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Catalysts Containing Depleted Uranium Compounds

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Abstract

The review is devoted to considering the features of physicochemical properties of uranium oxides. Chemical processes involving catalysts those contain depleted uranium compounds are analyzed and systematized. The review contains the materials published within the period from 1964 to 2009.

Key words: uranium oxides, catalyst, depleted uranium

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INTRODUCTION

Naturally occurring uranium consists of the mixture of three isotopes – U^{238} , U^{235} and U^{234} , and the fraction of isotope U^{238} in this mixture amounts to 99.27 % [1]. The main field of its application represents nuclear industry where uranium enriched with respect to isotope U^{235} (3–4 %) is employed. A by-product of the enrichment is referred to as depleted uranium; the main part of radioactive isotopes (U^{235} and U^{234}) is extracted at the stage of enriching. The depleted uranium is less radioactive as compared to uranium ore containing 0.2–0.4 % of U^{235} .

Other application areas of uranium compounds are known, too. So, in 19–20 centuries

uranium oxides were used for colouring glass and ceramics. Up to 1980ths the depleted uranium was employed in stomatology. Now both naturally occurring and depleted uranium are used in manufacturing containers for transportation of radioactive materials and in making especially strong and chemically stable alloys for mechanical engineering, as well as ballast in aircraft [2, 3]. It should be noted that the recycling of vast man-caused stocks of depleted uranium stored as uranium hexafluoride, the main by-product of uranium enrichment, represents a global problem. One of prospective ways to recycle the stocks of uranium hexafluoride consists in the manufacture of catalysts based on uranium oxides obtained from urani-

um hexafluoride through intermediate products such as uranyl salts.

The chemistry of uranium compounds is sophisticated enough; there are various oxidation states and a lot of thermodynamically stable phases [1, 4–9]. The structure of the external electron shell of uranium atom $5f^36d^17s^2$ allows the element to exhibit such oxidation degree as +2, +3, +4, +5 and +6 respectively; in the system U–O there are several stable phases those are of interest for catalysis: UO_2 , U_3O_8 , UO_3 , as well as a great number of non-stoichiometric phases and polymorphic modifications. For example, uranium trioxide UO_3 exhibits seven polycrystalline modifications and one modification with an amorphous structure [10]. Moreover, the phase transition from one structure to another can proceed with a very low activation energy value, and there are a number of metastable oxides in system U–O. Figure 1 demonstrates a phase diagram for uranium–oxygen system [11]. A wide range of phases of uranium oxide compounds with non-stoichiometric composition occurring could be explained by the fact that there is enough space for oxygen incorporation in the lattice of uranium oxides.

The prevailing consumption of uranium in the form of uranium dioxide is made by the enterprises of atomic power engineering, thus oxygen-containing compounds of uranium were investigated most completely with the purpose of manufacturing nuclear fuel. At the same time, due to the aforementioned variety of uranium valent states of within its oxides as well as to the features of their mutual transformations, uranium oxides represent promising catalysts for a wide range of chemical reactions. The studies on catalytic properties of uranium compounds are being carried out since 1940ths [12]. The oxides and other compounds of uranium could be used both as individual catalysts, and as promoters or carriers for others oxides or metals.

In the present review, we have considered physicochemical properties of uranium oxides are considered, generalized the methods for preparing uranium oxide catalysts, analyzed research methods and the possibility of applying them. The literature data for last four decades concerning the studies on catalysts based on uranium oxides have been systematized.

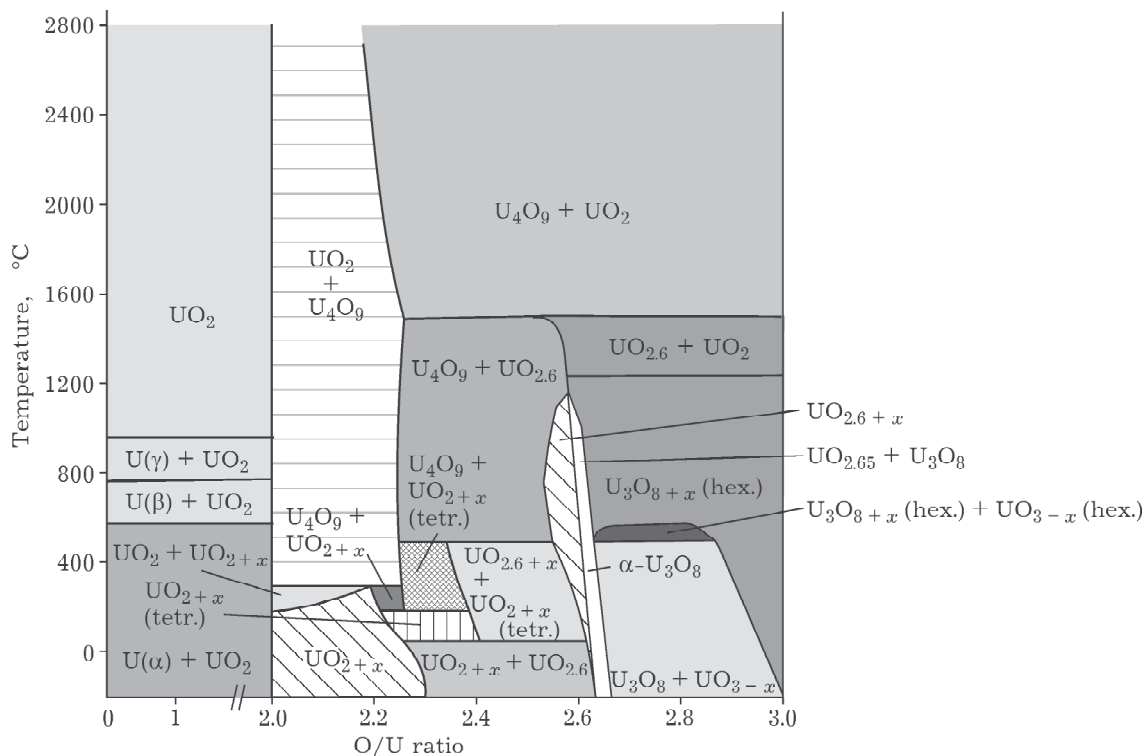


Fig. 1. Phase diagram of U–O system [11].

In the review we have demonstrated the advantages and promise of employing uranium oxide catalysts in the reactions of obtaining hydrogen from synthesis gas, Fisher–Tropsch process, the processes of partial oxidation, cracking, hydrotreating and purifying gas emissions those contaminate the environment. The advantages of employing uranium oxide catalysts include the possibility for varying the valent state of uranium as well as the stoichiometry of oxides over a wide range, their resistance with respect to the action of catalytic poisons (for example, sulphur, water, chlorine, coke) and the opportunity of replacing expensive industrial catalysts based on precious metals by more efficient catalysts such as UO_x .

PHYSICOCHEMICAL FEATURES OF URANIUM OXIDES

The U–O system represents one of the most complicated double metal–oxygen systems. This is caused not only by the fact that several oxidation levels, or states, are inherent in uranium, but also by the fact that in this system there are numerous polymorphic modifications and solid solutions, there are a lot of compounds with variable composition as well as metastable phases. Data available from various literature sources point out the existence of at least 10 oxides of uranium and 14 modifications of them [6]. Below we consider the properties inherent in uranium compounds employed in order to prepare catalysts, as well as in uranium oxides those can be used as carriers, active components or modifying additives for different kinds of catalysts.

The oxidation degree +6 for uranium is the most stable in aqueous solutions. It is customary to assume that uranium (VI) exists as UO_2^{2+} ion [13]. Under calcination the catalysts prepared *via* impregnation technique, decomposition of compound contained in the impregnation solution is observed to occur. In most cases in order to obtain uranium oxide catalysts one uses to employ uranyl nitrate hexahydrate $UO_2(NO_3)_2 \cdot 6H_2O$. The process of this compound decomposition to produce uranium trioxide is multy-stage one. It is believed that the decomposition of nitrate involves, in general, the following reactions:
 $UO_2(NO_3)_2 \cdot 6H_2O \leftrightarrow UO_2(NO_3)_2 \cdot 3H_2O + 3H_2O$
 $UO_2(NO_3)_2 \cdot 3H_2O \leftrightarrow UO_2(NO_3)_2 \cdot 2H_2O + H_2O$



Equilibrium pressure constants of and the heat of transition were determined for each stage [14].

Obtaining ammonium polyuranates is of a certain practical interest in the preparation of bulk uranium oxides, since ammonium polyuranates under calcination could be rather readily converted into pure uranium oxide U_3O_8 [15]. Now the majority of technological process for obtaining uranium oxides provides such final operation as the calcination of ammonium polyuranates to yield uranium oxide. Ammonium diuranate samples one uses to obtain *via* adding an aqueous solution of ammonium to a solution of uranyl nitrate up to gaining pH 11, a dense yellow precipitate is filtered, washed and dried to obtain constant mass. Under the precipitation of uranium by ammonium hydroxide from uranyl nitrate solutions the precipitate formed deposit usually mistaken for $(NH_4)_2U_2O_7$, exhibits a non-stoichiometric structure. The process of ammonium polyuranates decomposition in air and in inert media occurs in five stages:

- 1) 298–403 K – the removal of adsorption water;
- 2) 403–473 K – the removal of a part of constitutional water;
- 3) 473–623 K – the removal of other part of the constitutional water and a part of ammonia;
- 4) 623–723 K – β - UO_3 formation (in air), self-reduction and U_3O_8 formation U_3O_8 (in an inert medium);
- 5) >723 K – U_3O_8 formation (in air) and oxygen loss of at elevated temperature values with the formation of U_3O_{8-x} .

The process of thermal decomposition in hydrogen proceeds *via* the same stages, but the latter stage, *i. e.* the reduction of U_3O_8 to produce UO_2 proceeds through the formation of intermediate phases $UO_{2.25}$ and UO_{2+x} [6].

