickel catalysts [20,21]. Unfortunately, they are too expensive for wide, industrial scale use. Due to this fact, gold which is significantly cheaper than others noble metals, has become the subject of our interest. Furthermore, according to theoretical simulation gold seems to be good promoter of Ni catalysts [22].

The effect of chemical composition of  $\text{MgO--Al}_2\text{O}_3$  on reducibility, structural properties, activity and stability of supported Ni and Ni–Au catalysts in partial oxidation of methane was investigated in this paper.

### 2. Experimental

#### 2.1. Catalysts preparation

Supports  $\text{Al}_2\text{O}_3$ , MgO and  $(\text{MgO})_x(\text{Al}_2\text{O}_3)_y$  supports were prepared by precipitation and co-precipitation of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and

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Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O aqueous solution with ammonia. All supports were dried at 100 °C/4 h/air and calcined at 400 °C/4 h/air. The following composition of binary oxides support were prepared and in the text will be used their short cuts:

Support composition	Short cut of support
(MgO)(Al <sub>2</sub> O <sub>3</sub> ) <sub>2</sub>	Mg <sub>0.25</sub> Al
(MgO)(Al <sub>2</sub> O <sub>3</sub> )	Mg <sub>0.5</sub> Al
(MgO) <sub>4</sub> (Al <sub>2</sub> O <sub>3</sub> )	Mg <sub>2</sub> Al

The catalysts 5%Ni and 5%Ni–2%Au were prepared by wet impregnation of precursors: Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and HAuCl<sub>4</sub>. The composition of metal phase was determined as the best to achieve high catalytic performances in POM reaction, what was confirmed in previous studies (these results are not showed in this work). Additionally 2% of gold addition was suitable for the physicochemical measurements. Then obtained catalysts were dried 100 °C/4 h/air and calcined at 400 °C/4 h/air. The catalytic tests were carried out without any preliminary reduction procedure of catalysts.

## 2.2. Catalytic activity and stability tests

The activity tests in partial oxidation of methane (CH<sub>4</sub> + 1/2 O<sub>2</sub> → H<sub>2</sub> + CO) were carried out in the temperature range 200–900 °C under atmospheric pressure. The experiments were performed in the quartz flow reactor with an inner diameter of 4 mm placed in electric furnace equipped with a temperature controller. A K-type thermocouple was inserted at the bottom of the catalyst bed to check the bed temperature. The reactor was heated with the rate of 10 °C min<sup>-1</sup>. The catalyst sample 0.1 g making about 5 mm of bed highest was used in catalytic tests. The steam of reactant gas including: methane (5% CH<sub>4</sub>/He) and oxygen (5% O<sub>2</sub>/He) were supplied in molar ratio 2:1 at total flow rate 100 ml min<sup>-1</sup> (GHSV = 60,000 ml (h g cat)<sup>-1</sup>). All reagents of POM reaction were analyzed using GC technique. Gases mixture consisting of CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub>, and CO was analyzed by GC Varian 3300 (Varian Inc.) instrument equipped with CTR-1 column working at 35 °C and TCD detector running at 120 °C with 130 mA. The analysis of H<sub>2</sub> was carried out using CHROM-4 gas chromatograph (Laboratorni Pristroje Praha)—molecular sieve 4A, temperature 110 °C with TCD detector (100 mA, temperature 120 °C). Conversion (X) and selectivity (S) were calculated according to the following equations:

$$X_{\text{CH}_4} = \frac{\text{CH}_{4\text{in}} - \text{CH}_{4\text{out}}}{\text{CH}_{4\text{in}}} \quad (1)$$

$$S_{\text{CO}} = \frac{\text{CO}_{\text{out}}}{\text{CO}_{\text{out}} + \text{CO}_{2\text{out}}} \quad (2)$$

$$S_{\text{H}_2} = \frac{\text{H}_{2\text{out}}}{(\text{CH}_{4\text{in}} - \text{CH}_{4\text{out}}) \times 2} \quad (3)$$

The stability tests were carried out during 24 and 72 h run in POM reaction. The carbon deposition was analyzed by total organic carbon analyzer—TOC measurements.

## 2.3. Catalysts characterization

The temperature programmed reduction measurements (TPR<sub>H<sub>2</sub></sub>) were performed in automatic TPR system AMI-1. Samples (0.1 g) pre-calcined at 400, 700, and 900 °C were reduced in hydrogen stream (5% H<sub>2</sub>–95% Ar) with the gas volume velocity 40 ml min<sup>-1</sup> with the linear heating rate 10 °C min<sup>-1</sup>. The TPR studies were conducted in the temperature range 25–900 °C. Hydrogen consumption was monitored by a thermal conductivity detector.

