Catalysis Today 157 (2010) 217–222

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Characterization of alumina-supported uranium oxide catalysts in methane oxidation

Z.R. Ismagilov*, S.V. Kuntsevich, N.V. Shikina, V.V. Kuznetsov, M.A. Kerzhentsev, V.A. Ushakov, V.A. Rogov, A.I. Boronin, V.I. Zaikovsky

Boreskov Institute of Catalysis, 5, Pr. Akad. Lavrentieva, 630090 Novosibirsk, Russia

ARTICLE INFO

Article history:
Available online 25 March 2010

Keywords:
Uranium oxides
Nanoparticles
Uranyl nitrate
Supported catalyst
XPS
HRTEM
Methane oxidation

ABSTRACT

Synthesis of alumina-supported uranium oxide catalysts and their characterization in methane oxidation have been performed. The catalysts containing 5% U were prepared by impregnation, solid-phase synthesis and mechanical mixing techniques. Samples were studied using BET, XRD, HRTEM and XPS methods. It was shown that physicochemical properties and activity of the catalysts depend on the preparation procedure and calcination temperature and are determined by the extent of the interaction between active component and support. Most active are the catalysts prepared by impregnation of alumina with an aqueous solution of uranyl nitrate. It was found that the $5\%U/Al_2O_3$ catalyst calcined at 1000 °C has the highest catalytic activity, and it is explained by the formation of highly active nanodispersed state of uranium on the surface of the support.

1. Introduction

Uranium oxides are rather attractive for catalysis as their stoichiometry can be varied in a wide range, and valence state of uranium can be changed depending on temperature and oxygen to uranium ratio (O/U) [1,2]. G.J. Hutchings showed that uranium oxide catalysts are active at low temperatures in the reactions of deep oxidation of hydrocarbons, in particular chlorine-containing ones, and resistant to such catalytic poisons as sulfur, water and halogens [3,4]. Uranium oxide catalysts are successfully employed in partial oxidation processes [5,6]. Mixed Ni–U oxide compositions are efficient in methane conversion to syngas [7,8]. Our analysis over the last years revealed more than 70 patents which show that many industrial processes can be efficiently performed with application of uranium oxide catalysts [9]. Earlier we prepared variety of bulk uranium oxide catalysts by precipitation and thermal decomposition of uranyl salts (nitrate, acetate and oxalate) and studied their physicochemical and catalytic properties in relation to the nature of a precursor and preparation procedure [10]. We have shown that uranium oxides obtained by precipitation of uranyl nitrate and by direct thermal decomposition of the salt differ in their porous structure, morphology, phase composition and activity in TPR with hydrogen and complete oxidation of butane. Collected experience with bulk uranium oxides having low specific surface area stimulated us to synthesize and study uranium catalysts on supports with high surface area, aiming at their prospective advanced performance.

This paper is focused on the preparation and study of supported catalysts—uranium oxide on alumina containing 5 wt% U.

Samples were studied using BET, XRD, HRTEM and XPS methods to reveal information on the interaction between active component and support and to establish the dependences of physicochemical properties and activity of the catalysts on the preparation procedure and calcination temperature.

2. Experimental

Three techniques were used for the preparation of uranium oxide catalysts supported on γ-Al_2O_3 and containing 5 wt% U:

(1) Impregnated catalysts were prepared via incipient wetness impregnation of support with aqueous solutions of uranyl nitrate $UO_2(NO_3)_2{\cdot}6H_2O$. Spherical γ-Al_2O_3 (grain size 0.5–1.0 mm or 1.0–1.6 mm) was obtained by the method reported elsewhere [11]. After impregnation, the samples were dried at 100 °C and then calcined at 500, 600 or 900 °C for 4 h and at 1000 or 1100 °C for 3 h. One of the samples was calcined at 1000 °C for 18 h.

(2) Solid-phase catalysts containing 5 wt% U were prepared by mixing UO_3 with the γ-Al_2O_3 support powder [11]. The UO_3 powder was obtained by precipitation from aqueous solution of uranyl nitrate with 25% aqueous ammonia and subsequent calcination

---

* Corresponding author. Tel.: +7 383 3306219; fax: +7 383 3306219.
E-mail address: zri@catalysis.ru (Z.R. Ismagilov).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.02.020

of the sediment at 500 °C [10]. A mixture of the powders was pounded in an agate mortar for 10 min, and then the resulting powder was pressed into pellets and calcined at 500, 600 or 900 °C for 4 h and at 1000 °C for 3 h. A 0.5–1.0 mm fraction was used for the determination of specific surface area and catalytic activity.