There is some evidence in the literature for the fact that the following uranium oxides exist: UO_3 , U_3O_8 , U_2O_5 , U_5O_{13} , U_3O_7 , U_7O_{16} , U_4O_9 , UO_2 and UO [8]. Among all the compounds listed, mainly the following three oxides are employed in catalysis; they are UO_2 , U_3O_8 and UO_3 .

Uranium dioxide UO_2 represents a substance of dark brown colour with CaF_2 type crystal structure [1, 5]. This non-stoichiometric com-

pound can exhibit the composition ranging from $UO_{1.6}$ to $UO_{2.25}$, the density amounting to 10.96 g/cm^3 . Uranium dioxide can be obtained via reducing uranium trioxide or U_3O_8 either by hydrogen or by carbon monoxide at $500\text{--}600^\circ\text{C}$. The powder of UO_2 with entirely stoichiometric composition ($O/U = 2.00$) is almost impossible to obtain in practice. Usually researchers can obtain such oxide with either deviation from stoichiometry. The stability of uranium dioxide powder with respect to oxidation is determined by the prehistory of its obtaining [16]. In the presence of oxygen, the UO_2 is capable of dissolving oxygen within its own bulk, with the conservation of cubic structure to form the phase such as UO_{2+x} , where x depends on temperature. Uranium dioxide does not react with water and water vapour up to 300°C , it is insoluble in hydrochloric acid, however it can be dissolved in nitric acid, aqua regis as well as in the mixture of HNO_3 and HF . Under dissolving in nitric acid, the formation of uranyl ions UO_2^{2+} occurs. A crystalline hydrate of uranium dioxide $UO_2 \cdot 2H_2O$ is known representing black sediment precipitating due to hydrolyzing the solutions of uranium.

Uranium oxide U_3O_8 represents a non-stoichiometric compound that has several modifications depending on the conditions of preparing [1, 6]. By the present time it is established,

that uranium oxide U_3O_8 has three crystal modifications. The modification such as $\alpha\text{-}U_3O_8$ is most completely studied. The substance is coloured from green to olive-green and black; the U_3O_8 density is equal to 8.39 g/cm^3 . Uranium oxide U_3O_8 is formed under uranium dioxide oxidation in air of calcining any uranium oxide, oxide hydrate or uranium salts in air at $650\text{--}900^\circ\text{C}$ with any volatile base or acid. Oxide U_3O_8 is sometimes considered to be $UO_2 \cdot 2UO_3$. However, it is evidenced that all the atoms of uranium in U_3O_8 are structurally equivalent and carry an equal positive charge. This compound is not soluble in water and in diluted acids, but it can be slowly dissolved in the concentrated mineral acids with the formation of the mixture of uranium and uranyl salts. In HCl and H_2SO_4 solutions, a mixture of uranium salts is formed with the oxidation level of 4 and 6, whereas in only uranyl ion can be formed. Incomplete dissolving U_3O_8 in sulphuric acid results in the formation of U_2O_5 , which cannot be obtained *via* reducing uranium oxides with hydrogen on heating. Uranium oxide U_3O_8 contains hydrate $U_3O_8 \cdot H_2O$ which does not crystallize and can be very readily oxidized to yield uranium trioxide hydrate.

Uranium trioxide UO_3 represents orange-yellow powder existing in one amorphous and five crystalline modifications, the density rang-

TABLE 1
Methods for obtaining uranium trioxide

Final products	Obtaining conditions
UO_3 (amorph.)	Thermal decomposition of uranium peroxide $UO_4 \cdot 4H_2O$ (as well as $UO_3 \cdot 2H_2O$, $UO_2C_2O_4 \cdot 3H_2O$, $(NH_4)_4[UO_2(CO_3)_3]$) washed from nitrate ion, in air at $673\text{--}723 \text{ K}$
$\alpha\text{-}UO_3$	1) UO_3 (amorph.) calcination in an oxygen atmosphere at a pressure of 4 MPa and the temperature of $773\text{--}825 \text{ K}$; 2) Hydrated uranium peroxide containing nitrate ion, calcination at 723 K
$\beta\text{-}UO_3$	1) U_3O_8 calcination in an oxygen atmosphere at a pressure of 4 MPa and the temperature of $773\text{--}823 \text{ K}$; 2) Slow heating of ammonium polyuranate containing a nitrate ion, up to 723 K ; 3) Fast heating of uranyl nitrate hexahydrate, up to 723 K
$\gamma\text{-}UO_3$	1) $UO_2(NO_3)_2 \cdot 6H_2O$ thermal decomposition in air, first heating up to 473 K , then (after homogenization) heating up to 773 K ; 2) Calcination of $\alpha\text{-}$, $\beta\text{-}$, $\gamma\text{-}$ modifications and UO_3 (amorph.) in an oxygen atmosphere at a pressure of 7 MPa and the temperature of 923 K
$\delta\text{-}UO_3$	$\beta\text{-}UO_3 \cdot H_2O$ calcinations in air at 648 K during 24 h
$\varepsilon\text{-}UO_3$	U_3O_8 oxidation by means of gaseous NO_2 at $498\text{--}573 \text{ K}$
$\eta\text{-}UO_3$	The phase exists at a pressure of $1500\text{--}6000 \text{ MPa}$ up to 1773 K

TABLE 2

Parameters of various uranium trioxide UO_3 modifications

Modifications	Colour	Density, g/cm^3		Structure	Heat of formation, kcal/mol
		Picnometric	X-ray		
UO_3 (amorph.)	Orange	6.8	no data	no data	-290.8
$\alpha\text{-UO}_3$	Brown	7.04	8.34	Hexagonal $a = 3.97, c = 4.17 \text{ \AA}$	-291.8
$\beta\text{-UO}_3$	Orange-red	8.25	no data	no data	-294
$\gamma\text{-UO}_3$	Yellow	7.28	7.27	Orthorhombic $a = 13.61 \text{ \AA}, b = 15.48 \text{ \AA}, c = 4.17 \text{ \AA}$	-293
$\delta\text{-UO}_3$	Dark red	6.99	6.67	Cubic $a = 4.16 \text{ \AA}$	-294
$\epsilon\text{-UO}_3$	Red	8.54	no data	Orthorhombic	-293
$\text{UO}_{2.9}$	Olive-green	7.72	8.42	no data	no data

ing within $5.92\text{--}7.54 \text{ g}/\text{cm}^3$ [7]. It is thermodynamically stable in air up to the temperature of $600 \text{ }^\circ\text{C}$. Uranium trioxide is obtained via oxidation of UO_2 or U_3O_8 by oxygen at a pressure of $30\text{--}100 \text{ atm}$ at the temperature about $500 \text{ }^\circ\text{C}$ or through the calcination of uranium peroxide hydrate $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ or of uranyl nitrate hydrate $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or of ammonium diuranate $(\text{NH}_4)_2\text{U}_2\text{O}_7$.

The properties of uranium trioxide depend in many respects on the method of its obtaining. Data concerning the methods of obtaining and interdependence between various modifications of UO_3 are presented in Table 1 [6].

Data generalization concerning some properties of various UO_3 modifications is presented in Table 2 [7].

Uranium trioxide is amphoteric compound: with acids, it forms uranyl salts, for example UO_2SO_4 , whereas the reaction with alkalis results in the formation of the uranium salts acid, for example $\text{Na}_2\text{U}_2\text{O}_7$. Several crystalline hydrates of uranium trioxide are known those could be considered to be acids.

Most well studied triple oxides – urinates – are formed due to the amphoteric nature of uranium in six-valent state [1]. Uranates represent the compounds of uranium oxides with more basic oxides of other elements. Uranates

could be considered to be the salts uranic (H_2UO_4), hypothetical diuranic ($\text{H}_2\text{U}_2\text{O}_7$) and polyuranic ($\text{H}_2\text{U}_n\text{O}_{3n+1}$) acids are coloured yellow or yellow-orange. There are uranates of alkaline, alkali-earth, as well as transition metals existing. As opposite to the systems such as uranium-oxygen, the addition and loss of oxygen in uranates are reversible. Uranates are not water-soluble; they are well-soluble in mineral acids and can be decomposed by carbonate solutions. These compounds are obtained *via* sintering stoichiometric amounts of UO_3 with other oxides.

CATALYSTS BASED ON URANIUM COMPOUNDS AND THEIR USE

Organic synthesis reactions

Let us consider separate examples of employing the compounds of uranium in catalytic reactions for organic synthesis. Further, we are presenting a systematic review concerning catalysts grouped according to more comprehensively investigated reactions and processes.

Paper [17] demonstrated the possibility of using the salts uranium tetrachloride, as well as uranyl chloride, fluoride and acetate in the Friedel – Crafts process (acylation of aromatic compounds). The authors consider such cata-

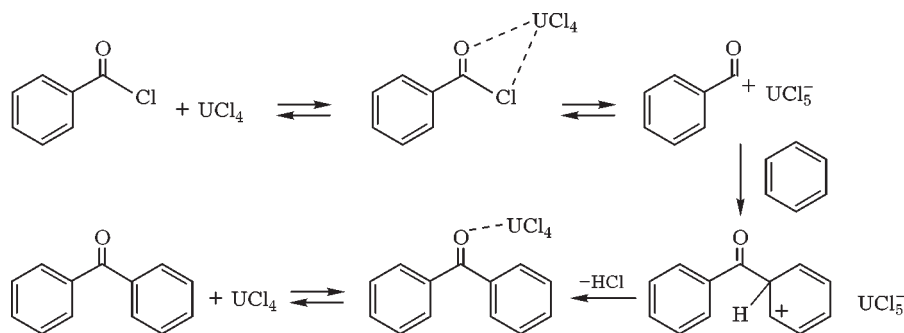


Fig. 2. Acylation reaction mechanism on uranium tetrachloride.

lysts to be inexpensive and commercially available. A probable mechanism of the reaction has been demonstrated therein. With uranyl salts a high yield of mono- and biacylation products is achieved as a result of the reaction under dry air conditions. Catalysts based on uranium salts are easy for recycling, whereas reaction products can be readily purified. It has been revealed that complexes of U^{4+} и U^{6+} are bright coloured, readily forming acylated ions, not forming complexes with ketones and aromatic esters. A possible mechanism for acylation reaction involving uranium salts is presented in Fig. 2.