The X-ray diffraction (XRD) measurements were carried out for two series of catalysts samples. The 5%Ni and 5%Ni–2%Au/(MgO)<sub>x</sub>(Al<sub>2</sub>O<sub>3</sub>)<sub>y</sub> systems were calcined at 400 °C and

**Table 1**  
Specific surface area m<sup>2</sup> g<sup>-1</sup>.

Catalyst	Specific surface area [m <sup>2</sup> g <sup>-1</sup> ]	
	400 <sup>a</sup>	900 <sup>a</sup>
Al <sub>2</sub> O <sub>3</sub>	237	137
MgO	30	20
Mg <sub>0.25</sub> Al	170	97
MgAl <sub>2</sub>	152	83
Mg <sub>4</sub> Al	125	66
5%Ni/MgAl <sub>2</sub>	119	52
5%Ni–2%Au/MgAl <sub>2</sub>	100	47

<sup>a</sup> Calcination temperature [°C].

reduced (flow rate of gas—50 ml min<sup>-1</sup>) at 900 °C. The various pre-treatment of catalyst samples follows from the need to obtain structural information about the nature of catalysts at the beginning and the end of POM reaction. It is a well known fact, that conditions of partial oxidation of methane changes from oxidative in low temperature (up to 400 °C) to reductive in higher temperature (above 500 °C) and high CH<sub>4</sub> conversion is achieved at about 900 °C [11]. X-ray diffraction patterns were collected using PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano reflecting geometry. Copper CuK radiation from a sealed tube was utilized. Data was collected in the range 5–90° 2θ with step 0.0167° and exposition per one step of 27 s.

Carbon content was determined by TOC technique (TOC—5000 Shimadzu with SSM 5000A—solid sample module). Samples (0.1 g) were oxidized at 900 °C in oxygen stream (150 ml min<sup>-1</sup>). An IR detector was used for quantitative analysis of exhausted CO<sub>2</sub>.

## 3. Results and discussion

### 3.1. Specific surface area measurements

The effect of calcination temperature on the specific surface area of Mg<sub>x</sub>Al<sub>y</sub> supports and 5%Ni and 5%Ni–2%Au/Mg<sub>x</sub>Al<sub>y</sub> catalysts is presented in Table 1. The surface area for mono oxides MgO and Al<sub>2</sub>O<sub>3</sub> amounted to 30 and 237 m<sup>2</sup> g<sup>-1</sup> after calcination at 400 °C and 20 and 137 m<sup>2</sup> g<sup>-1</sup> at 900 °C, respectively. The surface area for mixed oxides (Mg/Al ratios 0.25–2) supports changes from 170 to 125 m<sup>2</sup> g<sup>-1</sup> at 400 °C and decreased to 97 and 66 m<sup>2</sup> g<sup>-1</sup> at 900 °C. Koo et al. postulated the decrease of surface area attributing to the collapse of MgO–Al<sub>2</sub>O<sub>3</sub> support structure during the high temperature calcination process, which resulted also in the increase of Ni particles sizes [15]. The 5%Ni and 5%Ni–2%Au catalysts supported on Mg<sub>0.5</sub>Al characterized enough high surface area (119 and 110 m<sup>2</sup> g<sup>-1</sup>, respectively) ensured high activity of catalysts. The maximum of surface area after calcination at 450 °C and a further decrease of it with growth of temperature was reported also by Jiratova et al. [25].

### 3.2. TPR characterization

The temperature programmed reduction measurements were carried out for monometallic 5%Ni (Fig. 1) and bimetallic 5%Ni–2%Au catalysts (Fig. 2) supported on MgO, Al<sub>2</sub>O<sub>3</sub> and Mg<sub>x</sub>Al<sub>y</sub>. The samples were pre-calcined at 400, 700, and 900 °C. The TPR profiles for 5%Ni and 5%Ni–2%Au/Al<sub>2</sub>O<sub>3</sub> (Figs. 1a and 2a) presented consumption of hydrogen at low temperature, beginning at 300 °C, which was associated to the reduction of free nickel oxide species. Second peak observed at above 600 °C is connected to reduction of NiO species being in interaction with Al<sub>2</sub>O<sub>3</sub> support. The nickel and nickel–gold catalysts supported on MgO showed higher hydrogen consumption than supported on Al<sub>2</sub>O<sub>3</sub>. They showed not too intensive effects in the range of low temperature (Figs. 1b and 2b).