(3) Mixed catalysts were prepared by intensive mixing of the γ-Al_2O_3 powder preliminarily calcined at 500, 600, 900 or 1000 °C, with uranium oxide powders obtained by precipitation from aqueous solution of uranyl nitrate with 25% aqueous ammonia and calcined at 500, 600, 900 or 1000 °C corresponding to the alumina calcination temperatures. Two powders of the same calcination temperature were mixed and pressed into pellets. A 0.5–1.0 mm fraction was used for the determination of specific surface area and catalytic activity.

Specific surface area of the catalysts (S_{BET}, m^2/g) was determined by thermal desorption of argon using a SORBIN.4.1 instrument.

XRD analysis of the samples was made in a HZG-4C (Freiberger Prazisionsmechanik) diffractometer with monochromatic cobalt radiation in the 2θ angle range of 20–80° at a scan rate of 1°/min. Phases were identified using the JCPDS database. The content of U_3O_8 phase in the catalyst samples was found from the calibration plots obtained for mechanical mixtures of Al_2O_3 and U_3O_8 powders, each of them being calcined at a temperature corresponding to the studied catalyst calcination temperature.

Mean particle size was evaluated by Sherrer equation:

$$D = \frac{n \times \lambda}{\beta \times \cos\theta}$$

where D is coherence diffraction area size, λ is radiation wave length, θ is diffraction angle; β is line broadening on diffraction picture, n is coefficient dependent on particle size.

The high-resolution transmission electron microscopy (HRTEM) study was performed in a JEM-2010 electron microscope (accelerating voltage 200 kV, resolution 1.4 Å). Energy Dispersive X-ray Analysis (EDX) of the samples element composition was carried out using a Phoenix EDAX spectrometer with Si(Li) detector, energy resolution not exceeding 130 eV, and diameter of the electron probe up to 100 Å. The composition is expressed as atomic percent of Al and U calculated from the signal intensity ratio Al*K*:U*M*. Diameter of the analyzed region was up to ca. 100 Å, detection sensitivity for heavy atoms was ca. 0.1 at.%. Catalyst particles were deposited on a holey carbon film supported on a copper grid.

The X-ray photoelectron spectroscopy (XPS) study was carried out with an ES-300 (KRATOS Analytical) photoelectron spectrometer at constant analyzer pass energy. The X-ray tube equipped with two anodes, Mg and Al, served as a source of photons. The working regime of the X-ray tube operation was as follows: the anode potential 15 kV and emission current 13 mA. The energy scale was calibrated against the binding energies of $Au4f_{7/2}$ and $Cu2p_{3/2}$, which were equal to 84.0 and 932.7 eV, respectively. The qualitative analysis was made using a survey scan with high sensitivity.

Experiments on temperature-programmed reduction with hydrogen (TPR) were carried out in a flow reactor loaded with ca. 100 mg of the catalyst under study. The reaction mixture consisting of hydrogen (10 vol.%) and argon was fed into the reactor. Temperature was raised from 40 to 900 °C at a rate of 10 °C/min. Activity of catalysts supported on γ-Al_2O_3 was tested in the reaction of deep oxidation of methane in a flow tubular quartz reactor under variation of the reactor temperature from 200 to 500 °C. Catalyst loading was 1 cm^3. The initial reaction mixture containing 1 vol.% CH_4 in air was fed into the reactor at GHSV equal to 1000 h^{-1}. Composition of the reaction mixture before and after the reactor was analyzed using gas chromatographic analysis.

3. Results and discussion

Specific surface area (S_{BET}) and phase composition of the catalysts prepared by different techniques and containing 5% U on Al_2O_3 are presented in Table 1.

Phase composition of uranium oxides in the solid-phase catalyst at respective calcination temperatures is similar to that in the mixed catalyst. In the samples calcined at low temperature (500 °C) the active component consists of β-UO_3 phase, which transforms to α-U_3O_8 during calcination at a higher temperature (600–1000 °C). In case of impregnated catalysts the uranium oxide phase U_3O_8 appears in the diffraction pattern only after calcining at 1000 °C. The absence of uranium oxide phases in the diffraction pattern of impregnated samples calcined at temperatures below 1000 °C can be attributed either to high dispersion of uranium oxides, which does not allow the XRD identification of the phase, or to the formation of an interaction phase, which is also not identified by XRD. In the case of existence of the interaction phase, it can be destructed at the rise of the calcination temperature with high-dispersed oxides formation. The active component is sintered to roughly dispersed particles with a size more than 400 Å at an increase of the calcination temperature up to 1100 °C or an increase of calcination duration at 1000 °C. The amount of observable coarse U_3O_8 phase, as determined by XRD analysis from the calibration plots of the prepared mixtures, varies with the type of catalyst calcined at 1000 °C: in the impregnated catalyst, the amount of this phase constitutes 20%; in the solid-phase catalyst 30%; and in the mixed catalyst it attains 100% of the actually introduced uranium amount.