The authors of [18] have demonstrated that some ligands can form a variety of bonds with uranium. As a result, such inert molecules as nitrogen and carbon dioxide become reactive, being in the complex with uranium. Due to the fact that uranium is capable of involving external f electrons for binding ligands, this element exhibits catalytic properties for the realization of reactions those are impossible with the use of traditional catalysts on the basis of transition metals.

The advantage of uranium over lanthanoids and transition metals consists in the fact that the atom has a rather large ionic radius exhibiting the ability of forming high coordination numbers. Uranium is noteworthy for a variety of stable oxidation states, as opposite to trivalent lanthanoids. Thus, it is known, that uranium coordination compounds are efficient in the process of alkane hydrogenation [19–23], as well as oligomerization, dimerization, hydroamination of alkynes [24–26].

Acetaldehyde interaction with the surface of uranium oxides such as UO_2 , $\alpha\text{-U}_3\text{O}_8$,

$\beta\text{-UO}_3$ was considered by the authors of [27, 28]. It has been demonstrated that the reaction products depend on U/O ratio in formula U_xO_y . Due to the fact that the structure of UO_2 allows placing within itself a significant amounts oxygen, there is formation of one molecule of organic compound from two ones occurring on the surface dioxide with oxygen abstraction from the two latter. So, two acetaldehyde molecules are combined to give the molecule of butene. On the surface of $\alpha\text{-U}_3\text{O}_8$ there is aldol condensation of two acetaldehyde molecules occurring to produce croton aldehyde. For $\beta\text{-UO}_3$, the products of reaction depend on the surface covering level by adsorbate. At a low covering level one can register the formation of furan, whereas when the covering level is high there are furan and croton aldehyde observed to be formed.

The interaction of formaldehyde with the surface uranium oxides such as monocrystalline UO_2 (111) and polycrystalline UO_2 was studied in [29]. Ethylene formation is observed on the surface of UO_2 (111) to occur at a room temperature. For the polycrystalline surface within the temperature range of 88–200 K one can observe the formation of poly- and dioxymethylene groups. These groups resulted in the formation of stable formates those decomposed at a temperature above 550 K. It has been revealed that on the surface of both mono-, and polycrystalline samples there are identical products formed, except for the formation of the traces of methylformates in the case of a powder catalyst. However, UO_2 (111) was observed to be more active than polycrystalline UO_2 .

Behaviour of carboxylic acids on the surface of monocrystalline UO_2 was investigated [30]. The authors hold that the phenomenon of interaction between the molecules of gases with uranium compounds is connected their adsorption capability. Under adsorbing HCOOH one can observe CO_2 and H_2 formation at 630 K as well as CO and H_2O formation at 700 K. On the surface with oxygen deficiency there was CO_2 and formaldehyde formation occurring, with a significant amount of ethylene. Formaldehyde was desorbed at 550 and 630 K.

The authors of [31] investigated the process of furan formation from acetylene on the surface of $\beta\text{-UO}_3$. It has been revealed that on $\alpha\text{-U}_3\text{O}_8$ furan is formed in trace amounts, whereas on UO_2 there is no furan formation from acetylene occurring. It has been demonstrated that there is two mechanisms for the formation of furan from C_2 molecules; they are aldol condensation and oxidative dimerization with the participation of catalyst's surface oxygen [32].

A possibility has been demonstrated for the reactions of dehydration and dehydratation on the surface of UO_2 [33]. Temperature programmed desorption of ethanol was investigated at 370 and 570 K. At a high temperature, the desorption of ethanol, ethylene and acetaldehyde occurred. For the calibration of the covering level of the surface and for determining the adsorption coefficient the authors employed Auger spectroscopy. The authors of [33] have demonstrated that the selectivity of the reaction does not depend on the covering level for the surface of the catalyst. The formation of furan from ethanol on $\beta\text{-UO}_3$ was studied in [34].

The adsorption of methanol CH_3OD was studied for the surface of uranium and uranium dioxide [35] within the temperature range of 90–500 K. The adsorption on uranium at 90 K resulted in the formation of methoxy groups. The adsorption at room temperature resulted in the formation of the mix of methoxy groups and uranium oxycarbide. The further heating up to 400 K resulted in decomposing the surface groups with the formation of methane and uranium oxycarbide with the formula $\text{UO}_{0.66}\text{C}_{0.34}$. The desorption of hydrogen and deuterium was observed within the range of 325–450 K. From the surface of uranium dioxide, CH_4 , H_2 , HD , D_2 and CO were observed to desorb. The au-

thors of [36] investigated the behaviour of formic acid (HCOOD and DCOOH) on the surface of uranium and UO_2 . The interaction with the surface has been investigated employing the methods of thermal desorption mass spectroscopy, XPS and ionization mass spectroscopy. The adsorption of formic acid on the surface of uranium at 100 K results in the formation of formate as main product. A number of products are formed at 200 K: formate, hydroxyl groups, adsorbed oxygen and hydrogen (deuterium). The formate adsorbed was observed to decompose at 300 K. Carbon on the surface was produced in the form of carbide. On the surface uranium oxide UO_2 one can observe the formation of much more stable formate groups as compared to the surface of uranium. Within the range of 100–300 K, prevailing products on the surface are presented by the formate and hydroxyl groups. At the temperature ranging within 300–350 K one can observe the formation of water on the surface. Formates decompose at 400–500 K to produce CO и H_2CO (D_2CO) groups. On heating higher than 500 K, carbon has not been found out on the surface of oxide. Carbon-containing compounds either are desorbed with the formation of CO -containing products, or can migrate within the near-surface layer of the catalyst.

It has been demonstrated that uranium triiodide represents an efficient acid catalyst for the Mukayama reaction [37, 38] and a precursor for $\text{UI}_3(\text{THF})_4$ catalyst in Diels–Alder reactions (the reactions of cyclic and acyclic dienes – dienofiles) those are carried out under soft conditions in the presence of a small amount of the catalyst. The coordination compound $\text{UI}_3(\text{THF})_4$ was been prepared via the reaction between amalgamated uranium and iodine in tetrahydrofurane (tetramethylene oxide) medium [39].

Many uranium-containing catalysts for the reactions of organic synthesis are protected by a number of patents. The process of preparation of organic urethanes via the interaction between organic compounds containing nitro- and hydroxyl groups and CO is carried out in the presence of a catalyst. The catalytic system contains the compound of a precious metal, a heteroaromatic nitrogen-containing compound and thorium or uranium oxide [40].

A process has been offered for the methylation of phenols in the gas phase with the formation 2,6-xylenol on magnesium oxide promoted by titanium uranium, chromium ions as well as sulphate ions [41].

The process of olefin epoxidation by organic hydroperoxides is performed on an uranium-containing catalyst applied onto titanium dioxide and SiO₂. The catalyst can be promoted by a compound of magnesium, calcium, strontium, barium, as well as by the oxides or hydroxides of boron, tin, niobium, tantalum, chromium, molybdenum, rhenium, bismuth or rare earth elements (REE) [42].

A manufacture of oxiranes (epoxides) was proposed *via* the reaction of olefins with organic hydroperoxides employing such catalysts as naphthenates and carbonyls of uranium as well as those of molybdenum, titanium, tungsten, vanadium, rhenium, niobium, tantalum, selenium, chromium, zirconium, and tellurium. Examples have been given for the interaction between ethylbenzene hydroperoxide and propylene with the formation of propylene oxide and phenylethyl alcohol as well as other lower olefins [43, 44].

The obtaining of 4-methyl-1-pentene employed as a monomer in the production of polyolefins is carried out under contacting C₃H₆ with a catalyst containing a hydride complex of uranium [45].

The alkylation of phenols on uranium-containing catalysts has been claimed in the patent [46].

Unsaturated hydrocarbons, including benzene, are hydrogenated on a catalyst containing nickel applied onto such carrier as calcium phosphate promoted by barium and uranium. The catalytic activity of the mentioned catalysts is

high enough to perform the processes, including the liquid-phase hydrogenation of aromatic molecules, under moderate conditions, which causes the lifetime of the catalysts to increase [47].

In order to perform hydroreforming and isomerisation of hydrocarbons, a catalyst was proposed consisting of such carrier as a refractory mineral oxide, a combination of halogen and metal in the free form or as compounds being from the following groups: metals of the platinum group (0.02–2 %), tin (0.2–2 %), a metal chosen from such group as Sc, Y, Th, U and other REE (0.01–5 %) [48, 49].

Obtaining synthesis gas on nickel-uranium catalysts

The authors of [50] studied the influence of adding thorium, uranium, zirconium oxides upon the activity of nickel and cobalt catalysts in the reaction of partial methane oxidation. The following sequence of the activity of catalysts has been established: NiO–TiO₂ > NiO–UO₂ > NiO–ZrO₂. The disadvantage of these catalysts consists in a considerable deactivation owing to their carbonization, however, adding cobalt results in essential hindering the process of coking. The reaction was carried out under the conditions of short contact time (GHSV = 5.2 · 10⁵ h⁻¹), C_{CH₄} = 66 mol. %, C_{O₂} = 34 mol. %. Data concerning the activity of non-reduced catalysts are presented in Table 3. Data concerning the activity of catalysts preliminary reduced by hydrogen at 500 °C are presented in Table 4.

