

Catalytic Activity and Physicochemical Properties of Ni–Au/Al₃CrO₆ System for Partial Oxidation of Methane to Synthesis Gas^{1,2}

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Abstract—This work is focused on the role of gold and Al₃CrO₆ support for physicochemical properties, and catalytic activity of supported nickel catalysts in partial oxidation of methane (POM). Catalysts, containing 5% Ni and 5% Ni–2% Au active phases dispersed on mono- (Al₂O₃, Cr₂O₃) and bi-oxide Al₃CrO₆ support, were investigated by TPR, BET and XRD methods, and the activity tests in POM reaction were carried out. Bimetallic Ni–Au catalysts dispersed on Al₃CrO₆ support remained highly stable and active. The amorphous binary oxide Al₃CrO₆ can stabilize considerable amount of Cr⁴⁺, Cr⁵⁺, and Cr⁶⁺ species in Ni–Au/Al₃CrO₆ catalyst network during its calcination in the air. Nickel supported on binary oxide Ni/Al₃CrO₆ can form Ni(III)CrO₃ bi-oxide phase in reductive conditions. During TPR H₂ reduction of Ni–Au/Al₃CrO₆ catalyst chromium(II) oxide Cr(II)O phase is observed. After POM reaction the existence of bimetallic Au–Ni alloy was experimentally confirmed on mono-oxide Al₂O₃ support surface, but its formation was not identified on bi-oxide Al₃CrO₆ support.

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INTRODUCTION

Reforming of hydrocarbons to synthesis gas is a very important branch of industrial chemistry. The use of methane to syngas production is applied in several ways of methane reforming reactions [1].

	Kind of reaction	ΔH_{298}^0 , kJ/mol
Steam reforming	$\text{CH}_4 + \text{H}_2\text{O} \longrightarrow \text{CO} + 3\text{H}_2$	206
CO ₂ reforming	$\text{CH}_4 + \text{CO}_2 \longrightarrow \text{CO} + 2\text{H}_2$	247
Partial oxidation	$\text{CH}_4 + 1/2\text{O}_2 \longrightarrow \text{CO} + 2\text{H}_2$	–38

Steam reforming process is common way to obtain syngas. Unfortunately this process, and also CO₂ reforming are highly endothermic reactions, what causes the necessity of large expenditure of energy. Partial oxidation of methane can be an alternative method of synthesis gas production. POM reaction is mildly

exothermic process, which gives synthesis gas with H₂/CO = 2 : 1. Such composition of gaseous mixture is suitable for methanol and Fisher Tropsch synthesis. Syngas is formed in high-temperature conditions (800–1200°C). The use of noble metals, such as: Pt, Pd, Ru, Rh [2], permits to achieve good efficiency of POM process. Unfortunately, these metals are unacceptably expensive, but nickel is relatively cheap and highly effective catalyst material for POM reaction. However, nickel catalysts are susceptible for sintering and they are not resistant for coke deposition, taking place on Ni-catalyst surface during POM reaction. Resistance to carbon deactivation follows the decreasing order Ru, Rh ≫ Pd > Ni [3]. The prevention of coke accumulation is possible, when high degree of nickel dispersion on catalyst support surface is achieved. Also, the use of promoters, for example: noble metals or alkaline earth metal oxides reduces coke formation [4]. It is probably connected with a surface segregation of metals. Among noble metals: Ru, Rh, Au, and the others can be used for promoting Ni catalysts. The addition of gold can result in Ni–Au alloy formation on catalyst support surface assuring better dispersion of Ni. In this way supported Ni–Au catalysts are expected much more resistant to carbon species accumulation [5].

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² Based on a report at the VII Russ. Conf. on Mechanisms of Catalytic Reactions (with international participation), St. Petersburg, July 2–8, 2006.

Catalytic activity in POM reaction depends on a kind and a content of applied metal phase and also, on the properties of support. Until now, alumina oxide was commonly applied as supporting material. The addition of such components, as chromia or magnesia to alumina improves considerably the catalytic properties [6]. The most common method of preparing bi-oxide supports is coprecipitation. In this way, it is possible to obtain well-mixed binary oxide spinel type Al₃CrO₆ structure. Both Al₃CrO₆ and Al₂MgO₄ spinel oxides contribute to higher activity of metal/support catalyst in POM reaction, when compare with Al₂O₃ support alone [7, 8].