Easier polymorphous transformation of impregnated catalyst support (γ-Al_2O_3 → θ-Al_2O_3) and the faster dynamics of specific surface area decrease in comparison with solid-phase and mixed samples are other factors that indirectly point to the existence of the interaction phase. This behavior of the impregnated catalysts at the rise of the calcination temperature is similar to that of aluminum–manganese catalysts. Previous study [12] of a genesis of aluminum–manganese catalysts calcined at temperatures up to 1100 °C established that their activity in the hydrocarbon oxidation reactions sharply increased after calcination at 900–1000 °C. The thermal activation of the catalyst is explained by destruction of a manganese ions solid solution in the structure of alumina at these temperatures with the formation of corundum and emergence of X-ray amorphous highly dispersed manganese oxide clusters on the support surface.

The HRTEM study of impregnated 5%U/Al_2O_3 catalysts showed different states of uranium on the surface of Al_2O_3 support for the samples calcined at different temperatures.

According to Fig. 1a, morphology of the sample calcined at 600 °C is represented by γ-Al_2O_3 acicular particles with the typical size 50 Å × 500 Å. In HRTEM images one can see the interplanar distances, dn: 4.5, 2.8, 2.4 Å, etc. corresponding to the γ-Al_2O_3 lattice. The structure of this phase has some defects: numerous interblock boundaries and a stepwise relief of the crystal surface. Phase transition γ-Al_2O_3 → θ-Al_2O_3 (see Table 1), which occurred after calcining the catalyst up to 1000 °C, resulted in considerable changes of the support morphology. The nascent θ-Al_2O_3 particles have a more isometric shape and sizes of 300 Å × 1000 Å (Fig. 1b). HRTEM images show the lattice planes with interplanar distances 4.5 and 5.4 Å corresponding to θ-Al_2O_3 [13,14]. The structure of these particles is less defective compared to γ-Al_2O_3, although surface steps are also observed here.

Uranium oxide particles were not detected by HRTEM in the aggregates of catalyst particles calcined at 600 and 1000 °C. Although XRD data indicate the presence of uranium oxide phase in the sample calcined at 1000 °C (Table 1), its amount is low and this phase is not seen in HRTEM images.

Table 1
Phase composition and specific surface area of 5%U-Al_2O_3 catalysts prepared by impregnation, solid-phase synthesis and mixing.

Catalysts	T_{calc}, °C	Phase composition	Specific surface area, m^2/g
Impregnated	500	γ-Al_2O_3	160
	600	γ-Al_2O_3	167
	900	δ- and γ-Al_2O_3	78
	1000	θ-Al_2O_3 α-U_3O_8 The presence of α-$UO_{3.01}$ or α-$UO_{2.92}$ is possible	40
	1000 18 h	θ-Al_2O_3 Trace amounts of α-Al_2O_3 α-U_3O_8 with particle size exceeding 400 Å	32
	1100	θ-Al_2O_3 Trace amounts of α-Al_2O_3 α-U_3O_8 The presence of α-$UO_{3.01}$ or α-$UO_{2.92}$ is possible	33
Solid-phase	500	γ-Al_2O_3 β-UO_3 with particle size exceeding 400 Å	156
	600	γ-Al_2O_3 Trace amounts of β-UO_3 with particle size exceeding 400 Å α-U_3O_8 with particle size exceeding 400 Å	140
	900	δ+γ-Al_2O_3 α-U_3O_8 with particle size exceeding 400 Å	95
	1000	δ+γ-Al_2O_3 α-U_3O_8 with particle size exceeding 400 Å	70
Mixed	500	γ-Al_2O_3 β-UO_3 with particle size exceeding 400 Å	156
	600	γ-Al_2O_3 α-U_3O_8 with particle size exceeding 500 Å	163
	900	δ+γ-Al_2O_3 α-U_3O_8 with particle size exceeding 500 Å	104
	1000	δ+γ-Al_2O_3 α-U_3O_8 with particle size exceeding 500 Å	75

Nevertheless, a noticeable signal of U is present in the EDX spectra obtained from individual γ-Al_2O_3 (600 °C) and θ-Al_2O_3 particles (1000 °C), the amount of U in atomic ratio to Al comprising 3–5%. Dark contrasting points on the surface of alumina particles are observed in HRTEM images for the samples calcined at 600 and 1000 °C (Fig. 1a and b). Note that in the images of pure alumina (without uranium) this effect is not observed, hence the contrasting dark points are related to electron scattering on heavy U atoms that decorate the aluminum oxide particles. In combination with EDX data, this gives ground to conclude that in these cases uranium is in the ultimately dispersed-ionic state on the surface or incorporated into alumina particles.

