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An Active Phase Transformation on Surface of Ni–Au/Al_2O_3 Catalyst during Partial Oxidation of Methane to Synthesis Gas[1]

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Abstract—It was studied the influence of gold addition on physico-chemical properties and catalytic activity of bimetallic Ni–Au/Al_2O_3 catalyst in partial oxidation of methane (POM). The reduction behavior in hydrogen, XRD crystal structure, XPS spectra and POM catalytic activity were investigated. The reduction of Ni–Au catalyst is a prerequisite condition to catalyze POM reaction. The formation of Ni–Au alloy during high temperature reduction in hydrogen and also in the conditions of POM reaction was experimentally proved. The addition of gold to Ni/Al_2O_3 system improves catalyst stability and activity in POM reaction.

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Synthesis gas is one of the main products of a large-scale chemical industry. The main method of syngas production is steam reforming of methane. A major disadvantage of this endothermic process is a large consumption of energy:

$$CH_4 + H_2O \longrightarrow CO + 3H_2, \quad \Delta H^0 = 206 \text{ kJ/mol.} \text{ (I)}$$

The same problem exists in the case of dry reforming of methane by carbon dioxide:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2, \quad \Delta H^0 = 247 \text{ kJ/mol.} \text{(II)}$$

Partial oxidation of methane can be used alternatively for syngas production [1, 2]. This process is mildly exothermic, and it allows to proceed this reaction in isothermal conditions:

$$CH_4 + 1/2O_2 \longrightarrow CO + 2H_2, \quad \Delta H^0 = -38 \text{ kJ/mol.} \text{ (III)}$$

Despite intensive researchers' efforts the nature of catalytic system for partial oxidation of methane to syngas (POM) is relatively little known. The POM process catalyzed by many metals, such as Pt, Ru, Rh, Ni, and others [1, 2], can be used in syngas production alternatively for dry and/or steam reforming of methane. Although noble metals effectively catalyze POM process, they are unacceptably expensive. In industrial practice nickel is the most commonly used catalytic material for methane activation [3, 4]. It is often supported on alumina doped with magnesium or calcium [5, 6].

Gold has been extensively used at the last years for low temperature CO and hydrocarbons deep oxidation processes. However, there is no literature data referring to the application of gold in high temperature reactions, such as POM. This paper is focused on the active phase transformations which occur on the surface of Ni–Au/Al_2O_3 catalysts during POM process. The addition of gold improves the activity and stability of supported Ni/Al_2O_3 catalysts and such behavior can be referred to alloy formation between Ni and Au on alumina surface. There are many data devoted to the formation of nickel-gold alloys [7–9], however there are lack of information about catalytic properties of such intermetaloides. The liquids and solid solutions of the Ni–Au alloy were studied first in the works [10–12]. Gold can form alloy with nickel in full weight concentration range above 600°C. Those alloys have a wide application in industry, jewelry, dental techniques and many others [13]. However we can not found any data devoted to XRD measurements of such alloys. A few works can be found in literature devoted to nickel-gold supported catalysts [14, 15], especially for high temperature reaction processes [16]. In those works there were no observed increase of catalysts activity but significant inhibiting effect on carbon deposition was shown [17].

The reduction behavior of Ni–Au/Al_2O_3 catalysts in hydrogen, their XRD crystal structure, the results of XPS analysis and POM catalytic activity were investigated.

[1] The article is published in the original.

Table 1. The influence of calcination temperature (4 h in air) on specific surface area Al_2O_3 support and 10% Ni/Al_2O_3 and (8% Ni–2% Au)/Al_2O_3 catalysts

Calcination temperature, °C	Specific area, m^2/g		
	Al_2O_3	10% Ni/Al_2O_3	(8% Ni–2% Au)/Al_2O_3
400	130	110	112
900	80	70	68

EXPERIMENTAL

Catalyst Preparation

The conventional wet aqueous impregnation method was applied for the preparation of Ni–Au/Al_2O_3 catalysts. As a support, commercial alumina FLUKA 507C was used (S_{BET} = 138 m^2/g). Bimetallic (8% Ni–2% Au) and monometallic 10% Ni and 10% Au catalysts were prepared by co-impregnation method in aqueous solutions $Ni(NO_3)_2$ and $HAuCl_4$. After drying they were calcined for 4 h in air at 400°C. In XRD studies, a reference material consisting of NiO and Au mixture with the weight ratio Ni : Au (4 : 1), also calcined for 4 h in air at 400°C was used.