EXPERIMENTAL

Catalyst Preparation

Mono and bimetallic supported catalysts, containing 5% Ni and 5% Ni–2% Au, were prepared. As precursors of Ni and Au metal phases Ni(NO₃)₂ · 6H₂O and HAuCl₄ compounds were applied. Metal/support catalysts were prepared by conventional wet impregnation method. The appropriate compounds Cr(NO₃)₃ · 9H₂O and Al(NO₃)₃ · 9H₂O were used as precursors of supports. Mono (Al₂O₃, Cr₂O₃) and bi-oxide (Al₃CrO₆) supports were obtained by precipitation and co-precipitation with ammonia. Supports were dried and calcined 4 h in air at 400°C before impregnation step. The co-precipitated binary aluminum-chromium oxide, containing Al and Cr in molar ratio 3 : 1 gave the chemical formula Al₃CrO₆. The influence of chromium oxide on the physicochemical properties of γ -Al₂O₃ was studied [8, 9], but researchers did not clearly describe correlation between chromium content in mixed oxides and their catalytic activity. Based on our studies of Cr/Al mixed oxide (molar ratio Al/Cr = 3 : 1, 0.3 : 1, 0.1 : 1), the most active was sample for molar ratio 3. The chromium/aluminum mixed oxides was used just because as support of nickel-gold catalysts. Nickel and gold phase were impregnated on supports and then the supported catalysts were dried and finally calcined in the same conditions at 4 h in air at 400°C for. Additionally, series of supports calcined for 4 h in air at 400, 900, 1200°C were prepared.

Methods of Characterization

Temperature programmed reduction. TPR H₂ of supports and metal/support catalysts was performed by automatic TPR system AMI-1 Altamira Instruments, in temperature range 25–900°C with the linear heating rate 10 K/min. Samples (about 100 mg) were reduced in hydrogen stream (5% H₂–95% Ar) with the gas volume velocity 60 cm³/min. A thermal conductivity detector was used. A *phase composition* of catalysts was analyzed by XRD diffraction method using PANanalytical X'Pert MPD diffractometer (in 2 θ range (20°–80°)). The catalyst *specific surface area* and *porosity* was obtained by BET method using Sorp-

The influence of calcination temperature (4 h in air) on specific surface area of supports and supported catalysts

Kind of sample	Calcination temperature, °C	Specific surface area, m ² /g
Al ₂ O ₃	400	237
	900	137
	1200	5
Cr ₂ O ₃	400	6
	900	1
	1200	<1
Al ₃ CrO ₆	400	93
	900	70
	1200	5
5% Ni/Al ₃ CrO ₆	400	70
(5% Ni + 2% Au)/Al ₃ CrO ₆	400	54

tomatic 1900 equipment. Samples were outgased at 250°C during 12 h evacuation and, after that, low temperature nitrogen adsorption-desorption runs were carried out. The *activity tests* in partial oxidation of methane were carried out in a flow quartz reactor. A catalyst sample 100 mg was used in all runs. Both reactants: methane (5% CH₄/He) and oxygen (5% O₂/He) were mixed and supplied to reactor as a gaseous stream containing CH₄ and O₂ in molar ratio 2 : 1. The reaction was studied in temperature range 25–900°C. A gas chromatographic analysis of reactant/product mixture (CH₄, O₂, CO₂, CO) was carried out using GC Varian 3300 (Varian Inc) instrument, CTR-1 column, temperature 35°C with TCD detector (130 mA, temperature 120°C). An analysis of hydrogen was carried out using CHROM-4 gas chromatograph (Laboratori Prístroje Praha), molecular sieve 4A, temperature 110°C with TCD detector (100 mA, temperature 120°C). The quantitative determination of hydrogen content involves special calibration method, which is described in literature [10].

The amount of total organic carbon TOC deposited on the catalyst during POM reaction was determined by an automatic carbon analyzer TOC 5000 (Shimadzu) equipped with a solid sample module (SSM-5000 A).