The HRTEM study of the impregnated 5%U/Al_2O_3 catalyst revealed also an unusual behavior of γ-Al_2O_3 and θ-Al_2O_3 supports containing the surface U ions. Radiation-thermal effect of high-intensity electron beam changes the morphology of Al_2O_3 particles. Electron beam appears to create hollow regions in alumina particles (shown by white arrows in Fig. 1a). At the same time spherical bumps (up to 50 Å in size) emerge nearby on the surface (shown by black arrows in Fig. 1a). The high energy of electron beam also causes phase transformation of some of alumina, because the EDX study shows the presence of δ-Al_2O_3 or θ-Al_2O_3 in the formed bumps, as opposed to the rest of the particle represented by γ-Al_2O_3. The similar phenomenon was found for the uranium catalyst supported on θ-Al_2O_3 (see Fig. 1b) with the exception that the same high-temperature θ-modification of alumina was observed both on the original particle surface and the formed bumps.

Such changes are not observed in the case of Al_2O_3 support without uranium, although electron beam has the same intensity. In this work we did not investigate in detail the observed phenomenon; however, it is evident that the enhanced rearrangement of support material initiated by electron beam is caused primarily by the presence of U ions in the crystal lattice of alumina. It is not improbable that U ions penetrate into the lattice, filling the vacant cationic

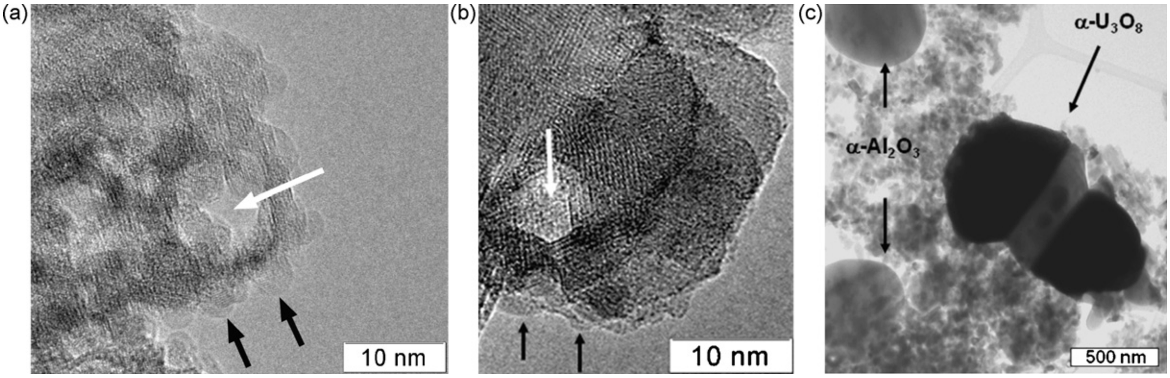

Fig. 1. HRTEM images of catalyst 5%U-Al_2O_3 prepared by impregnation calcined at: (a) 600 °C; (b) 800 °C; (c) 1100 °C; in (a) and (b), a white arrow shows a hollow region formed at the site of focusing an electron beam when taking the EDX spectrum, black arrows show areas of the Al_2O_3 surface changed under the action of electron beam with emerging spherical bumps.