Methods of Characterization

Thermo-programmed reduction (TPR) of supports and metal/support catalysts was performed in automatic TPO–TPR system AMl-1 "Altamira Instruments" in the temperature range 25–900°C with the linear heating rate 10°C/min. Samples (weight about 0.1 g) were reduced in hydrogen stream (5% H_2 + 95% Ar) with the gas volume velocity 60 cm^3/min, thermal conductivity detector was used.

Phase composition of catalysts was analyzed in situ by XRD method using PANanalytical X'Pert MPD diffractometer. The samples were heated at the nominal rate of 1°C/min, starting from 25°C and ending at 880°C in (5% H_2 + 95% Ar) gas mixture or (1.67% O_2 + 3.33% CH_4 + 95% Ar) reactant mixture.

Specific surface area and porosity of the catalyst were measured by BET method using Sorptomatic 1900 equipment. Samples were prepared at 250°C during a 12 h evacuation and after that low temperature nitrogen adsorption–desorption was carried out.

Hydrogen chemisorption measurements were carried out on ASAP 2010C instrument made by "Micromeritics." Sample weight was about 0.5 g. The following procedure was applied: preliminary evacuation and heating at 200°C (1 h), the flow of hydrogen at the same temperature (1 h), evacuation at 200°C (2 h), cooling down to 35°C, leak test and finally the measurement of hydrogen chemisorption isotherm at 35°C.

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% CH_4 + 95% He) and oxygen (5% O_2 + 95% He)—were supplied to the reactor as a gaseous stream containing CH_4 and O_2 in molar ratio 2 : 1. Total flow rate was 100 cm^3/min. The reaction was studied in the temperature range 25–900°C. A gas chromatography analysis of reactants and products mixture (CH_4, O_2, CO_2, CO) was carried out using GC Varian 3300 instrument ("Varian Inc.") with CTR-1 column at the temperature 35°C and TCD detector (130 mA, temperature 120°C). An analysis of hydrogen was performed by CHROM-4 gas chromatograph (Laboratorni Pristroje) on column with molecular sieve 4 Å at 110°C and with the TCD detector (100 mA, temperature 120°C).

X-ray photoelectron spectra (XPS) were obtained using a spectrometer ES-300 Kratos Analitical equipped with a monochromatic Mg-K_α X-ray source. Spectra were recorded with analyzer pass energy 15 eV.

RESULTS AND DISCUSSION

The results of specific surface area measurements for Al_2O_3 support and $Ni–Au/Al_2O_3$ catalysts after their calcination (4 h in air at 400 and 900°C) are presented in Table 1. Depending on the treatment temperature (400 or 900°C) the specific surface area of Al_2O_3 decreases from 130 to 80 m^2/g and for supported catalysts from 110–112 to about 70 m^2/g. The further decrease of surface area by 10–20 m^2/g can be assigned to the impregnation procedure with nickel or gold.

The metal dispersion estimated by hydrogen chemisorption was rather low (1.5% for $Ni–Au/Al_2O_3$ catalysts and 3% for $Ni–Au/Al_2O_3$ catalyst after 900°C reduction in hydrogen stream). After reaction metal dispersion was similar (1.4 and 2.0%, respectively). Such low dispersion degree can be explained by kind of nickel precursor as well as using of gold deposition method. Some literature data suggest that is not possible to achieve high degree of nickel dispersion in the case of use nickel nitrate as a precursor [18–26]. If organic salt of nickel was used the degree of metal dispersion may be in the range 1–10% [19] depending on metal loading and treatment conditions.