The investigation of the surface of catalysts has demonstrated that the specific sur-

TABLE 3

Catalytic oxidation of methane into synthesis gas on mixed oxide catalysts

Catalysts	Reaction temperature, °C	CH ₄ conversion level, %	Selectivity level, %		H ₂ /CO
			H ₂	CO	
NiO–ThO ₂	800	94.2	96.8	97.1	1.99
	700	90.0	94.8	95.1	1.99
NiO–UO ₂	800	79.4	88.8	95.5	1.86
	700	71.2	82.2	93.4	1.76
CoO–ThO ₂	800	62.1	76.5	91.9	1.67
	700	58.6	73.6	88.5	1.67
CoO–UO ₂	800	52.1	72.3	87.8	1.65
	700	40.0	64.6	81.8	1.58

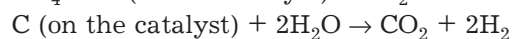
TABLE 4

Catalytic oxidation of methane into synthesis gas on preliminary reduced mixed oxide catalysts

Catalysts	S_{sp} , m ² /g	CH ₄ conversion level, %	Selectivity, %		H ₂ /CO	Carbon precipitation, 10 ² g/(g · h)
			H ₂	CO		
NiO-UO ₂	2	78.7	92.4	95.2	1.94	0.2
CoO-UO ₂	0.5	49.8	64.2	81.3	1.58	—
NiO-CoO-UO ₂	0.8	58.6	86.6	90.6	1.58	0.03

face area of nickel-containing catalysts is in general higher than this value for cobalt-containing catalysts. It should be noted that the preliminary reduction of catalysts before the reaction has insignificantly affected their activity that is comparable to the activity of non-reduced catalysts.

The authors of [51] reported the process of hydrogen obtaining in the reaction of methane steam reforming at a low temperature (500 °C) in two parallel catalytic reactors with varied feeding by gas mixtures CH₄ + N₂ and H₂O + N₂ into the reactors. The process included two simultaneous reactions: catalytic decomposition of methane into hydrogen and carbon and water vapour interaction with carbon on the catalyst with the formation of hydrogen and CO₂:



Owing to such organization of the process on Ni/UO₃, the hydrogen yield equal to 3.1 mol/mol of methane has been achieved.

We have demonstrated in [52] that the introduction of uranium (from 0 up to 30 %) to the comp of Ni-U/Al₂O₃ catalyst results in a considerable increase in the catalytic activity in the reaction of methane steam conversion. So, on 10 % Ni/Al₂O₃ catalyst (an analogue of the industrial catalyst) the conversion level of methane amounts to 40 %, whereas the yield of hydrogen is 23 % at 850 °C and 50 000 h⁻¹. Under the same conditions the conversion level of methane and the yield of hydrogen in the reaction of methane steam conversion on Ni-30U/Al₂O₃ catalyst amount to 77 and 42 %, respectively.

For the reaction of methane conversion, an increase in the content of uranium in the catalyst results in a decrease of coke formation. Adding 30 % U to the composition of the catalyst results in an almost complete inhibition of coke

formation (the yield of carbon at 850 °C amounts to ~0.4 %), whereas for the industrial analogue the yield of carbon at 850 °C amounts to 14 %.

Catalysts containing uranium oxides as well as the mixed nickel-uranium catalysts were investigated in the reaction of partial methane oxidation. The introduction of uranium in the structure of traditional partial oxidation catalysts based on nickel allows one to increase the yield of hydrogen. The yield of hydrogen at 800 °C on uranium-containing catalysts amounts up to 65 % as compared to 40 % for an analogue of industrial Ni/Al₂O₃ catalyst under the same conditions.

The influence of Ni and Ru content in the catalyst, of the temperatures and contact time upon catalytic activity in the reaction of methane steam reforming was investigated by the authors of [53, 54]. The process was carried out at a pressure $P = 1$ atm and $T = 600$ – 780 °C. Under these conditions, the yield of hydrogen amounted up to 17–18 cm³/s per 1 g of the catalyst. Before the reaction the catalysts reduced by hydrogen at 700 °C during 1 h. Figure 3 demonstrates the conversion level of methane depending on the contact time for ruthenium-uranium and nickel-uranium catalysts. For the comparison, data concerning the activity of industrial Ni/Al₂O₃ catalyst are presented.

For the steam reforming of propylene, a catalyst was proposed containing by 5–15 % of nickel, uranium, thorium, as well as alkaline or alkali earth metal, for example 0.5–1.5 % of potassium. The catalyst is prepared employing the method of refractory carrier impregnation with the melts of metal nitrates. The yield of hydrogen in this case can amount to 68.3 % [55].

Methods have been offered for the preparation of nickel-uranium catalysts *via* impregnation of Al₂O₃ or spinel with the solutions of the salts of these metals [56]. There is also a

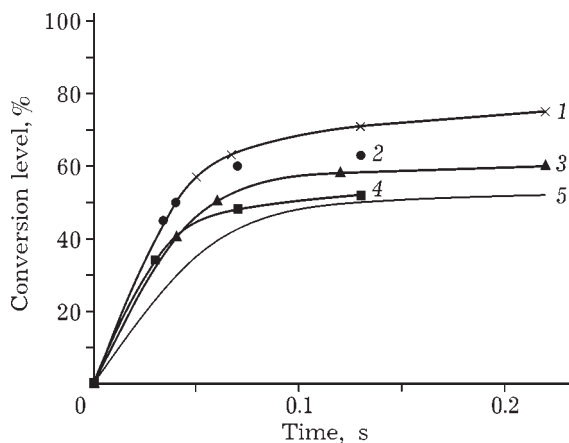
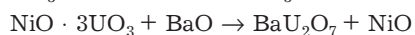
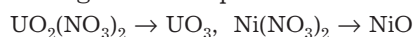


Fig. 3. Conversion level of methane depending on the contact time on catalysts with 0.8 mass % of Ru/U₃O₈ (1, 3) and 9 mass % of Ni/U₃O₈ (2, 4) at 750 (1, 2) and 700 °C (3, 4). Solid line (5) corresponds to the sample of industrial catalyst with 7.5 mass % of Ni/Al₂O₃.

method for carrier preparation *via* mixing the powders of UO₃ and Al₂O₃ and the subsequent sintering within the temperature range of 600–1650 °C [57]. The authors of [58] proposed thermal decomposition of uranyl and nickel acetates to occur in the presence of a carrier. Oxides are formed under calcination on the carriers. Uranium oxide completely reacts with nickel oxide to produce nickel urinate when the latter is in excess.

Further catalysts are calcinated in a reducing atmosphere for the formation of active components in the form of metals. The nickel-uranium catalyst claimed in the patent [59] was exposed to from four to six redox cycles. The active component of the ready catalyst consists of metal nickel reduced from nickel oxide, nickel uranate and U₄O₉. Then the catalysts are impregnated with aqueous solutions of salts or hydroxides of alkali and alkaline earth metals, for example Ba.

During the synthesis of the catalyst the following reactions proceed:



Notwithstanding the fact that the addition of alkali earth metal results in decreasing the amount of nickel uranate, which causes reducing the catalytic activity in the reaction of steam reforming, this procedure is necessary in order to increase the ability for preventing

carbonaceous formations to appear. The catalyst synthesized can contain 2–60 % of nickel (as calculated for metal), 5–15 % of uranium and up to 43 % of an alkaline or alkali earth metal, preferably 1.7–12 %. The volume flow rate of the process was varied within the range of 3000–7000 h⁻¹. The yield of hydrogen resulted from various types of hydrocarbons amounted up to 56–63 % at the temperature of 500–700 °C. The composition of a carrier could be added with magnesium oxide [60].

In the process of methane steam reforming an efficient catalyst was used, whose active component represented nickel oxide or nickel as well as one or more uranium oxides [61, 62]. The uranium to nickel ratio within the mentioned catalysts ranged from 0.62 : 1 to 0.74 : 1, whereas the total content of active components in the catalyst does not exceed 10–20 % with respect to the total mass of the catalyst. The content of alkali metal in the catalyst amounts to 0.05–0.15 %. Aluminium oxide such as α-Al₂O₃ can serve as a carrier for the mentioned catalyst. One could use also γ-Al₂O₃, molecular sieves, zirconium silicates, silicon carbide, SiO₂, clay and aluminosilicates. The catalyst was prepared via the method of impregnation. The products of the reaction were presented by hydrogen (62 %), methane (13.83 %), CO (7.96 %), CO₂ (16.67 %), C₂H₆ (0.0059 %), C₂H₄ (0.002 %), C₃H₈ (0.002 %).

For the steam reforming of hydrocarbons with the formation of hydrogen, methane, CO and CO₂ one can use a catalyst containing ruthenium applied on a zirconium carrier, as well as an element belonging to the group of transition metals and REE including uranium [63].

An impregnated catalyst containing nickel and uranium applied onto calcium phosphate at a ratio Ca : P = 1.4 : 1–2.3 : 1 has been tested in CO reaction with water vapour. This catalyst prepared via impregnating the gel of calcium phosphate of by uranium compounds demonstrated a good activity in the reforming of hydrocarbons (for example, cyclohexane) by water vapour [64, 65].

Uranium as a promoting additive is successfully applied in the production of reducing gases. The process of producing the gas containing 94 % of hydrogen and CO *via* partial oxidation of C₁–C₇ hydrocarbons by means of an oxy-

gen-containing gas is carried out by way on the catalyst containing uranium and 3–15 mass % of nickel on Al_2O_3 or SiO_2 , as well as their mixtures and MgO [66].

A composition has been claimed for a catalyst of steam reforming of hydrocarbons contained in petroleum [67]. It represents a nickel-cobalt catalyst mainly containing one or more metals of the platinum group, a promotor presented by the compound of beryllium, magnesium or an element belonging to III–VII groups of the Periodic Table with the atomic number not higher than 90, as well as uranium oxides.

Obtaining hydrocarbons from synthesis gas (Fisher–Tropsch process)

Catalytic oligomerization processes with the formation of both linear and cyclic polymers were studied concerning the powder of metal uranium [68]. In this work, a special attention was given to the role of the *f* orbitals of metals in the formation of carbon–carbon bond under polymerization and in the reaction of obtaining hydrocarbons from synthesis gas [69]. Further, within the framework of the same concept experimental data were analyzed concerning the obtaining of hydrocarbons under the decomposition of methylene iodide, diazomethane and ketenes on an uranium catalyst. The authors consider the formation of the products of these reactions such as C_1 and C_4 alkanes and alkenes to occur due to the participation of methyl radicals. The Fisher–Tropsch reaction of synthesis gas at an atmospheric pressure and at the temperature of 250 °C resulted in obtaining a mixture of hydrocarbons, alcohols and ethers: methane (60–70 %), CH_3OH (20–25 %), $\text{C}_2\text{H}_5\text{OH}$ and $\text{CH}_3\text{OCH}_2\text{OCH}_3$. In this case it is assumed that the mechanism of the process occurs through the formation of uranium alkoxides, however, with no formation the phase of uranium oxide. In order to explain the reaction mechanism suggested the authors studied the pyrolysis of uranium alkoxides $\text{U}(\text{OCH}_3)_5$, $\text{U}(\text{OC}_2\text{H}_5)_5$ и $\text{U}(\text{OCH}_3)_6$ and have demonstrated the similarity of product composition for these reactions.