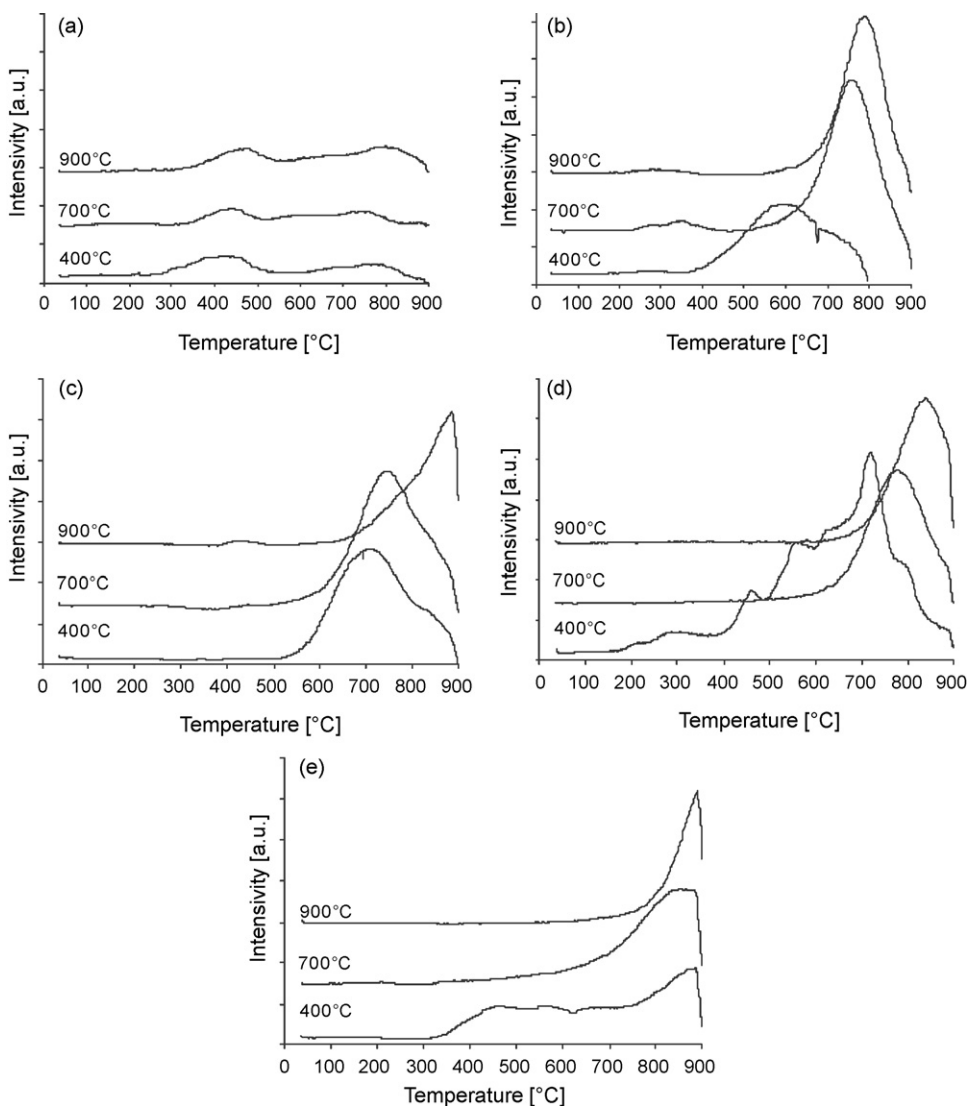


Fig. 1. The TPR profiles for 5%Ni/support catalysts (support: (a)  $\text{Al}_2\text{O}_3$ , (b)  $\text{MgO}$ , (c)  $\text{Mg}_{0.25}\text{Al}$ , (d)  $\text{Mg}_{0.5}\text{Al}$ , and (e)  $\text{Mg}_2\text{Al}$ ).

Additionally their shift towards higher temperature from 300 to 400 °C might be a result of NiO–MgO solid solution formation during the preparation step as was also reported by Shishido et al. [26].