Obtained results show that gold addition has no strong influence on metal crystalline size.

TPR profiles for Ni/Al_2O_3 and $Ni–Au/Al_2O_3$ catalysts after their different treatments (calcination for 4 h in air at 400°C, TPR run up to 900°C and reoxidation at 600°C and after partial oxidation of methane) are presented in Fig. 1. These profiles differ considerably. The reduction of monometallic 10% Ni/Al_2O_3 catalyst after its calcination for 4 h in the air at 400°C

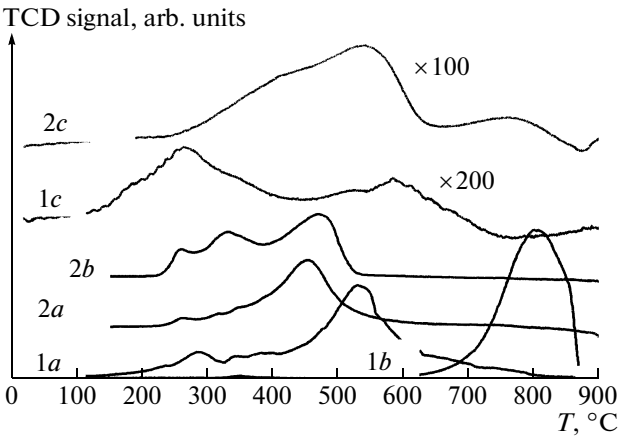

Fig. 1. TPR profiles for Ni/Al_2O_3 and Ni–Au/Al_2O_3 catalysts: *1a*—10% Ni/Al_2O_3, calcination for 4 h in air at 400°C; *2a*—(8% Ni–2% Au)/Al_2O_3, calcination for 4 h in air at 400°C; *1b*—10% Ni/Al_2O_3, TPR run up to 900°C and reoxidation at 600°C; *2b*—(8% Ni–2% Au)/Al_2O_3, TPR run up to 900°C and reoxidation at 600°C; *1c*—10% Ni/Al_2O_3, POM reaction at 800°C; *2c*—8% Ni–2% Au)/Al_2O_3, POM reaction at 880°C.

(*1a*) occurs in temperature range 200–600°C, whereas after the first TPR and catalyst reoxidation at 600°C reduction effect is observed only above 600°C (*1b*). Low temperature reduction effects in the temperature range 100–400°C can be attributed to the reduction of large crystallites of nickel(II) oxide, not strongly interacting with the support. Similar behavior was observed in work [27]. The reduction of nickel oxide strongly interacting with alumina surface takes place above 400°C. The reduction effect above 600°C can be attributed to nickel aluminate $NiAl_2O_4$ reduction and this fact has been generously confirmed by researches from many laboratories [28–30]. Gold addition does not change considerably the first cycle TPR profiles characteristic of bimetallic Ni–Au catalyst, both after the first calcination at 400°C (*2a*), and after second catalyst reoxidation at 600°C (*2b*). Thus one can assume that the gold prevented the formation of nickel aluminate [27]. The TPR profiles for Ni/Al_2O_3 (*1c*) and Ni–Au/Al_2O_3 (*2c*) catalysts after their involvement in POM reaction differ considerably in comparison with the TPR profiles of previously calcined samples. The overall reduction effects are smaller by about 100–200 times. Such small reduction