In the patent [70] the authors have proposed the catalysts consisting of carriers based on the oxides of such chemical elements as Si, Al,

Ti, Zr, Sn, Zn, Mg or Ln; the active component consisting of cobalt, an element belonging to the group of precious metals, uranium, as well as molybdenum and tungsten.

A cobalt catalyst, promoted by Zr, Hf, Ce, U, is efficient in the process of methanol or synthesis gas conversion into hydrocarbons. Methanol with the addition of hydrogen or synthesis gas reacts on the catalyst with the formation of linear paraffins and olefins with the subsequent obtaining a high-quality fuel [71, 72].

For the process of synthesis gas conversion into liquid hydrocarbons, one could employ copper, iron, thorium, zinc, uranium or zirconium as an active component of the catalyst. Either Fe-containing zeolite or an inorganic carrier containing iron ions or iron oxide of can be used as a carrier. Metals belonging to VIII group are added in order to prevent the system from the formation of coke. The hydrocarbons obtained contain 70 % of C_3 series hydrocarbons with less than 10 mass % of methane [73].

The process of synthesis gas conversion into hydrocarbons and aromatics (benzene) was carried out on a catalyst containing gallium or indium oxide and metal, chosen from the groups VIIB or VIII of the Periodic Table. The most preferable metals were Ce, U, Th. The catalyst can also contain additional components, for example zeolite which in some cases could be used as a carrier. The mentioned process results in a low yield of C_1 and C_2 , the synthesis gas used has a low H_2/CO ratio [74].

Partial oxidation processes on uranium oxide catalysts

Oxidative ammonolysis. The authors of [75, 76] were engaged in the development of U–Sb-catalyst and have demonstrated its high efficiency in the reaction of oxidative ammonolysis of propylene with the obtaining of acrylonitrile. XRD data have confirmed the formation of $\text{USb}_3\text{O}_{10}$ and USbO_5 phases. The authors have assumed that the oxidation and ammonolysis of propylene occurs through the formation of allylic intermediate species. The active centre of the catalyst is five-valent antimony that is stabilized and regenerated through the interaction with uranium. Catalytic oxidation of propylene on $\text{USb}_3\text{O}_{10}$ has been investigated in

[77]. From the results of the experiments in a flow-through microreactor it is seen that the catalyst can be used for the oxidation of propylene to produce acrolein [78–80].

In the studies of impregnated uranium oxide catalysts applied onto TiO_2 , a strong synergistic effect has been revealed between UO_x phase and the phase of carrier in the reaction of isobutene partial oxidation [81]. The reaction was carried out in a microreactor with fixed catalytic layer. The load of the catalyst amounted to 100–200 mg, grain size being within the range of 50–150 nm. The flow represented a mixture of C_4H_8 , O_2 and He. The total flow rate amounted to 38 mL/min; the flow rate of helium was equal to 30 mL/min. The results of the studies are presented in Fig. 4. The content of uranium oxides in the catalyst was varied within the range of 3–29 mass % (0.5–9 mol. %). The reaction products were presented by formaldehyde and metacrolein with trace amounts of acetone and light alkanes. Introducing even a small amount of uranium into the catalyst resulted in an increase in the selectivity with respect to target products of the reaction (Fig. 5).

The authors of [82–88] investigated the reactions of isobutene oxidation on MoO_3 – UO_3 – SiO_2 catalysts, the effects of temperature, of water content and of butene/oxygen ratio on the activity of these catalysts. UO_2MoO_4 и MoO_3 have been determined in the system with the use of XRD method. The synergistic effect appears as the result of contact between these two phases and it is manifested in the activity

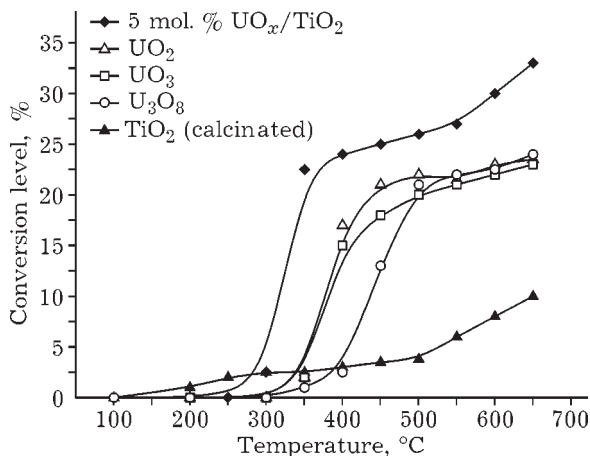


Fig. 4. Effect of temperature on isobutene conversion level on bulk TiO_2 , UO_x and applied UO_x/TiO_2 catalysts.

of the catalyst in the reaction of isobutylene conversion. The activation of olefins (electron donors) and oxygen (an electron acceptor depends on acid-base properties of the catalysts). The activation of the mentioned olefin occurs on more electronegative (acid) centres of the catalyst such as Mo^{6+} и U^{6+} . It has been revealed that the more strong is the acidity, the more strong is the olefin–metal bond and higher is the probability of the formation of complete oxidation products.

The processes of propane partial oxidation up to acrolein and acrylic acid on the catalysts containing uranium are claimed in the patents [89–92].

The process of the gas phase catalytic oxidation of isobutane in the presence of a catalyst containing divanadyl pyrophosphate and uranium compounds is described in [93].

Gas phase catalytic oxidation of an unsaturated aldehyde by molecular oxygen at 200–500 °C with obtaining corresponding carboxylic acid was performed in the presence of a catalyst containing uranium, Mo, P and other chemical elements. This catalyst is especially efficient for obtaining methacrylic acid from metacrolein, having a long lifetime [94, 95].

The ammoxidation of propane was carried out on a catalyst containing the oxides of Fe,

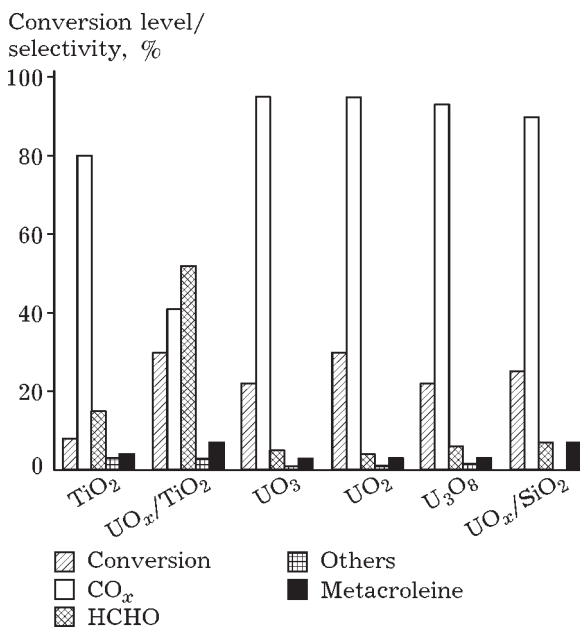


Fig. 5. Synergistic effect on UO_x/TiO_2 catalyst in the reaction of isobutene partial oxidation at 600 °C. The activity of UO_x/SiO_2 catalyst is presented for comparison.

Co, Bi and Mo and uranium [96].

Mixed metal oxide catalysts based on antimonates containing uranium have been patented for the process of propylene ammoxidation into acrylonitrile [97, 98]. The patent [97] presents a method for preparing a mixed metal oxide catalyst on the basis of uranium antimonite with the general formula $U_aFe_aSb_bMo_cBi_eO_f$ where the values a and a' are varied within the range of 0.1–1.0. The mentioned catalyst is successfully used by the Solutia Co. (the USA) for the manufacture of acrylonitrile from propylene and ammonia.

The process of terpene oxidation by oxygen is performed on the catalyst containing bismuth molybdates or antimony oxide promoted by iron oxide or uranium oxide [99].

For the process of the preparation of unsaturated nitriles *via* ammoxidation and oxidation of olefins to yield corresponding unsaturated aldehydes have been offered a catalyst has been proposed containing mixed Fe, Sb, U, Bi, Mo oxides. The catalyst is especially successfully used for obtaining acrylonitrile from propylene, ammonium and an oxygen-containing gas [100–103].

The process of methanol or formaldehyde ammoxidation to produce HCN was carried out on a catalyst containing metal belonging to the group of Fe, Co, Ni, Zn, B, U, as well as phosphorus oxides with an atomic ratio metal to phosphorus ranging from 0.8 : 1 to 2.0 : 1 [104].

The oxidation or ammoxidation of olefins has been proposed to carry out in the presence of a catalyst consisting of a mixture of uranium and tellurium oxides with an atomic ratio U : Te = 2–5 [105].

A uranium-containing catalyst for the production of polyamines has been proposed. The catalyst contains up to 80 % of nickel, chromium, copper, palladium, ruthenium, iron being promoted by uranium and other metals (up to 30 %) [106].

Partial oxidation of alcohols. An influence of acid-base properties upon the activity of catalysts in the process partial methanol oxidation into formaldehyde has been investigated [107]. The gas phase process was carried out in the presence of excess air. Methanol was oxidized on U_3O_8 . The conditions of the reaction are as it follows: the temperature being of 300 °C, the catalyst load amounting to 10 g, the concentration of CH_3OH in air being equal to

TABLE 5

Methanol oxidation for the catalysts based on U_3O_8

Catalysts (atomic ratio)	Specific surface, m^2/g	HCHO yield, mol. %
U	5.5	41.2
U–Mo (9 : 1)	4.1	20.1
U–P (9 : 1)	4.6	35.4
U–K (9 : 1)	5.2	82

2.5 mol. %, the total flow rate being equal to 1 L/min. It has been demonstrated that there is a connection between the selectivity with respect to formaldehyde and the acidity of the catalyst. The authors have concluded that the activation of methanol by acid centres represents a necessary condition for the formation of formaldehyde, whereas the variation of a ratio between metal oxides allows one to achieve optimum acid properties.