The binary oxides supports  $\text{Mg}_x\text{Al}_y$  are not reducible compounds and TPR results of their studies are not presented in this work, however, the TPR profiles for nickel and nickel–gold catalysts supported on  $\text{Mg}_x\text{Al}_y$  are presented in Figs. 1c–e and 2c–e. The 5%Ni and 5%Ni–2%Au/ $\text{Mg}_x\text{Al}_y$  did not show any reduction effects at the low temperature regardless on composition of supports and temperature of calcination. The TPR results of 5%Ni/ $\text{Mg}_{0.25}\text{Al}$  (Fig. 1c) showed  $\text{H}_2$  consumption at 700–900 °C, which is definite as a reduction of stable  $\text{Ni}^{2+}$  compounds (NiO–MgO or  $\text{NiAl}_2\text{O}_4$  formed during calcination) [28]. The TPR profiles of samples with higher magnesium addition pre calcined at 400 °C showed wide reductive effects which began at lower temperature (300 °C) in comparison to 5%Ni/ $\text{Mg}_{0.25}\text{Al}$  (500 °C). Those results are agreed with studies of Koo et al. [15]. The samples pre calcined at 900 °C exhibit TPR peaks above 800 °C due to strong metal oxide to support interaction (SMSI). The SMSI occurs as interactions for highly dispersed nickel particles and support, while the larger agglomeration of metal oxide have a weak connection with a carrier [15]. Additionally, Au promotion of Ni catalysts (Fig. 2) caused insignificant shifts of the peaks towards the lower temperature.

### 3.3. X-ray diffraction analysis

Fig. 3 shows the results of XRD investigations of  $\text{Mg}_x\text{Al}_y$  supports pre-calcined at 400 °C. X-ray diffraction pattern for  $\text{Mg}_x\text{Al}_y$  supports with molar ratio  $\text{Mg}/\text{Al} = 0.25$ –2 indicated the presence of  $\text{MgAl}_2\text{O}_4$  spinel, additionally Mg-rich sample ( $\text{Mg}/\text{Al} = 2$ ) showed also the occurrence of MgO phase ( $2\theta = 43.06^\circ$  and  $62.53^\circ$ ) [28]. Furthermore, the increasing intensity of XRD signals with MgO loading to  $\text{Al}_2\text{O}_3$  confirmed the growth of crystalline size of supports.

Figs. 4 and 5 demonstrate the phase composition of 5%Ni and 5%Ni–2%Au/ $\text{Mg}_x\text{Al}_y$  catalysts pre-calcined at 400 °C and pre-reduced at 900 °C, respectively. The NiO phase for catalysts pre-calcined at 400 °C was not observed, probably due to partially  $\text{Ni}^{2+}$  inclusion in support network and formation of  $\text{NiAl}_2\text{O}_4$  spinel [24,29]. It is hard to distinguish the XRD patterns of  $\text{MgAl}_2\text{O}_4$  ( $2\theta = 19.03^\circ, 31.27^\circ, 36.85^\circ, 44.83^\circ, 59.37^\circ, \text{ and } 65.24^\circ$ ) from the  $\text{NiAl}_2\text{O}_4$  ( $2\theta = 19.07^\circ, 31.41^\circ, 37.01^\circ, 44.99^\circ, 59.66^\circ, \text{ and } 65.54^\circ$ ) because they overlap. However, those results are agreed with TPR profiles, which showed the presence of strong metal oxide to the support interaction (SMSI).

Additionally, the XRD patterns confirmed the presence of metallic Au for 5%Ni–2%Au/ $\text{Mg}_x\text{Al}_y$  catalysts after both pre-treatment conditions—calcination at 400 °C and reduction at 900 °C.