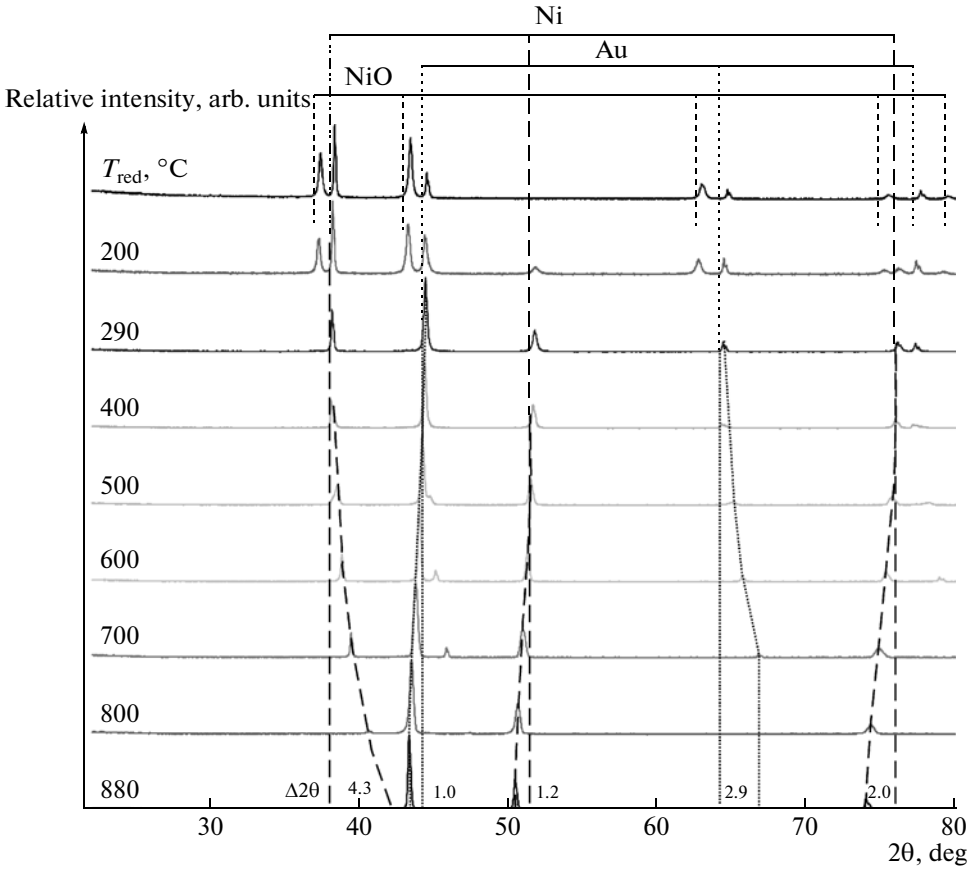

Fig. 2. XRD patterns for nickel oxide (80%)–gold (20%) mechanical mixture reduced in situ in (5% H_2 + 95% Ar) gas mixture at different temperatures.

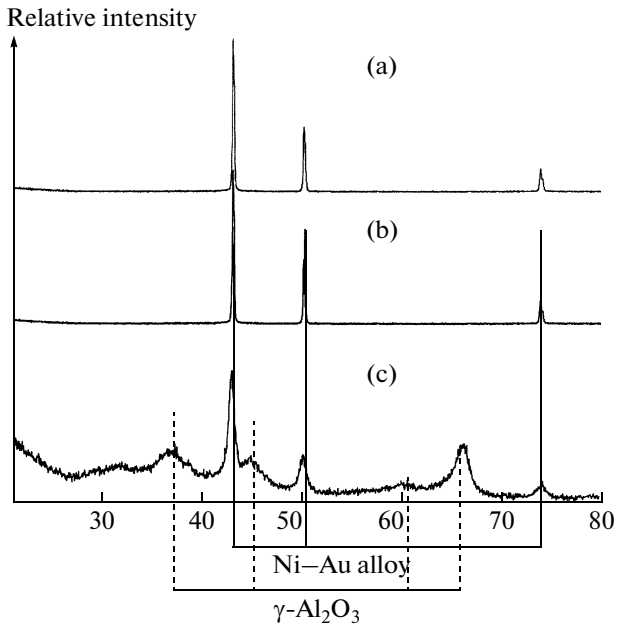

Fig. 3. XRD patterns for (80% NiO–20% Au) mixture after POM reaction at 880°C (a) and after reduction in (5% H_2 + 95% Ar) at 880°C (b) and for (8% Ni–2% Au)/Al_2O_3 catalyst after POM reaction at 880°C (c).