RESULTS

Catalyst Surface Area and Porosity

Results of specific surface area for supports: Al₂O₃, Cr₂O₃, Al₃CrO₆, calcined at 400, 900, 1200°C/4 h/air and supported catalysts: 5% Ni/Al₃CrO₆, 5% Ni–2% Au/Al₃CrO₆ calcined at 400°C/4 h/air are presented in Table 1.

The specific surface area of supports and catalysts considerably decreased with the increase of calcination

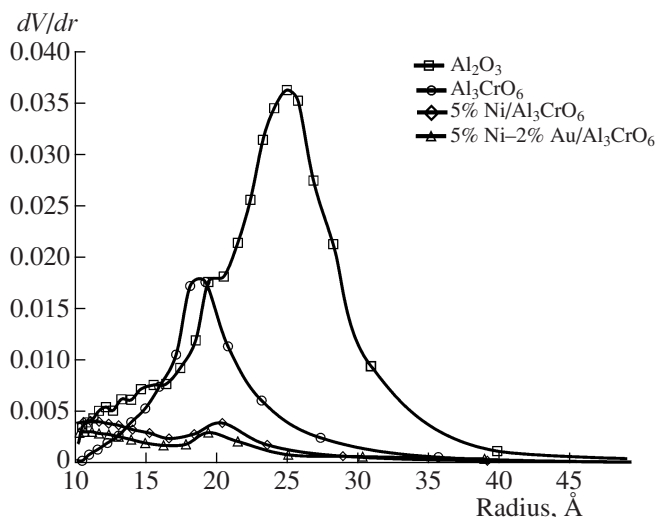


Fig. 1. The pore size distribution of supports: Al_2O_3 , Al_3CrO_6 and catalysts: 5% $\text{Ni}/\text{Al}_3\text{CrO}_6$, 5% $\text{Ni}-2\% \text{Au}/\text{Al}_3\text{CrO}_6$.

temperature. The highest surface area $237 \text{ m}^2/\text{g}$ was observed for Al_2O_3 (after calcination at 400°C) and it was lowered to $5 \text{ m}^2/\text{g}$ (after calcination at 1200°C), because of $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ phase transition. Chromium (III) oxide after calcination at 400°C had got a very small surface area, below $6 \text{ m}^2/\text{g}$. Binary oxide Al_3CrO_6 support, had surface area of $93 \text{ m}^2/\text{g}$

after calcination at 400°C , other studies show similar results for it [11]. This calcinations procedure for support or metal/support catalyst showed that impregnation lowered considerably specific surface area of Al_3CrO_6 support from 93 to $70 \text{ m}^2/\text{g}$, for 5% $\text{Ni}/\text{Al}_3\text{CrO}_6$, catalyst and to $54 \text{ m}^2/\text{g}$ for 5% $\text{Ni}-2\% \text{Au}/\text{Al}_3\text{CrO}_6$ catalyst. It was probably a result of support transformation in acid solution originating from HAuCl_4 and $\text{Ni}(\text{NO}_3)_2$, taking place during impregnation step.

The pore distribution of catalyst system is showed in Fig. 1. Alumina support, with the highest specific surface area, was identified as mezzo-porous bimodal structure with main pore radius about 24 \AA and additional one at 18 \AA . In the case of binary oxide system Al_3CrO_6 the main pore size about 18 \AA dominated. For supported catalysts 5% $\text{Ni}-2\% \text{Au}/\text{Al}_3\text{CrO}_6$ and 5% $\text{Ni}/\text{Al}_3\text{CrO}_6$ the their porosity decreased substantially.