Bulk uranium oxide U_3O_8 is efficient in the process of obtaining formaldehyde; the formation of by-products being insignificant, but the activity is lower in comparison with V_2O_5 . The results of the investigations are presented in Table 5.

In previous paper, the authors of [108] reported an environmentally safe process of benzyl alcohol oxidation on a number of catalysts such as Au/MgO, Au/ Al_2O_3 , Au/ ZrO_2 and Au/ U_3O_8 prepared employing a method of homogeneous precipitation. Au/ U_3O_8 catalyst has appeared the most active in the mentioned process. In the work [109] this process was considered in more detail. The greatest activity in this reaction is demonstrated by Au/ U_3O_8 catalyst prepared using the method of homogeneous precipitation, and calcinated at 400 °C. This catalyst has demonstrated the ability to be reusable. The selectivity with respect to benzaldehyde increases as the temperature increased from 130 to 160 °C.

For the process of methanol conversion into liquid hydrocarbons the authors of [110] proposed using a uranium-containing catalyst including a porous carrier made of SiO_2 or Al_2O_3 or their mixture, cobalt and a promotor chosen from the group of Zr, Ti, Cr, Ru, Fe, Mg, Zn, Th. It has been demonstrated that the presence of uranium increases to a considerable extent the conversion level of methanol into

formaldehyde. The catalyst can be both non-applied, and applied onto aluminium oxides, aluminosilicates, SiO_2 , molecular sieves, silicon carbide, zirconium silicates. The active components containing compounds of uranium, were matched in such proportions that to provide the formation of the following stoichiometric complexes: uranyl molybdate $\text{UO}_2(\text{MoO}_4)$, uranyl paramolybdate $(\text{UO}_2)_3(\text{MoO}_3)_7$, uranium octamolibdate $\text{UO}_3(\text{MoO}_3)_8$ or molybdenum uranate [111].

Partial oxidation of toluene on Bi-U catalysts. Bi-U catalyst has been successfully employed in the process of toluene conversion into benzene at 400–500 °C. It has been demonstrated that for achieving a high selectivity with respect to benzene the reaction is required for carrying out in the absence of gaseous oxygen, using bismuth uranate as an oxidizer. The reduced uranate obtained can be readily reoxidized by air within the process. The selectivity and productivity depending on the ratio of Bi/U is presented in Fig. 6. It is seen that the maximal selectivity and productivity can be achieved at the ratio $\text{Bi}/\text{U} = 2$. It is obvious that an active component is presented by the phase of bismuth uranate Bi_2UO_6 . An assumption has been put forward concerning two possible mechanisms of the reaction: 1) toluene oxidation up to benzaldehyde with the subsequent dissociation to produce benzene and CO; 2) oxidation to give benzoic acid with the subsequent dissociation to yield benzene and CO_2 . Dependences of the reaction rate have been studied depending on the reagent flow rate and the concentration of toluene [112–116].

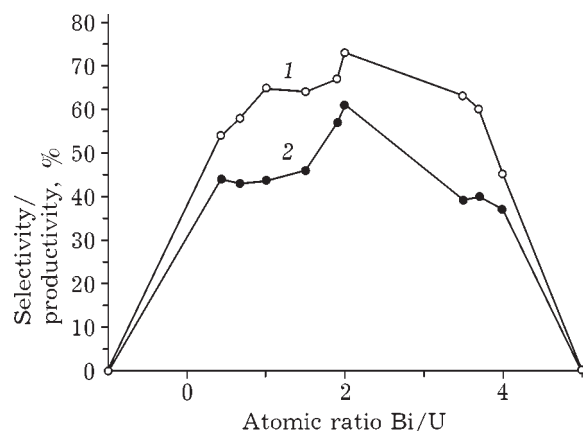


Fig. 6. Selectivity (1) and productivity (2) depending on the catalyst composition.

Obtaining of aldehydes. Series of mixed metal oxide catalysts have been prepared and tested in the process of propane and propylene oxidation. Mixed catalyst U/Sb with the composition $\text{USb}_3\text{O}_{10}$ has demonstrated the selectivity in the formation of acrolein from propylene. Remarkable results for the selective oxidation of propane and propylene into formaldehyde have been obtained on Fe/U catalyst prepared in the proportion of 0.5 : 3 and 1 : 3 [117]. Data concerning the specific surface area and the phase structure of catalysts are presented in Table 6. The testing procedures were carried out in a microreactor at the volume flow rate amounting to 9600 h^{-1} . At 450 °C the selectivity with respect to formaldehyde has reached 44 % at the conversion level of propane equal to 42 %. For the mentioned catalyst the selectivity with respect to formaldehyde remained high even at 500 °C and at the conversion level of propane equal to 40 %.

Olefins $\text{C}_3\text{--C}_4$ were oxidized on the uranium-containing catalyst in the presence of molecular oxygen at 200–450 °C for obtaining corresponding aldehydes and acids [118]. The process of obtaining unsaturated esters of carboxylic acids was carried out in the presence of a catalyst containing uranium. Unsaturated esters of carboxylic acids including vinylacetate, are obtained via the reaction of olefins and aliphatic or aromatic compounds with molecular oxygen or air in the gas phase at elevated temperatures. The catalyst contains palladium acetate, alkali metal acetate and one or more compounds of uranium applied onto a carrier. In the preparation of the catalyst the carriers (silicic acid, kieselguhr, silica gel, diatomite alumina, aluminosilicate, aluminophosphate, pumice, silicon carbide, asbestos or activated coal) were impregnated with aqueous solutions of palladium acetate, uranyl acetate and alkali metal acetate [119, 120].

TABLE 6
BET and XRD data for Fe-U catalyst

Atomic ratio	$S_{\text{sp}}, \text{ m}^2/\text{g}$	Identified phase
0.5/3	18	UO_3
1/3	116	UO_3

TABLE 7

Results of testing Mo-U catalysts in the reaction of methanol oxidation ($GHSV = 50\,000\text{ h}^{-1}$)

Mo/U ratio	T, °C	Conversion level, %		Selectivity, %		
		O ₂	CH ₄	CH ₃ OH	CO	CO ₂
1.9 : 1	537	42	1	39	55	7
1 : 2.2	543	76	2.2	43	52	6

Uranium oxides are used in the gas phase processes of direct methylbenzene oxidation to produce corresponding aldehyde derivatives, for example, in the conversion of toluene into benzaldehyde. The catalyst contains uranium oxides and molybdenum combined with Pb, Sn, Zr, Cd, Sb, Ni oxides [121]. The process of toluene oxidation in to benzaldehyde was carried out in the presence of a catalyst containing copper, iron, uranium, lead, tellurium, molybdenum, phosphorus oxides and some promoting elements. The catalyst has been prepared using a method of three-stage hydromixing. At the temperature of 500 °C the conversion level of toluene amounted to 37.79 %, the selectivity with respect to benzaldehyde was equal to 63.7 % [122, 123].

The obtaining of maleic anhydride is performed with the use of a catalyst containing uranium and vanadium [124].

Partial oxidation of methane into methanol.

Uranium-containing catalysts for partial methane oxidation to produce methanol have been tested in a high-pressure circular reactor [125]. The maximal selectivity with respect to methanol for $\text{MoO}_3 \cdot \text{UO}_2 / \text{SiO}_2(\text{Al}_2\text{O}_3)$ catalyst amounted up to 43 %. The results concerning the selectivity and conversion level are presented in Table 7.

Hydrocracking processes

The authors of [126] proposed two types of catalysts on the basis of uranium oxides for cracking heavy hydrocarbons and obtaining gasoline with simultaneous hydrorefining. The catalysts were prepared via impregnation of an alumina carrier with the solution of uranyl nitrate. Uranium oxide catalysts contained 10 mass % of UO_3 , and this amount is considered to be an optimum value for a monolayer covering of aluminium oxide. It has been dem-

onstrated that uranium oxide applied onto aluminium oxide with adding to a cobalt-molybdenum catalyst promotes a considerable increase in the conversion level of heavy oil into light products *via* hydrocracking.

The process was carried out at a pressure of 200 atm within the temperature range of 430–540 °C. The addition of uranium to aluminium oxide resulted in an increase in sulphur removal level. It has been demonstrated that the process of hydrocracking on a cobalt-molybdenum-uranium catalyst proceeds at lower temperature values as compared to the cobalt-molybdenum catalyst (Fig. 7).

A catalyst for cracking and manufacturing gasoline with high content of aromatic hydrocarbons are described in the patent [127]. As much as 1 to 20 % of UO_3 was applied onto zeolite which has been applied onto a matrix consisting of $\text{SiO}_2\text{-Al}_2\text{O}_3$ combination. The process proceeds at the temperatures of 430–530 °C.

The process of cracking higher hydrocarbons on uranium-containing catalysts is described in patents [128, 129]. The hydrocarbons

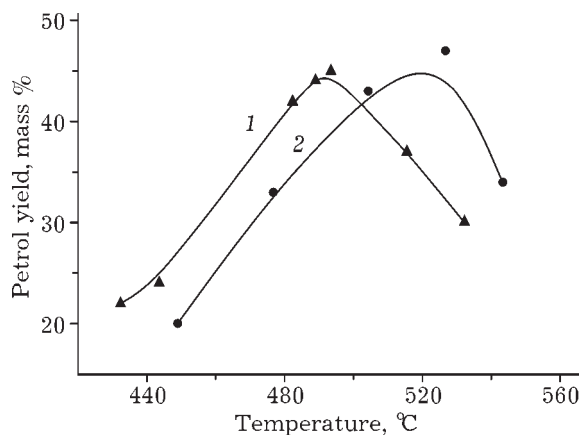


Fig. 7. Yield of petrol fractions in the process of hydrocracking for uranium-cobalt-molybdenum and cobalt-molybdenum catalysts.

are converted into a mixture of CO and methane or hydrogen. Air, CO or steam can serve as an oxygen-containing component. Oxide catalysts for the mentioned processes can contain lanthanum, cobalt, nickel, uranium, cerium and thorium applied onto the carrier presented by aluminium and magnesium oxides. Particle size of the catalyst is equal to less than 100 μm . The content of the metals amount up to 90 % for particle, 29 % for cobalt, 10 % for nickel, 8 % for uranium, 9 % for cerium and thorium.