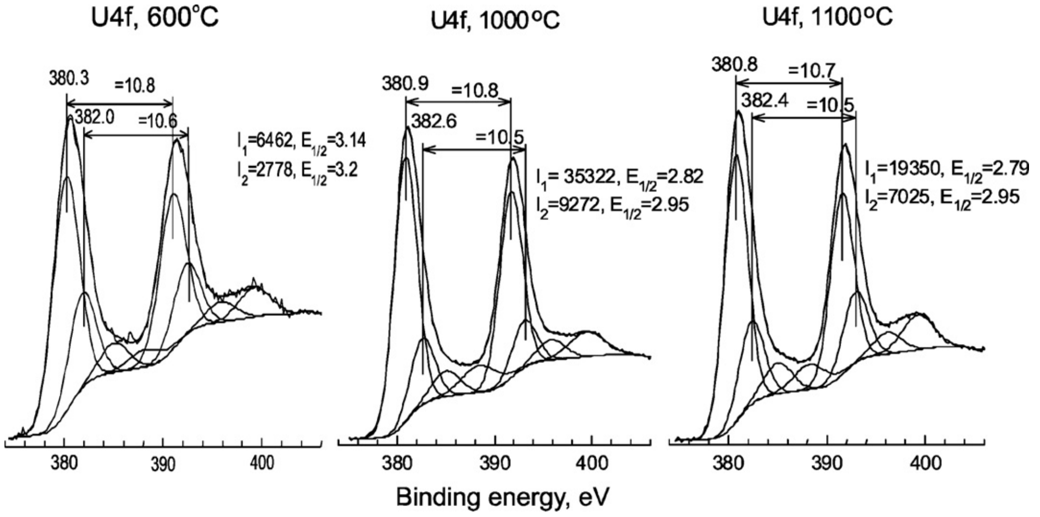

Fig. 2. Decomposition of XPS spectra of U4f into individual doublets after approximation of inelastic electrons scattering using the Shirley-type background for impregnated 5%U/Al_2O_3 catalysts calcined for 3 h at 600 °C, 1000 °C and 1100 °C.

positions in γ-Al_2O_3 or substituting for aluminum ions in θ-Al_2O_3, which destabilizes the crystal lattice of alumina and increases the diffusive mass transfer.

It is worth to note that such modification of support may underlie the observed effect of decreasing temperature of polymorphous phase transitions of alumina in the catalysts being studied.

At the next calcination temperature of the samples 1100 °C, according to HRTEM data the support comprises not only θ-Al_2O_3 particles, but also spherical α-Al_2O_3 particles of size 500–1000 Å indicated by arrows on the left in Fig. 1c. Hollow regions also do not form in θ-Al_2O_3 crystals subjected to the action of electron beam. The uranium oxide is present in this sample as coarse particles of α-U_3O_8 indicated by an arrow on the right in Fig. 1c, with the size ranging from 200 nm to 2–3 μm. HRTEM images did not show the presence of U ions on the surface of alumina particles. Thus, calcination at 1100 °C leads to abrupt transition of U from ionic state on alumina (θ-Al_2O_3) to the state of macrocrystalline oxide phases, with the α-U_3O_8 species being predominant (Table 1).

XPS data for the impregnated 5%U/Al_2O_3 catalyst calcined at different temperatures are given in Fig. 2 and Table 2. As calcination temperature is raised from 600 to 1000 °C, intensity of U4f lines strongly increases, decreasing upon further heat treatment at 1100 °C (Table 2). This indicates a sharp increase of the surface uranium concentration that occurs at elevation of calcination temperature to 1000 °C, which is basically related to dispersion of uranium oxide. Further elevation of calcination temperature to 1100 °C results, on the contrary, in sintering of the active component.

Comparing our U4f spectra with literature data [15], one can see that although these spectra are more diffused, they are quite similar to that of a binary UO_2 oxide with strongly defected structure UO_{2-x}. The contribution of metallic uranium is absent. A peak at 398-400 eV is a satellite. More detailed analysis of presented different states of uranium, in particular U6+, requires fitting of spectra to individual components (Fig. 2).

Approximation of the spectra depicted in Fig. 2 was carried out in accordance with the literature data reported in [16]. In contrast to that work where only one component of spin-orbit doublet was described, we approximated full region of U4f. To get a satisfactory description of the entire experimental spectra in full region we had to initialize two doublets to describe valence states 4 and 6 of uranium atoms (doublets with $E_b(U4f_{7/2})$ = 380.3–380.9 eV and 382.0–382.6 eV, respectively) and additional satellite structure in the form of two doublets with $E_b(U4f_{7/2})$ ~385 eV and ~388.5 eV. According to recent publications on uranium oxides mixtures, the positions of $U4f_{7/2}$ component are at 380.7 and 382 eV for U4f(4+) and U4f(6+), respectively [16]. The experimental values obtained in our work coincide well with these literature data.

According to curve fitting (Fig. 2) and the data in Table 2, the contribution of U4+ and U6+ is different for these samples and the temperature dependence of the ratio of low oxidation state (U4+) to high oxidation state (U6+) follows the total uranium concentration in the surface layer.