Phase Composition

The influence of calcination temperature at 400 , 600 , 900 , and 1200°C per 4 h on XRD patterns for binary oxide Al_3CrO_6 support (curves 1–4) and for mono oxide $\alpha\text{-Cr}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ supports at 1200°C (curves 5 and 6) is presented in Fig. 2. The XRD patterns for binary oxide Al_3CrO_6 samples show rather low degree of crystallization irrespective of calcination

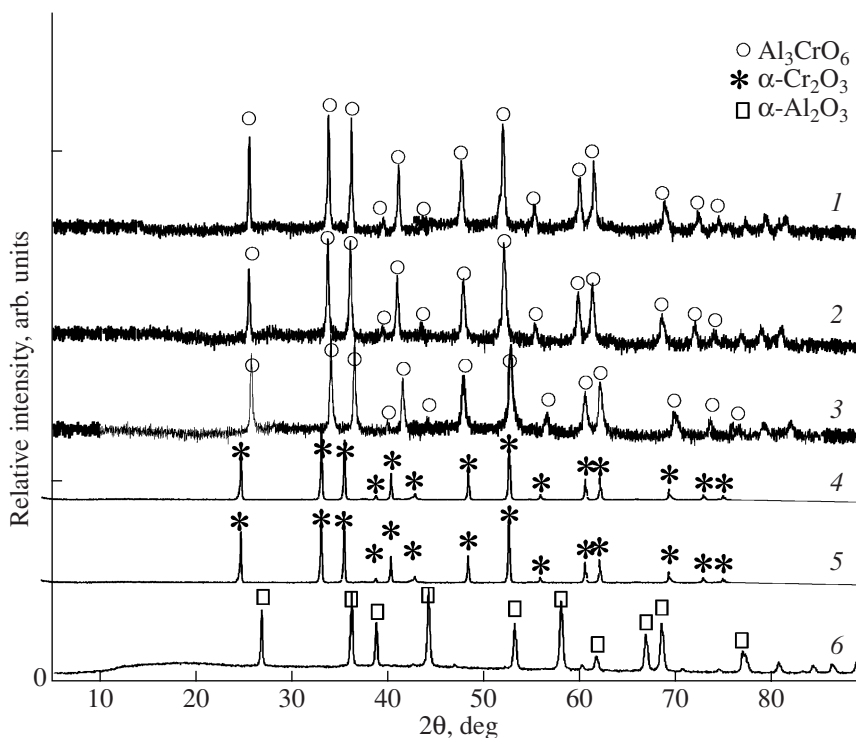


Fig. 2. The influence of calcination temperature (4 h in air) on XRD patterns for binary oxide Al_3CrO_6 support (curves 1–4 for 400 , 600 , 900 , and 1200°C , respectively) and for mono oxide $\alpha\text{-Cr}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ supports at 1200°C (curves 5 and 6).