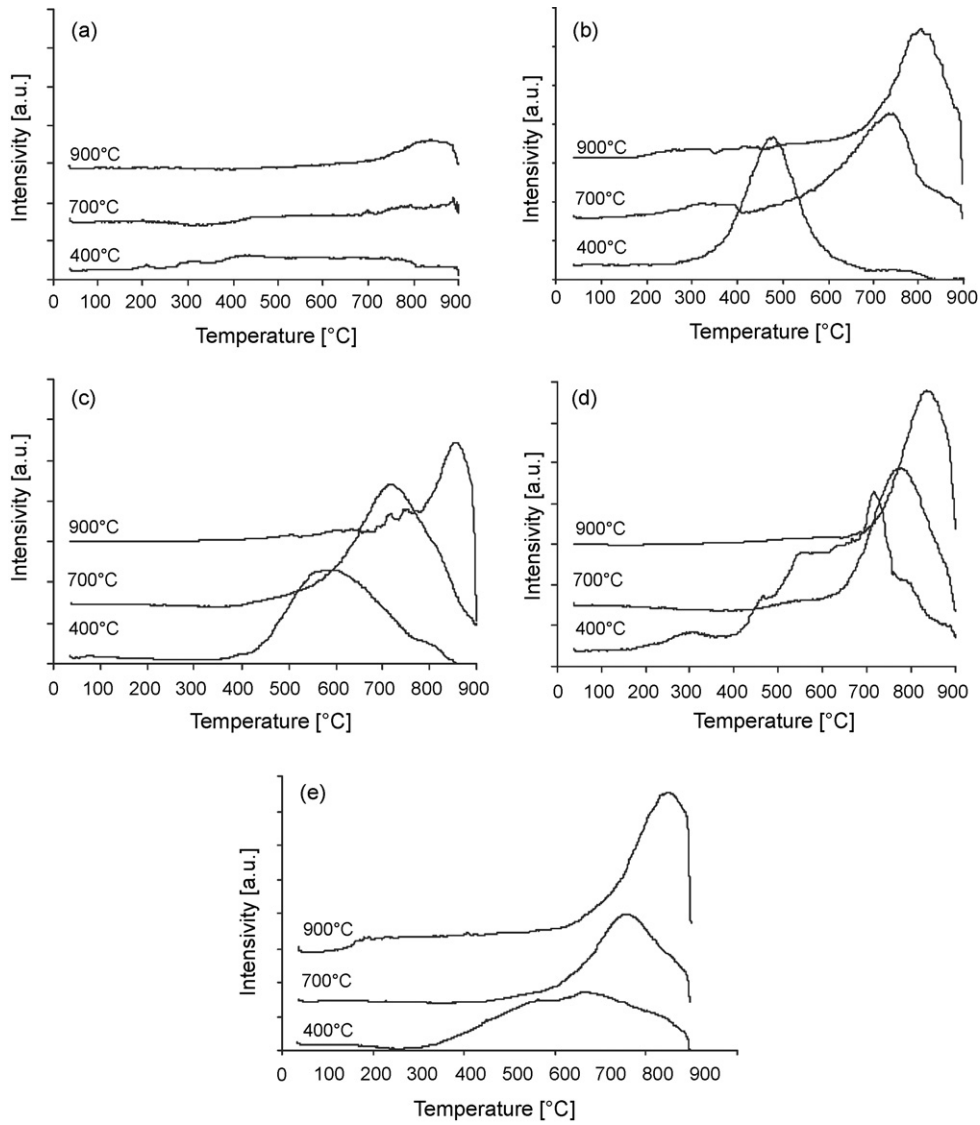


Fig. 2. The TPR profiles for 5%Ni–2%Au/support catalysts (support: (a)  $\text{Al}_2\text{O}_3$ , (b)  $\text{MgO}$ , (c)  $\text{Mg}_{0.25}\text{Al}$ , (d)  $\text{Mg}_{0.5}\text{Al}$ , and (e)  $\text{Mg}_2\text{Al}$ ).

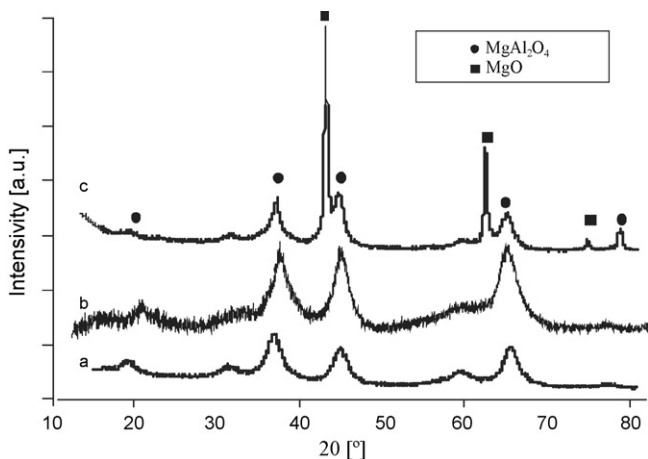


Fig. 3. XRD patterns for (a)  $\text{Mg}_{0.25}\text{Al}$ , (b)  $\text{Mg}_{0.5}\text{Al}$ , and (c)  $\text{Mg}_2\text{Al}$  supports.