Fig. 3 shows hydrogen TPR data obtained for the catalysts. The TPR curves for impregnated catalyst, characterizing the ability of samples to be reduced by hydrogen as a function of calcination temperature, strongly differ from the TPR curves for solid-phase and mixed catalysts. As the calcination temperature of impregnated catalysts increases, hydrogen consumption peaks shift to the low-temperature region (Fig. 3a), thus indicating the appearance of more reactive species of the active component. We attribute the thermal activation effect of impregnated catalysts to an increase of dispersion at raising the calcination temperature from 600 to 1000 °C and its decrease at 1100 °C, as it was shown previously. An additional effect may occur because the amount of U4+ in the sample calcined at 1000 °C is higher (according to XPS data) compared to the samples calcined at 600 and 1100 °C. During the long-term (18 h) calcining of the catalyst at 1000 °C its reactivity decreases due to sintering; TPR peak of this sample shifts to the high-temperature

Table 2
XPS data for samples of the impregnated 5%U/Al_2O_3 catalyst calcined at different temperatures.

5%U/Al_2O_3 sample	Binding energy of $U4f_{7/2}$, eV				Area of the doublet		U^{IV}/U^{VI}	Ratio of surface concentrations
	U^{IV}	U^{VI}	U^{IV}	U^{VI}	S (U^{IV})	S (U^{VI})		U/Al
600 °C	380.3	382.0	385.1	388.1	6462	2778	2.33	0.007
1000 °C	380.9	382.6	385.0	388.5	35322	9272	3.81	0.040
1100 °C	380.8	382.4	385.1	388.3	19350	7025	2.75	0.029

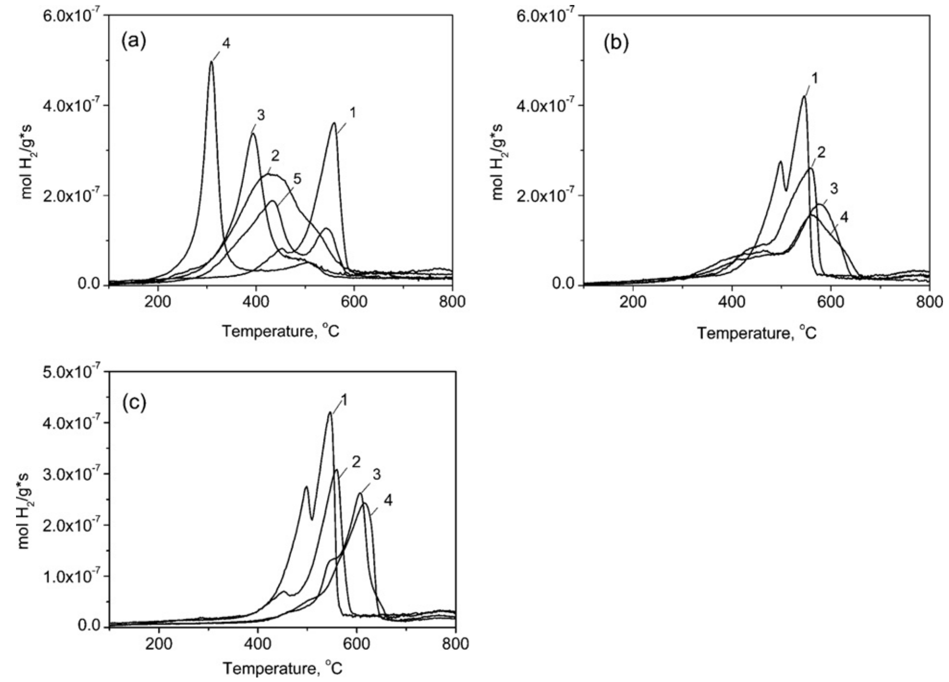

Fig. 3. TPR curves of 5%U-Al_2O_3 catalysts synthesized by various techniques and calcined at different temperatures: (a) impregnated catalyst calcined at (1) 500 °C; (2) 600 °C; (3) 900 °C; (4) 1000 °C; (5) 1000 °C for 18 h; (b) solid-phase catalyst calcined at (1) 500 °C; (2) 600 °C; (3) 900 °C; (4) 1000 °C; (c) mixed catalyst calcined at (1) 500 °C; (2) 600 °C; (3) 900 °C; (4) 1000 °C.

region with respect to the TPR peak of sample calcined at the same temperature for 3 h.