Hydrotreating processes on uranium oxide catalysts

The authors of [130, 131] have presented the results of studies on H_2S adsorption and desorption on polycrystalline oxide UO_2 at 100 and 300 K. The work was carried out aiming at the further employing of depleted uranium for the industrial purposes, in particular for oil hydrotreating. The samples prepared by means of sputtering UO_2 onto a molybdenum substrate in the form of thin film 10^3 \AA thick were tested in an ultra-high vacuum chamber with the corresponding equipment for analysis.

The results of the studies have demonstrated H_2S to dissociate initially on the surface at a low covering level *via* the reaction on defect centres and oxygen vacancies. Molecular H_2S at 100 K can be adsorbed with the covering level of one monolayer onto a polycrystalline surface. After annealing, H_2S is desorbed at 140 K. At 250 K, a recombination reaction occurs resulting in the further desorption. It has been also established that atomic sulphur is desorbed from the surface at 580 K. Sulphur compounds are adsorbed onto UO_2 in the form of H_2S , SH and atomic S. In this case H_2S is mainly bound with U surface centres, whereas sulphur atoms are bound with oxygen centres.

Catalysts based on aluminium oxide and an active component consisting of uranium oxide and a metal from the VIII group are successfully used in the processes of hydrotreating hydrocarbons [132, 133]. According to these patents, the mass fraction of uranium in the catalyst can amount up to 5–35 %. The catalyst could be modified by the metals of the VIII group, mainly iron, cobalt, nickel and ruthenium, with the mass fractions of the metals ranging within

0.1–10 % [132]. The catalyst is prepared *via* the impregnation of the carrier with an alcoholic solution of uranyl acetylacetonate [133].

A catalytic process for desulphurization of gases containing H_2S and SO_2 is presented in the patent [141]. The catalyst consists of a carrier (silicon carbide) and an active component (Ti, Zr, Y, La, U, Pb, Mo, Fe, Co, Cu, Ni, Zn, Cd salts or the same elemental metals).

Catalytic CO oxidation and selective NO reduction

The catalytic reduction of NO has been studied for applied uranium oxide catalysts those have demonstrated a considerable activity and selectivity as compared to traditional platinum catalysts, wherein an active phase UO_x ($2 < x < 2.5$) has been identified *in situ* according to XRD data. The reduction was carried out in a flow-through microreactor. The gas flow consisted of NO, CO and He. The flow rate amounted to 2300 h^{-1} . The authors of [142] have reported the data of testing those indicate a considerable promoting effect of uranium oxide applied onto $\gamma\text{-Al}_2\text{O}_3$ carrier with a high specific surface area on the conversion level of NO. It has been also demonstrated that bulk U_3O_8 catalyst is less active as compared to applied one (Fig. 8).

The authors of [142] have also compared the activity of catalysts depending on calcinations

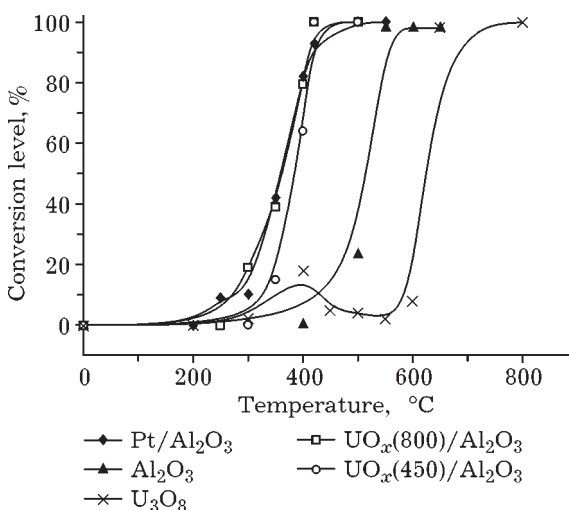
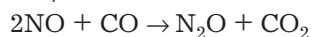


Fig. 8. NO conversion level depending on temperature for uranium oxide and platinum catalysts.

temperature. An $\text{UO}_x/\gamma\text{-Al}_2\text{O}_3$ catalyst, calcinated at 800 °C has appeared more active in comparison with the same catalyst calcinated at 450 °C: using the former results in the 100 % conversion level for NO at 400 °C. Using all the uranium catalysts at an initially low temperature results in the formation of the main conversion product such as N_2O . With the increase in the temperature the selectivity level of catalysts, both bulk and applied ones rapidly increases, whereas the 100 % selectivity level with respect to N_2 can be observed at 400 °C [143].

Uranium oxide catalysts applied onto $\gamma\text{-Al}_2\text{O}_3$ as well as onto amorphous and mesoporous SiO_2 have been tested in the reactions of CO/O_2 and NO/CO conversion:



As a precursor, the authors used uranyl nitrate. A significant improvement in the functioning of uranium oxide catalysts in the processes of CO oxidation and NO reduction could be achieved via embedding the active phase in mesoporous SiO_2 . The system obtained from uranyl nitrate applied onto SiO_2 keeps the activity up to 600 °C, whereas a similar catalyst on Al_2O_3 exhibits the loss of activity. The activity of uranium oxide catalysts in the process under consideration is comparable to the activity of traditional $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst. Usually chlorides make catalysts to be poisoned; however the use of UCl_4 as a precursor on Al_2O_3 in the oxidation of CO has resulted in an increase in the activity comparable to the best catalyst of the uranyl nitrate system.

The reaction of selective NO/CO reduction on the mesoporous catalyst demonstrates a zero kinetic order with respect to NO, and the reaction rate is proportional to $[\text{CO}]^{1.4}$. The reaction rate on bulk U_3O_8 depends on the concentration of NO.

The ability of applied uranium oxide catalysts for increasing the activity in the process of CO oxidation and selective NO reduction depends on the type of a carrier, precursor and preparation technique.

For the complete oxidation of CO and hydrocarbons a mixed uranium oxide catalyst is proposed which is prepared via combining the oxides having oxygen ionic conductivity of fluorite type (Ce, Zr, Th, U, Hf) with active transition metals (Mo, Cu, Co, Mg, Ni, Ag) [144].

For the conversion of CO, hydrocarbons and nitrogen oxides formed in internal combustion engines, a multifunctional catalyst has been proposed which contains a porous layer made of a refractory oxide (20–99 %), cerium oxide (0.8–70 %), uranium oxide (0.150 %) and 0.1–20 % of a metal from the group of Pt, Rh, Pd, Ru, Ir and Au. It has been demonstrated that the addition of uranium and cerium oxides improves the activity and stability of the catalyst [145, 146].

Another multipurpose catalyst consisting of a refractory inorganic carrier (50–99.7 %), uranium oxide (0.125 %), 0.1–35 % of a metal chosen from the group of Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, La, Pm, Nd, Gd, Y, as well as 0.1–20 % of a metal from the group such as Rh, Pd, Ru, Ir, has been proposed for the mentioned process [147, 148].

The process of nitrogen oxide reduction in a gas flow in the presence of ammonia was carried out on the uranium-containing catalyst prepared through the addition of vanadium oxide and the oxide of an element chosen from the group such as W, P, S, Cr, Zr, Mg, Cu, Co, Fe, to titanium dioxide with the formation of a mixture. The activation of the catalyst mixture [149, 150] has been established to be mechanochemical.

A catalyst containing U, Rh, Pt or Pd, spread over the porous surface of aluminium oxide is also employed successfully in the process of long and simultaneous conversion of CO, hydrocarbons and nitrogen oxides contained in hot gases, in particular in exhaust gases produced by internal-combustion engines. The ready catalyst contains 0.005–0.15 mass % of Rh, 0.1–0.6 mass % of Pt and 0.05–3 mass % of U applied onto aluminium oxide with a high specific surface area. In turn, the aluminium oxide is applied in the form of a film onto a cellular ceramic carrier with a rather low specific surface [152–154].

In order to purify exhaust gases the authors of [155–158] suggest to use catalysts containing nickel and uranium oxides. The active component can be applied onto aluminium oxide, bauxite or corundum, SiO_2 , kaolin, powdered brick or the oxide of an alkaline earth metal or of a mixture of metals. The mass fraction of nickel oxide in the catalyst amounts to 1–20 %, that for uranium oxide being equal to 2–15 %.

Deep oxidation of hydrocarbons including chlorine-containing ones

Industrial emissions of hydrocarbons and chlorine-containing organic molecules to the environment were always the focus of attention for researchers. As it is known, chlorine-containing pollutants are stable and can be destructed at the temperature higher than 1000 °C. This process results in the formation of highly toxic by-products such as dioxins and dibenzofurans. Catalytic combustion at low temperatures promotes a more efficient oxidation of pollutants with no formation of by-products.