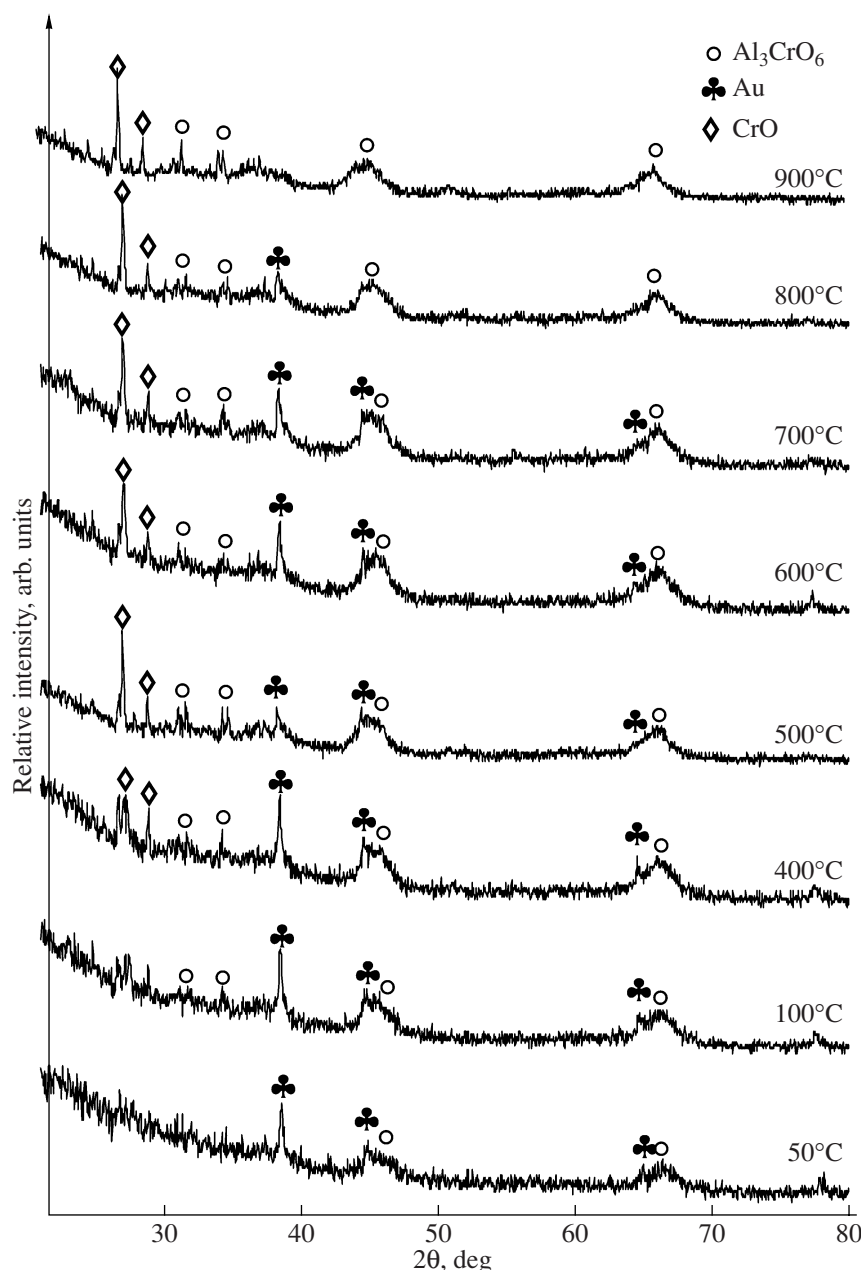


Fig. 3. The influence of reduction temperature on in situ XRD patterns of 5% Ni–2% Au/Al₃CrO₆ catalyst obtained during its reduction in 5% H₂–95% Ar gas stream.

temperature, which is evidenced by specific surface area values presented in table. The presence of crystalline Al₃CrO₆ phases is evident, but Al₂O₃ phase is not visible by XRD method. The reflexes coming from Al₃CrO₆ are very similar to α -Cr₂O₃ patterns being only shifted about 1°–2° 2 θ . The binary oxide spinel structure Al₃CrO₆ can be formed during preparation procedure. The similarity of γ -Al₂O₃ and α -Cr₂O₃ unit cells caused that they can form combined crystallographic network, of binary structure between appropriate monoxides.

The influence of temperature 50–900°C on in situ XRD patterns recorded during the reduction of 5% Ni–

2% Au/Al₃CrO₆ catalyst in 5% H₂–95% Ar gas stream is presented in Fig. 3. The catalyst appeared highly amorphous material with rather small and broad reflections characteristic for spinel Al₃CrO₆ and metal Au crystal phases. The gold phase is present only up to 800°C, above this temperature diffusion of Au into support network is observed and at 900°C XRD pattern of metallic gold disappears. The major changes of XRD patterns were assigned to the reductive formation of chromium(II) oxide CrO above 400°C. This phase is only stable in reductive atmosphere hydrogen or carbon monoxide whereas in oxidative atmosphere of air, oxy-