Behavior of the solid-phase catalysts in the TPR reaction is similar to that of mixed catalysts (Fig. 3b and c). As calcination temperature of these samples increases, TPR peaks shift to the high-temperature region, which is quite expectable and caused by decreasing dispersion of uranium oxide particles that compose these samples. However, when calcination is performed at 900 and especially at 1000 °C, effect of support shows up in the solid-phase samples: they are reduced at lower temperatures (some analogy with impregnated catalysts) as compared to the samples of mixed catalysts calcined at respective temperatures. Unlike the impregnated catalyst, whose samples are reduced by hydrogen in a wide range of temperatures with the peak maxima varying from 280

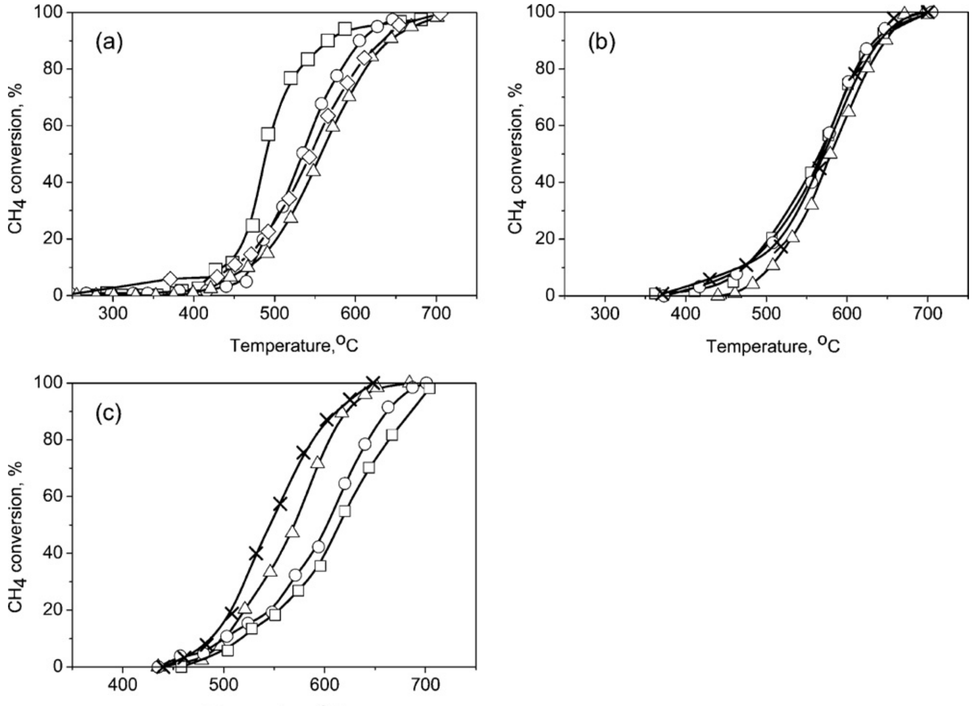

Fig. 4. Temperature dependences of methane conversion on 5%U-Al_2O_3 catalysts prepared by different techniques and calcined at different temperatures: (a) impregnated catalyst calcined at (△) 600 °C; (○) 900 °C; (□) 1000 °C for 3 h; (◊) 1000 °C for 18 h; (b) solid-phase catalyst calcined at (×) 500 °C; (△) 600 °C; (○) 900 °C; (□) 1000 °C; (c) mixed catalyst calcined at (×) 500 °C; (△) 600 °C; (○) 900 °C; (□) 1000 °C.

to 450 °C in dependence on calcination temperature, all samples of the solid-phase catalyst are reduced in a narrow temperature range with the peak maxima at 550–580 °C.

The indicated differences in the 5%U-Al_2O_3 catalyst activity in TPR manifest themselves also in the experimental data on catalytic activity in deep oxidation of methane presented in Fig. 4. The effect of impregnated catalyst thermal activation in TPR is observed also in the reaction of methane oxidation (Fig. 4a). Activity of the catalysts increases when calcination temperature is raised from 600 to 1000 °C. Calcination at 1100 °C as well as a long-term calcination at 1000 °C results in sintering of the active component phase, leading to a decrease of the catalytic activity. Samples of the solid-phase catalyst, irrespective of calcination temperature, show very close activity in methane oxidation (Fig. 4b), which resembles the behavior of these samples in the TPR reaction. The activity of mixed catalysts is dependent on the calcination temperature, and the catalysts calcined at low temperature are more active in methane oxidation (Fig. 4c).