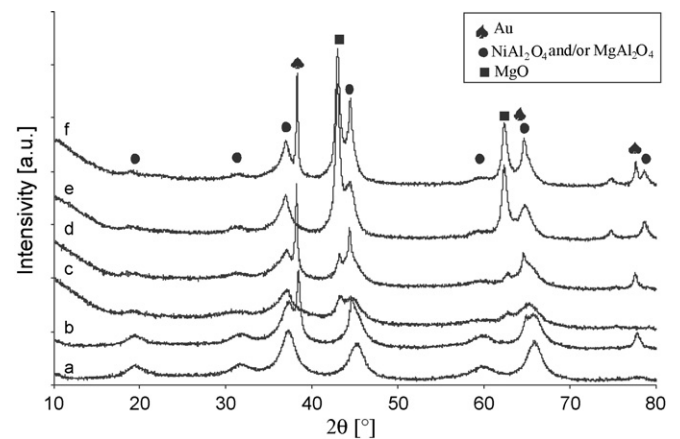
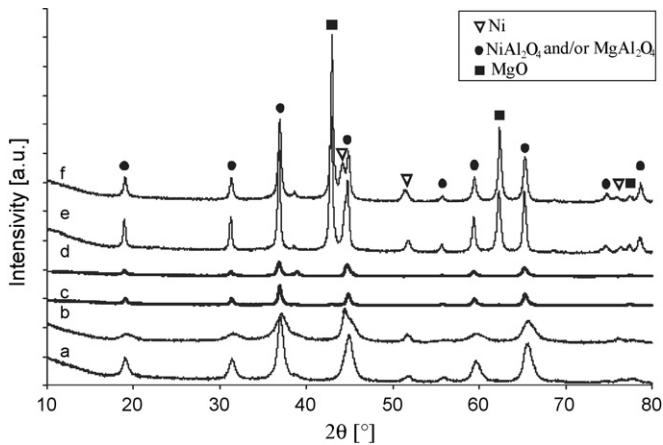


Fig. 4. XRD patterns for (a) 5%Ni/ $\text{Mg}_{0.25}\text{Al}$ , (c)  $\text{Mg}_{0.5}\text{Al}$ , (e)  $\text{Mg}_2\text{Al}$ , and (b) 5%Ni–2%Au/ $\text{Mg}_{0.25}\text{Al}$ , (d)  $\text{Mg}_{0.5}\text{Al}$ , (f)  $\text{Mg}_2\text{Al}$  pre-calcined at 400°C.

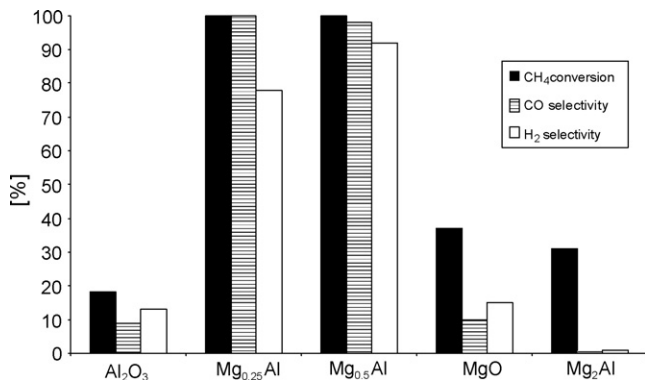


**Fig. 5.** XRD patterns for (a) 5%Ni/Mg<sub>0.25</sub>Al, (c) Mg<sub>0.5</sub>Al, (e) Mg<sub>2</sub>Al, and (b) 5%Ni–2%Au/Mg<sub>0.25</sub>Al, (d) Mg<sub>0.5</sub>Al, (f) Mg<sub>2</sub>Al pre-reduced at 900 °C.

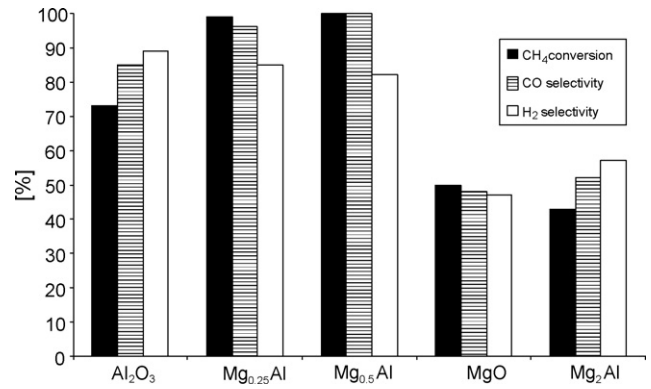
The reduction of 5%Ni and 5%Ni–2%Au/Mg<sub>x</sub>Al<sub>y</sub> catalysts at 900 °C (Fig. 5) resulted in the partial destruction of NiAl<sub>2</sub>O<sub>4</sub> structure and appearance of Ni phase for systems supported on Mg/Al = 0.25 and 2. The high temperature reduction caused also the disappearance of XRD signals coming from Au, probably owing to Ni–Au alloying which is confirmed also by shift of Ni pattern [30].