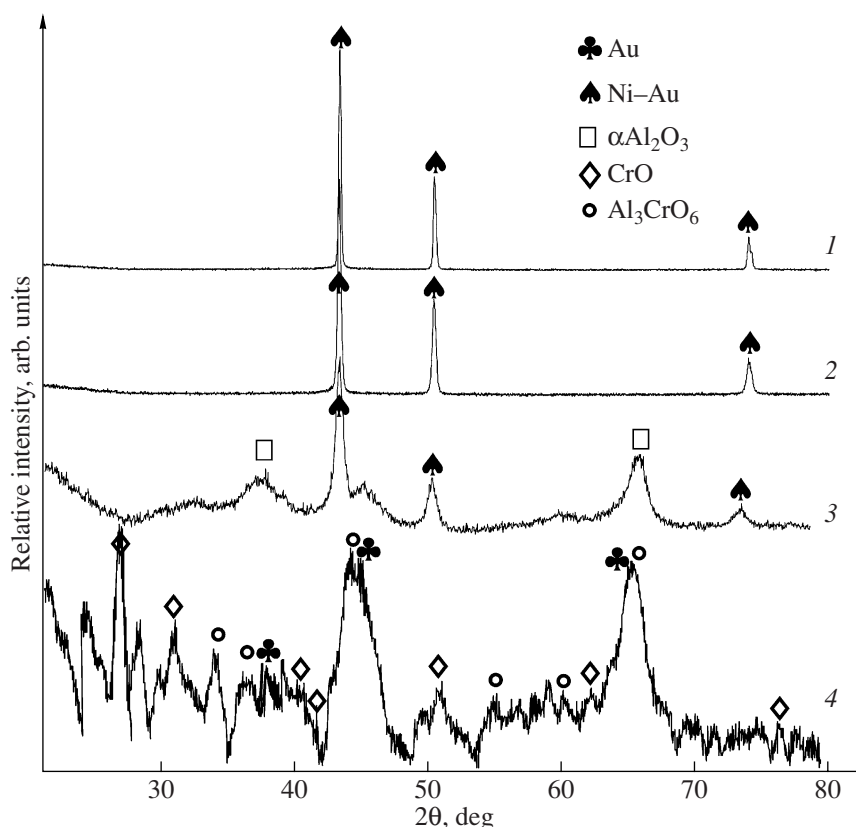


Fig. 4. XRD patterns showing the alloying effect for 80% Ni–20% Au physical mixture (prepared out support) after its reduction in hydrogen at 880°C (curve 1) and after POM reaction at 880°C (curve 2) and for 2% Au–8% Ni/Al₂O₃ (curve 3) and 2% Au–8% Ni/Al₃CrO₆ (curve 4) after POM reaction at 880°C.

gen or water it is oxidized to Cr(III) oxide. Both, nickel oxide NiO and metal Ni phases were not visible by XRD method, due to high degree of nickel dispersion on catalyst surface, and the anticipated reduction of nickel oxide to metallic nickel can not be confirmed.

The XRD studies show that metallic Ni–Au alloy can be formed depending on the kind of catalyst support and treatment conditions. The alloying behavior of metal phases of 5% Ni–2% Au/Al₃CrO₆ and 5% Ni–2% Au/Al₂O₃ catalysts was studied in the conditions of POM reaction, in the range of temperature 25–880°C. The analogical measurements were carried out for nickel-gold mixture prepared without support. A comparison of those selected results taken at 880°C is presented in Fig. 4. The Ni–Au alloy is formed in the case of 5% Ni–2% Au/Al₂O₃ catalyst, but it was not observed in the case of 5% Ni–2% Au/Al₃CrO₆ catalyst. The binary Al₃CrO₆ type structure and the unstable Cr(II)O phase were identified for 5% Ni–2% Au/Al₃CrO₆ catalyst during its work in the conditions of partial oxidation of methane at 880°C. At this temperature the conditions of POM process are reductive, caused by dominating products: CO and H₂ being a result of high methane conversion degree. XRD patterns were comparable for results after high temperature reduction in hydrogen and after POM reaction at

the same temperature 880°C. Figure 4 shows that the alloying process was obvious during reduction of Au–Ni mixture in hydrogen and it was also confirmed for 8% Ni–2% Au/Al₂O₃ catalyst, during its work in the high temperature of POM reaction. Nickel-gold alloying was observed also in previous work for Ni–Au/MgAl₂O₄ catalyst used for hydrocarbon steam reforming [12].