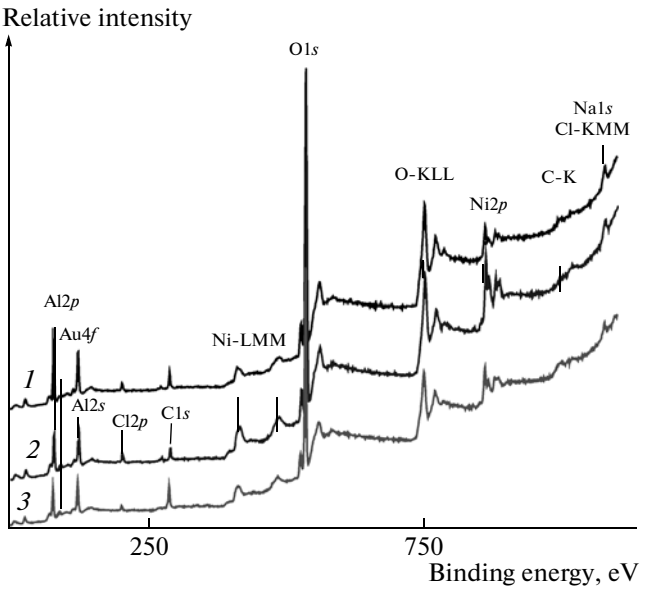

Fig. 4. XPS spectra for (8% Ni–2% Au)/Al_2O_3 catalyst after: *1*—2 h reduction in H_2 at 500°C, *2*—2 h calcination in air at 400°C, *3*—4 h POM reaction at 850°C.

effects can be explained by the reduction of catalyst in POM reaction conditions [31] (H_2 and CO products at 880°C). A quantitative analysis of TPR profiles shows that overall reduction effects for catalyst samples after POM reaction is about 1–2% of reduction effect of 10% Ni/Al_2O_3 catalyst calcined at 400°C. Gold addition increases about twice the observed reduction effects of the catalyst after POM reaction (curves *1c* and *2c*). This result is in good agreement with the XRD studies in situ (see Fig. 2). It is possible to suggest that metallic nickel is an active phase in this reaction, but part of the highly temperature treated compound seems to be in oxidized form during POM reaction [32]. A small reduction effect can be attributed to surface oxidized nickel. The degree of nickel reduction depends strongly on the reaction temperature and methane/oxygen ratio in reactant mixture. It was found in work [33].

The temperature programmed in situ XRD patterns for nickel oxide-gold mechanical mixture in (5% H_2 + 95% Ar) gas mixture are presented in Fig. 2. One can see that at ambient temperature two phases exist: metallic gold and nickel(II) oxide. The reduction of free nickel oxide takes place above 200°C. At the temperature 290°C only metallic nickel and metallic gold phases are detectable. Further increase of temperature up to 880°C leads to gradual shifts of 2θ values that characterize the nickel-gold alloy formation (the characteristic gradual shift of XRD lines up to 4°). At 880°C only XRD lines assigned to alloy of Ni–Au phase are visible. It is well known that the formation of alloys can modify considerably catalytic properties of catalyst active phase changing not only the surface chemical composition but also the size of metal crystallites or unit cell.

XRD patterns showing Ni–Au alloy formation in the mixture of 80% NiO and 20% Au after POM reaction at 880°C, reduction in (5% H_2 + 95% Ar) stream at 880°C and for working (8% Ni–2% Au)/Al_2O_3 catalyst after POM reaction at 880°C are presented in Fig. 3. The prerequisite condition of Ni–Au alloying is the reductive gas atmosphere of this process. After calcination of (8% Ni–2% Au)/Al_2O_3 catalyst at 850°C the spinel $NiAl_2O_4$ is formed [29] (see Fig. 1); but this phase is not detectable by the XRD method due to its low crystallinity and a high degree of spinel phase dispersion (see curve *c* in Fig. 3).