### 3.4. Catalytic activity tests

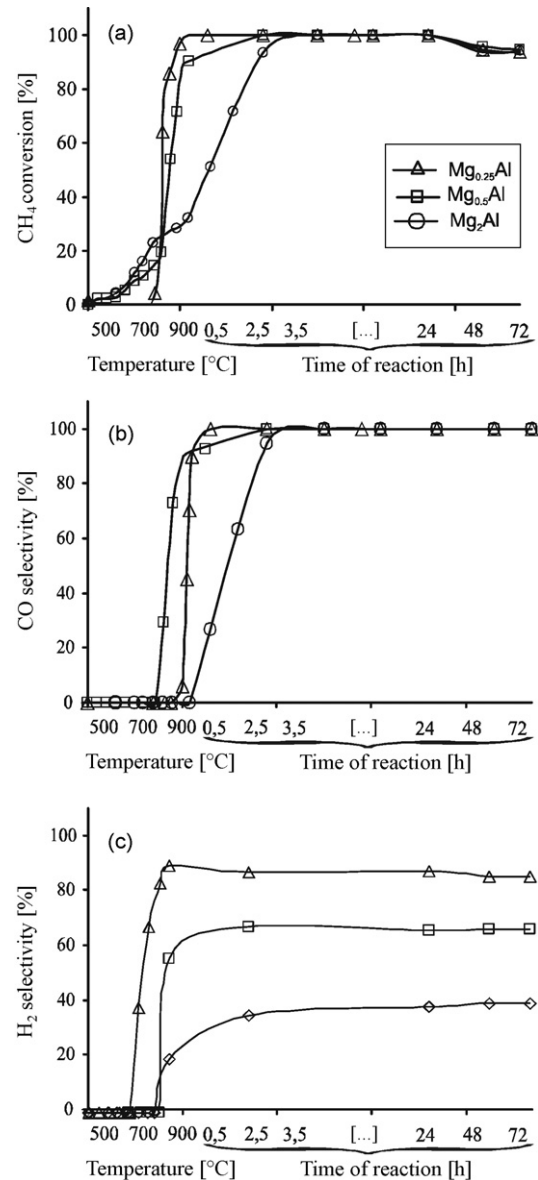
The 5%Ni and 5%Ni–2%Au/Mg<sub>x</sub>Al<sub>y</sub>, MgO and Al<sub>2</sub>O<sub>3</sub> catalysts were studied in partial oxidation of methane ( $\text{CH}_4 + 1/2 \text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$ ,  $\Delta H_{298\text{K}}^\circ = -36 \text{ kJ mol}^{-1}$ ). The reaction was carried out in the wide range of temperature (200–900 °C), but the synthesis gas formation started above 700 °C. The CH<sub>4</sub> conversion, CO and H<sub>2</sub> selectivity of nickel and nickel–gold catalytic systems at 900 °C are presented, respectively, in Figs. 6 and 7. The differences of catalytic performance between bimetallic and monometallic catalysts were observed. The higher activity of Ni–Au/Al<sub>2</sub>O<sub>3</sub> catalysts was observed in the first step of reaction, where they achieved 70% of CH<sub>4</sub> conversion (Fig. 7) while 20% of CH<sub>4</sub> conversion showed 5%Ni/Al<sub>2</sub>O<sub>3</sub> system (Fig. 6). The CH<sub>4</sub> conversion increased after several hours of POM reaction. The higher activity seems to be connected with higher amount of Ni<sup>0</sup> sites on the surface of bimetallic catalyst [31]. The facilitation of Ni sites reduction for them is probably achieved by CO adsorption on Au species and later reduction of NiO. What is more the changes of electron properties of elementary cells of Ni species being in Ni–Au alloy were responsible for activity the bimetallic catalysts [22,23].