Temperature Programmed Reduction

The TPR profiles of supports and catalysts are presented in Fig. 5. A reduction affinity in hydrogen, for Cr₂O₃, Al₃CrO₆ supports and supported nickel and nickel-gold catalysts after their calcination (400°C/4 h/air) were studied. A relatively low reducibility of α-Cr₂O₃ support is assigned to the reduction effects of chromium oxide species CrO_x (1.5 < x < 3) on chromia surface. The different behavior of bulk CrO₃ and supported CrO₃/SiO₂ was reported [13]. In the case of Al₃CrO₆ support, one major reduction peak located in temperature range 250–400°C and two minor reduction peaks below 250 and above 400°C were observed. The TPR effects were attributed to reduction reaction Cr⁶⁺ → Cr³⁺, but other species Cr⁵⁺, Cr⁴⁺ can not be neglected, especially when stabilized by aluminum(III)–chromium(III)

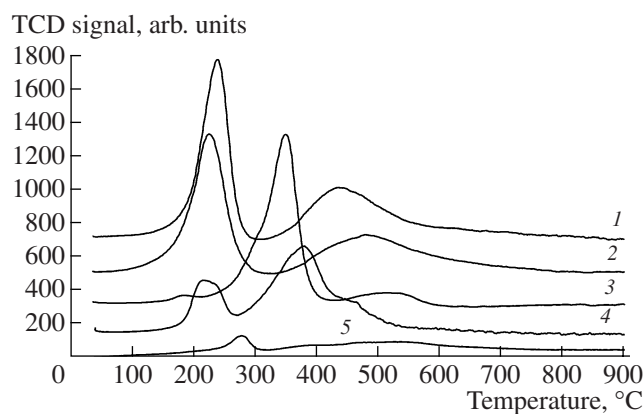


Fig. 5. TPR profiles for 5% Ni–2% Au/Al₃CrO₆, 5% Ni/Al₃CrO₆, Al₃CrO₆ (1–3) and 5% Ni/Cr₂O₃, Cr₂O₃ (4, 5) after calcination for 4 h in air at 400°C.

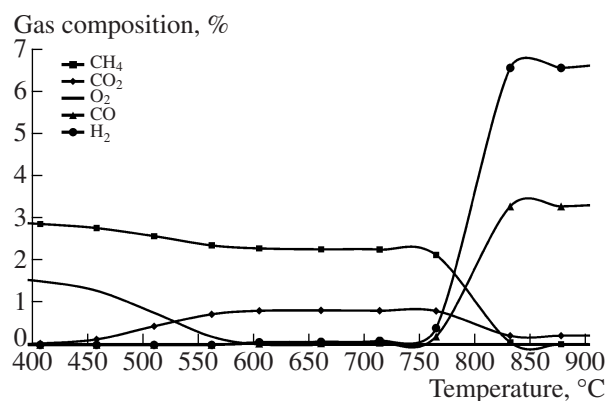


Fig. 6. The changes of concentration of gaseous reactants CH₄, O₂ and products CO, H₂ during temperature dependent combustion of methane on 5% Ni–2% Au/Al₃CrO₆ catalyst.

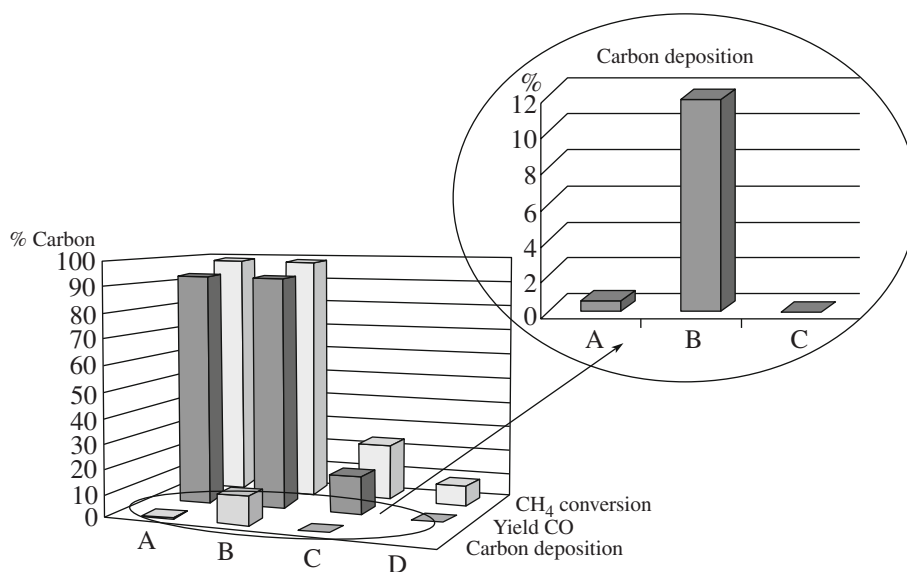


Fig. 7. CH₄ conversion, CO yield and carbon deposition in partial oxidation of methane at 800°C after 24 h on: (A) 5% Ni–2% Au/Al₃CrO₆, (B) 5% Ni/Al₃CrO₆, (C) Al₃CrO₆, (D) Al₂O₃.