The review of XPS spectra for (8% Ni–2% Au)/Al_2O_3 catalyst after reduction in H_2 at 500°C, calcination in air at 400°C and after POM reaction at 850°C are presented in Fig. 4. One can see the characteristic binding energy of photoelectrons originating from various atoms (Na, Al, Ni, Au, O, C, and Cl) present on bimetallic catalyst surface. The quantitative analysis of (8% Ni–2% Au)/Al_2O_3 catalyst surface is presented in Table 2. During POM reaction the concentration of surface gold increases in comparison with reduced or oxidized samples. Also, the increase of carbon concentration can be assigned to carbon deposit formation. A high and relatively constant value of chlorine content is referred to precursor of gold ($HAuCl_4$) used for catalyst preparation. The strong chlorine adsorption on alumina surface seems to be

Table 2. Chemical composition of (8% Ni–2% Au)/Al_2O_3 catalyst surface

Treatment	Content on the surface, %					
	Au	C	Ni	O	Cl	Al
4-h-long calcination in air at 400°C	0.06	8.90	7.41	55.36	1.59	26.68
POM reaction at 880°C	0.13	17.75	4.64	51.51	1.15	24.82
H_2 reduction at 500°C	0.06	10.51	3.42	58.87	1.39	25.75

responsible for its permanent presence on catalyst independently on treatment conditions, namely a high temperature and kind of atmosphere.

The detailed XPS spectra Au 4*f* and Ni 2*p* for (8% Ni–2% Au)/Al_2O_3 catalyst after reduction in H_2 at 500°C, calcination in the air at 400°C and after POM reaction at 850°C are presented in Fig. 5. One can see that metallic nickel and gold phases and various nickel(II) oxides are present on bimetallic catalyst surface. On the other hand, the existence of Ni–Au alloy can be inferred. Spectral lines Au 2*f* show that reduction is well. POM reaction increases binding energy, suggesting that during reduction and POM reaction massive gold on the surface is formed. Also XRD results show that Au–Ni alloy is formed in the reductive atmosphere of POM reaction. Presented results suggest that during reduction and POM reaction "bulk" Ni–Au alloy is formed, but its surface is enriched by gold.

Binding energy for Ni 2*p* line increases for the samples reduced in hydrogen as well as for the samples after their POM reaction. A complex character of all those spectra suggests that nickel appears in all its oxidation states. The character of lines as well as binding energy 855.9–856.1 eV are characteristic of nickel(III) oxide. The obtained results do not exclude the alloy formation on the support surface.

Catalytic activity tests of 8% Ni/Al_2O_3 and (8% Ni–2% Au)/Al_2O_3 catalysts are presented in Fig. 6. The gold addition lowers the ignition temperature of POM reaction, i.e., the temperature of changing the reactive atmosphere from oxidative to reductive (start CO and H_2 production) from 750 to 700°C. In the temperature range 400–700°C the total oxidation of methane ($CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$) takes place on the surface, whereas above 650°C for bimetallic (8% Ni–2% Au)/Al_2O_3 catalyst and above 750°C for nickel 8% Ni/Al_2O_3 catalyst POM reaction dominates ($CH_4 + 1/2O_2 \longrightarrow CO + 2H_2$). Above 800°C methane conversion degree is close to 100%.

CONCLUSIONS

1) The formation of Ni–Au alloy during high temperature POM reaction was experimentally proved on (8% Ni–2% Au)/Al_2O_3 catalyst surface.

2) Reduction of (8% Ni–2% Au)/Al_2O_3 catalyst is the prerequisite condition to catalyze POM reaction.