Thus, properties of the catalysts prepared by different techniques were found to depend on the preparation procedure and are determined by different extent of the interaction between active component and support. This interaction is evidently absent in the mixed catalyst, the catalyst properties being determined by the properties of individual components of oxides mixture. The impregnated catalyst shows a pronounced mutual effect of uranium compounds and alumina. Probably, an interaction phase between active component and support is formed, where uranium is mostly in the highly dispersed ionic state. As the calcination temperature increases to 1000 °C, the interaction phase is destructed to form high dispersed and reactive uranium oxides. During a long-term calcination at 1000 °C or after calcination at 1100 °C the high-dispersed species are sintered. Ultimately, the catalyst activity is determined by a ratio of phases composing the catalyst: the interaction phase, fine and coarse uranium oxides.

4. Conclusions

The effects of preparation procedure and heat treatment on physicochemical properties of supported uranium oxide catalysts and their catalytic activity in deep oxidation of methane have been studied.

It was found that properties of the catalysts prepared by various techniques depend on the preparation procedure and are determined by different extent of the interaction between active component and support. In the mixed catalysts this interaction is evidently absent, and catalytic properties are determined by the properties of individual components of the mixture. In the impregnated catalyst, as compared with solid-phase and mixed catalysts, mutual effect of uranium compounds and alumina is quite pronounced: at the rise of calcination temperature there occur intense sintering of the porous structure, substantial decrease of specific surface area and transition of γ-Al_2O_3 to the high-temperature modification θ-Al_2O_3. In the solid-phase catalyst, mutual effect of uranium and aluminum oxides shows up to a smaller extent compared to the impregnated catalyst.

The study of the catalytic activity shows that the catalysts prepared by the impregnation method are more active. It was found that the optimum calcination temperature to obtain the most efficient 5%U/Al_2O_3 catalyst was 1000 °C. The high activity of this catalyst is explained by the formation of highly active nanodispersed state of uranium on the support surface.

HRTEM and XPS study confirmed the formation of highly dispersed state of uranium on the support surface upon elevation of calcination temperature of the impregnated catalyst to 1000 °C, and sintering of the active component when the catalyst is calcined at a higher temperature (1100 °C).

It is concluded that the catalytic activity of 5%U/Al_2O_3 catalysts is determined by a ratio of phases composing the catalyst: the interaction phase, fine and coarse uranium oxides.

References

[1] G.T. Seaborg, J.J. Katz (Eds.), The Actinide Elements, first edition, New York, 1954.
[2] A.N. Zhiganov, V.V. Guzeev, G.G. Andreev, Technology of uranium dioxides for ceramic nuclear fuel, Tomsk, 2002.
[3] G.J. Hutchings, S.H. Taylor, Catal. Today 49 (1999) 105.
[4] G.J. Hutchings, C.S. Heneghan, I.D. Hudson, S.H. Taylor, Nature 384 (1996) 341.
[5] R.K. Grasselli, D.D. Suresh, J. Catal. 25 (1972) 273.
[6] V.C. Corberan, G. Kremenic, React. Kinet. Catal. Lett. 36 (1988) 235.
[7] Z.R. Ismagilov, S.V. Kuntsevich, V.V. Kuznetsov, N.V. Shikina, M.A. Kerzhentsev, V.A. Rogov, V.A. Ushakov, Kinet. Catal. 4 (2007) 544.
[8] L.G. Gordeeva, Y.I. Aristov, E.M. Moroz, N.A. Rudina, V.I. Zaikovskii, Y.Y. Tanashev, V.N. Parmon, J. Nucl. Mater. 218 (1995) 202.
[9] Z.R. Ismagilov, S.V. Kuntsevich, Chem. Sust. Dev. 17 (2009) 445.
[10] S.V. Kuntsevich, Z.R. Ismagilov, N.V. Shikina, V.A. Ushakov, N.A. Rudina, V.A. Rogov, V.V. Kuznetsov, V.V. Lazarchuk, V.G. Balakhonov, V.A. Matyukha, A.I. Drobyaz, A.L. Khlytin, Abstracts of the III International Conference "Catalysis: Fundamentals and Application", vol. 2, Novosibirsk, Russia, 2007, p. 270.
[11] Z.R. Ismagilov, R.A. Shkrabina, N.A. Koryabkina, Catal. Today 47 (1999) 51.
[12] S.A. Yashnik, Z.R. Ismagilov, V.V. Kuznetsov, V.V. Ushakov, V.A. Rogov, I.A. Ovsyannikova, Catal. Today 117 (2006) 525.
[13] Database: PCPDF, No. 10-0425.
[14] Database: PCPDF, No. 35-0121.
[15] S.D. Senanayake, et al., Catal. Today 120 (2007) 151.
[16] D. Kumar, et al., Phys. Chem. Chem. Phys. 5 (2003) 5477.