bi-oxide structure. The TPR profiles for supported Ni and Ni–Au catalysts were considerably different. Thus, the reduction peak, located in temperature range 150–250°C, probably represented two-step reduction Ni²⁺ → Ni combined with Cr⁶⁺ → Cr³⁺. The broad reduction effect, located in temperature range 300–600°C, was tentatively assigned to reduction of bulk oxidic Cr–Al phase, in which Cr⁶⁺–O–Al linkages dominated. The addition of gold to Ni/support catalysts did not hardly influences to the original TPR profile.

Activity Tests

The activity tests were carried out in the temperature range 25–900°C. A process of methane oxidation on Ni catalyst took place differently depending on temperature. Firstly, in the range 25–300°C methane did not

react with oxygen at all, then in the temperature range 300–700°C all oxygen is entirely exhausted in full oxidation of methane towards to CO₂ and H₂O. The synthesis gas (CO + H₂) was formed in high temperature range, above 750°C. The typical course of POM reaction on 5% Ni–2% Au/Al₃CrO₆ catalyst is presented in Fig. 6.

The total oxidation of methane on bimetallic 5% Ni–2% Au/Al₃CrO₆ catalyst started above 400°C, where the oxidative conditions dominate. The concentration of methane decreased and oxygen was entirely exhausted to form CO₂ and H₂O evolved as the main products. The reaction conditions changed from oxidative to reductive characteristic for POM process above 750°C. The conversion degree of methane, the yield of carbon mono-oxide formation in POM reaction at 800°C, and the total carbon deposition (after 24 h activ-

ity test) on 5% Ni–2% Au/Al₃CrO₆, 5% Ni/Al₃CrO₆, Al₃CrO₆, and Cr₂O₃ catalysts are represented as A, B, C, D in Fig. 7. Supports without metallic phase were considerably less effective than impregnated metallic supported catalysts. The conversion degree of CH₄ on both supports Al₂O₃ and Al₃CrO₆ was below 25% at 800°C, but CH₄ conversion degree was two times higher for binary support [14]. Catalysts containing active phase: 5% Ni/Al₃CrO₆ and 5% Ni–2% Au/Al₃CrO₆ appeared to be very active and the conversion degree of CH₄ was equal to 98% at 800°C. The Ni and Ni–Au catalysts showed similar activity in POM reaction, although nickel-gold catalysts were more stable and resistant for coke deposition after 24 h reaction at 800°C [12]. Total carbon deposit for 5% Ni/Al₃CrO₆ catalyst was 11.8%, whereas only 0.6% for 5% Ni–2% Au/Al₃CrO₆ catalyst.

CONCLUSIONS

- Ni–Au catalysts supported on aluminum-chromium oxide Al₃CrO₆ are highly active in partial oxidation of methane.

- Highly amorphous binary oxide Al₃CrO₆ can stabilize considerably amount of Cr⁴⁺, Cr⁵⁺, and Cr⁶⁺ species in Ni–Au/support network during its calcination in air at 400°C. Nickel supported on Al₃CrO₆ can form Ni(III)CrO₃ bi-oxide phase.

- Activity of Ni–Au and Ni/Al₃CrO₆ catalysts are comparable, but gold doped catalysts are more stable in reaction conditions and decreasing the formation of carbon deposition.

- Au–Ni alloy formation takes place on Al₂O₃ surface, but it does not on bi-oxide Al₃CrO₆ during high

temperature POM reaction. CrO phase is also observed during TPR H₂ reduction of Ni–Au/Al₃CrO₆ catalyst.

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