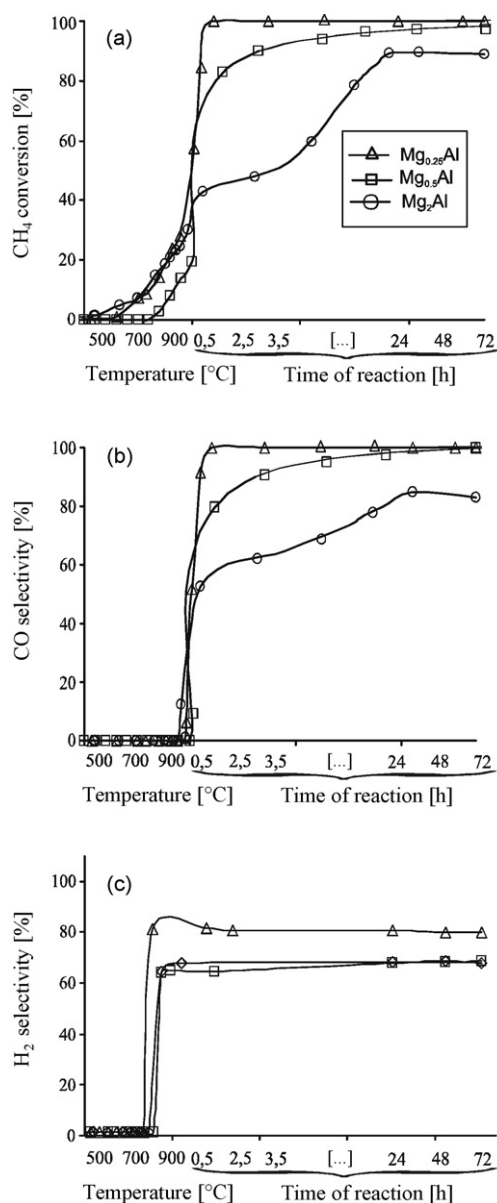
**Fig. 6.** The CH<sub>4</sub> conversion, H<sub>2</sub> yield and CO selectivity at 900 °C in POM reaction for supported nickel catalysts.



**Fig. 7.** The CH<sub>4</sub> conversion, H<sub>2</sub> yield and CO selectivity at 900 °C in POM reaction for supported nickel–gold catalysts.



**Fig. 8.** The (a) CH<sub>4</sub> conversion, (b) CO selectivity, and (c) H<sub>2</sub> selectivity of 5%Ni/support catalysts during 72 h of POM reaction.



**Fig. 9.** The (a) CH<sub>4</sub> conversion, (b) CO selectivity, and (c) H<sub>2</sub> selectivity of 5%Ni–2%Au/support catalysts during 72 h of POM reaction.

The catalysts supported on mono-oxide achieved lower activity than those supported on binary oxides. The highest activity (100% of CH<sub>4</sub> conversion, 90% of H<sub>2</sub> selectivity and 98% of CO selectivity) was achieved for catalysts supported on Mg<sub>0.25</sub>Al and Mg<sub>0.5</sub>Al, while Mg<sub>2</sub>Al similarly as MgO and Al<sub>2</sub>O<sub>3</sub> showed above two times lower CH<sub>4</sub> conversion. The decrease of activity for Mg-rich samples can be caused by excessive growth of alkalinity of studied systems [27].

Furthermore, the long term reactions performed at 900 °C during 72 h showed activation of 5%Ni and 5%Ni–2%Au/Mg<sub>2</sub>Al during first 3 h, after which the POM reaction runs with about 55% of CH<sub>4</sub> conversion and 70% of CO selectivity (Figs. 8 and 9). The POM reaction on monometallic Ni catalysts supported on Mg<sub>x</sub>Al<sub>y</sub> (Mg/Al=0.25–2) run with 100% of CO selectivity during 72 h test and the decrease of CH<sub>4</sub> conversion after this time was about 10% (Fig. 7a). The bimetallic nickel–gold catalysts showed a little higher ignition temperature, but after 72 h POM run they did not lose their activity (Fig. 8a).

The catalysts supported on Mg<sub>x</sub>Al<sub>y</sub> were much more resistant to carbon deposition than those on Al<sub>2</sub>O<sub>3</sub> carrier. The TOC analysis

showed only below 1 wt.% of carbon deposition after 24 h run of POM reaction. The carbon deposition about 23 wt.% was observed for Al<sub>2</sub>O<sub>3</sub>. The determination of the carbon type was impossible due to very small amount of deposition, however, one can suppose that it occurred as graphite like compounds.

#### 4. Conclusions

The co-precipitation of aluminium and magnesium binary oxides resulted in the formation MgAl<sub>2</sub>O<sub>4</sub> spinel, which showed suitable performance as a carrier of nickel catalyst for partial oxidation of methane. The highest activity and stability were achieved for 5%Ni and 5%Ni–2%Au/Mg<sub>0.25</sub>Al and Mg<sub>0.5</sub>Al pre-calcined at 400, which synthesizes the CO + H<sub>2</sub> mixture with 90–100% of CH<sub>4</sub> conversion and 100% of CO selectivity during 72 h run of POM reaction. The Mg-rich support Mg<sub>2</sub>Al, showed lower activity because of the presence of MgO besides MgAl<sub>2</sub>O<sub>4</sub> phase. The catalysts supported on Mg<sub>x</sub>Al<sub>y</sub> were highly resistant toward carbon deposition.

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