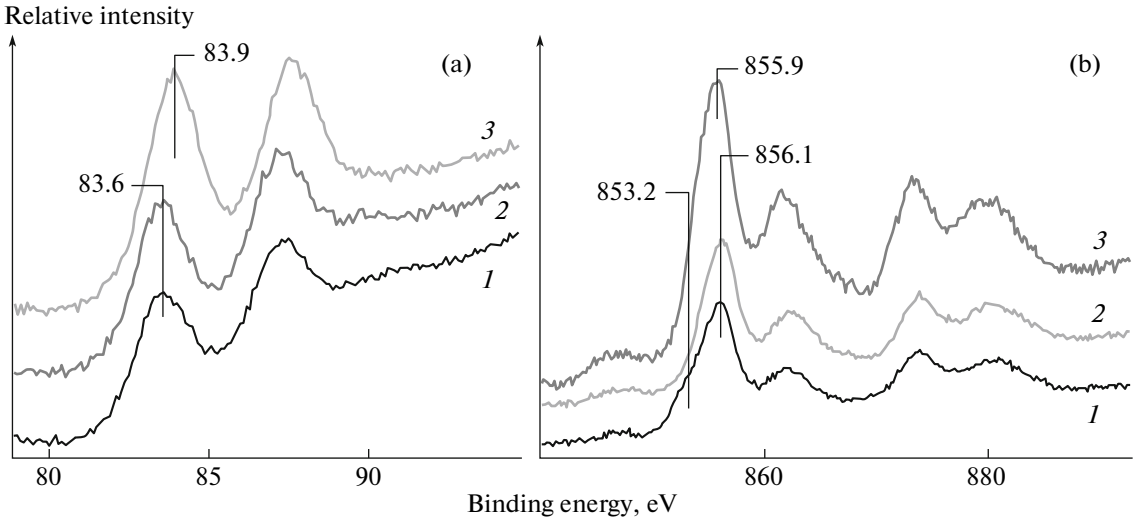

Fig. 5. Au 4*f* and Ni 2*p* XPS spectra (a and b, respectively) for (8% Ni–2% Au)/Al_2O_3 catalyst after: *1*—2 h reduction in H_2 at 500°C, *2*—2 h calcination in air at 400°C, *3*—4 h POM reaction at 850°C.

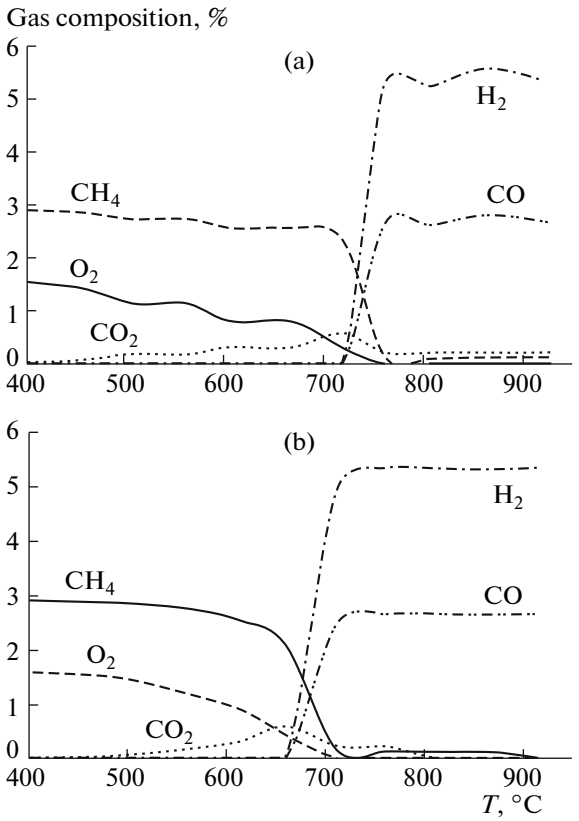

Fig. 6. Changes of gas composition during POM reaction on 8% Ni/Al_2O_3 (a) and (8% Ni–2% Au)/Al_2O_3 (b) catalysts.

3) The addition of gold to Ni/Al_2O_3 improves stability and activity of the catalyst in POM reaction.

4) The enrichment of gold on catalyst surface takes place during POM reaction.

5) TPR profiles after reoxidation previously reduced samples (up to 900°C) and POM reaction differ considerably probably due to nickel-gold alloy formation.

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