It is known that industrial catalysts based on precious metals are rapidly deactivated in such processes [159]. The authors of [160, 161] have demonstrated that uranium oxide catalysts are not deactivated under oxidation of hydrocarbons, including chlorine-containing ones. Benzene, toluene, chlorobutane and chlorobenzene can be oxidized at the temperature below 450 °C at sufficiently high values of volume flow rate even in much diluted mixtures (<1 %). Data concerning the oxidation of chlorobenzene (chlorobenzene conversion level) for various types of uranium oxide catalysts are presented in Table 8. The reaction conditions were as it follows: the concentration of chlorobenzene in air amounted to 1 %, the catalyst load being of 200 mg, the volume flow rate being equal to 70 000 h⁻¹. As much as 100 % selectivity with respect to CO_x was achieved for all the catalysts under investigation. It is significant that the products of chlorobenzene oxidation on uranium oxide catalysts are presented only by carbon oxides and HCl. In addition,

from the data presented in Table 8 it is seen that applying the U₃O₈ active phase onto SiO₂ has resulted in a little decrease in the activity. The authors assume that this fact could be connected with a decrease in the concentration of an active component. A comparative analysis has been performed concerning the activity of bulk U₃O₈ catalyst and the activity of Co₃O₄ notorious due to its efficiency with respect to deep oxidation of organic substances [162]. An almost 100 % conversion level of chlorobenzene on U₃O₈ has been observed at 350 °C, whereas at 600 °C on Co₃O₄ this value amounted to only 62 % under the same conditions. A number of mixed catalysts applied onto SiO₂ has been prepared in order to increase the selectivity of uranium oxide catalysts with respect to CO₂.

It has been demonstrated that uranium oxide catalysts are not deactivated after 400 h of their using as compared to catalysts based on precious metals, for example Pt/SiO₂ those, as it is known, are quickly deactivated by chlorine-containing compounds [163].

The results of oxidation of other volatile organic compounds on uranium oxide catalysts are presented in Table 9.

The authors of [161] have demonstrated that U₃O₈ represents an active catalyst for methanol oxidation. At the same time, U₃O₈ exhibits a low selectivity with respect to CO₂. The studies on a series of modified uranium oxide catalysts have demonstrated that the greatest selectivity concerning CO₂ is exhibited by such catalyst as Cu/U/SiO₂.

At the Oak Ridge National Laboratory (the USA), the preparation of uranium oxide catalysts employing the method of template synthesis has allowed researchers to obtain high-disperse systems on a mesoporous oxide carrier [164]. The catalysts were tested in the reactions of toluene, chlorobenzene and trichloroethylene oxidation. In this case applied catalysts are more active as compared to bulk one. The authors have demonstrated that the phase of U₃O₈ is much more active than the phase of UO₂. A catalyst with the ratio U : Si = 1 : 30 has appeared the most active.

Some metals (Cr, Co, K, Fe, V, Ca, Mg) those were used as promoters for uranium oxide catalysts have been considered. The results of testing the catalysts are presented in Ta-

TABLE 8
Chlorobenzene oxidation on powder catalysts

Catalysts	Temperature, °C	Conversion level, %
U ₃ O ₈	350	99.7
U-SiO ₂	400	99.9
Co-U-SiO ₂	400	99.9
Cu-U-SiO ₂	400	99.9
Fe-U-SiO ₂	400	99.9
Ni-U-SiO ₂	400	89
Mn-U-SiO ₂	450	99.9
Co ₃ O ₄	600	62

TABLE 9

Catalytic activity of uranium-containing catalysts in the reactions of volatile organic compounds (VOC) oxidation

Catalysts	VOC	Temperature, °C	Conversion level, %	Selectivity for CO _x , %
U ₃ O ₈ , granules	Benzene	400	99.9	100
U-SiO ₂ , granules	«	400	99.9	100
Cu-U-SiO ₂ , granules	«	400	99.9	100
U-SiO ₂ , powder	Toluene	400	99.9	100
U ₃ O ₈ , granules	Butane	600	81	100
U-SiO ₂ , granules	«	500	99.9	100
Cu-U-SiO ₂ , granules	«	450	95	100
U ₃ O ₈ , powder	Cyclohexanone	300	99.9	100
U-SiO ₂ , powder	«	300	99.9	100
U ₃ O ₈ , powder	Butylacetate	350	99.9	100
Cu-U-SiO ₂ , powder	«	350	99.9	100
Cu-U-SiO ₂ , powder	«	350	99.9	100

ble 10. It is seen that the addition of chromium to uranium oxide catalyst results in an increase in the activity only for the case of preparing by the method of joint synthesis. The consecutive impregnation does not exert any influence upon the activity. The addition of cobalt into

the U-SiO₂ system results in a small synergetic effect. The addition of uranium to titanium oxide also results in a synergetic effect in the activity of the catalyst with respect to the reaction of toluene oxidation and prevents TiO₂ from changing the phase at high temperature

TABLE 10

Results for testing the mixed catalysts such as uranium-transition metal in oxidation reactions of chlorine-containing volatile organic compounds

Catalysts	Composition	S _{sp} , m ² /g	T ₅₀ , °C		
			Toluene	Chlorobenzene	Trichloroethylene
U ₃ O ₈	Bulk	0.1	520	—	—
U-SiO ₂	U : Si = 1 : 10	—	460	—	—
U-SiO ₂	U : Si = 1 : 20	233	410	420	—
U-SiO ₂	U : Si = 1 : 30	267	—	410	—
U-SiO	U : Si = 1 : 40	337	—	470	—
U-SiO	U : Si = 1 : 50	267	—	490	—
(Cr-U)-SiO ₂	U : Cr : Si = 1 : 0.2 : 20	204	375	—	—
Cr/U-SiO ₂	U : Cr : Si = 1 : 0.2 : 20	253	418	—	—
Cr-SiO ₂	Cr : Si = 0.2 : 20	207	470	—	—
(Co-U)-SiO ₂	U : Co : Si = 1 : 0.23 : 20	242	440	—	—
Co/U-SiO ₂	U : Co : Si = 1 : 0.23 : 20	223	420	—	—
Co-SiO ₂	Co : Si = 1 : 85	224	420	—	—
TiO ₂ (350 °C)	Ti	128	365	500	—
TiO ₂ (600 °C)	Ti	18	425	—	—
TiO ₂ (800 °C)	Ti	3	550	—	—
U-TiO ₂ (350 °C)	U : Ti = 1 : 20	250	330	375	465
U-TiO ₂ (600 °C)	U : Ti = 1 : 20	108.6	325	375	465
U-TiO ₂ (800 °C)	U : Ti = 1 : 20	25	345	375	465
(U-Ti)-SiO ₂	U : Ti : Si = 1 : 1 : 20	205	380	—	—

TABLE 11

Data concerning the temperature for 1, 10, 50 % conversion level for alkanes on uranium oxide catalysts (T_1 , T_{50} , T_{100} , respectively), °C

Catalysts	Butane			Propane			Ethane			Methane		
	T_1	T_{10}	T_{50}	T_1	T_{10}	T_{50}	T_1	T_{10}	T_{50}	T_1	T_{10}	T_{50}
U ₃ O ₈	410	525	575	415	510	—	500	555	—	550	—	—
U ₃ O ₈ /SiO ₂	405	455	475	410	455	475	465	505	585	535	—	—
Cr/SiO ₂	350	450	600	365	425	505	375	470	—	520	—	—
Cr/U ₃ O ₈ /SiO ₂	300	305	325	300	400	435	325	455	525	485	560	—

values. The stability and activity of U–TiO₂ catalyst is comparable to 0.1 % Pt/Al₂O₃, the catalyst which is much more expensive. A by-product formed due to the oxidation of volatile organic compounds on U–TiO₂ catalyst represents benzaldehyde, but its yield does not exceed 10 %. It has been demonstrated that potassium is strong catalytic poison for uranium oxide catalysts, whereas iron magnesium and calcium reduce the activity of these catalysts in the reaction of chlorobenzene oxidation.

The authors of [165] performed studies concerning catalytic activity of uranium oxide in the oxidation of linear alkanes such as C₁–C₄. For the investigations, bulk catalyst U₃O₈ was prepared from uranyl nitrate using the method of thermal decomposition with the calcination temperature of 800 °C as well as impregnated catalysts containing 10 mol. % of uranium on SiO₂, 9 mol. % of uranium and 1 % of chromium on SiO₂. The catalytic activity of the catalysts was studied with the use of a flow-through reactor. The conditions of the reaction were as it follows: the concentration of volatile organic compounds in air was equal to 1 %, the volume flow rate being of 70 000 h⁻¹, with the catalyst load of 100–200 mg and the grain size of 0.6–1 mm. The processes under consideration are exothermic, and the temperature in the reactor is always higher than the temperature of

heating. The results of the studies on the activity of the samples are presented in Table 11.

Reaction rates for the oxidation of alkanes have been calculated with respect to 1 g of catalysts (Table 12).

Influence of water adding into the reaction mixture upon the activity of uranium oxide catalysts in the reactions of benzene and propane oxidation to produce carbon oxides was investigated. Adding small amounts of water (the optimum value determined amounted to 2.6 %) exerts a significant effect on the oxidation activity promoting complete oxidation. It has been demonstrated that the activity of U₃O₈ catalyst in the process of propane oxidation increases from a 50 % conversion level at 600 °C to 100 % one at 400 °C. Catalyst U₃O₈ has been compared with Mn₂O₃ catalyst of complete oxidation. It has been established, that such phenomenon is not observed for the manganese catalyst. There is no clear explanation concerning the increase in the activity. To all appearance, this fact could be connected with changing in the surface of the catalyst or appearing a new reaction pathway [166].

In the opinion of the authors of [167], the oxidation activity of uranium oxide catalysts depends on the structure of the oxygen lattice of the catalyst, since the catalysts operate according to the oxidation-reduction mechanism.

TABLE 12

Oxidation rate for alkanes on uranium oxide catalysts, mol/(g · s)

Reagents	Temperature, °C	U ₃ O ₈	U ₃ O ₈ –SiO ₂	Cr–U ₃ O ₈ –SiO ₂
Butane	450	7.68 · 10 ⁻⁸	1.70 · 10 ⁻⁶	2.49 · 10 ⁻⁵
Propane	450	4.61 · 10 ⁻⁷	1.22 · 10 ⁻⁶	1.82 · 10 ⁻⁵
Ethane	500	7.68 · 10 ⁻⁷	6.25 · 10 ⁻⁶	2.04 · 10 ⁻⁵
Methane	600	3.07 · 10 ⁻⁷	7.54 · 10 ⁻⁷	5.71 · 10 ⁻⁶

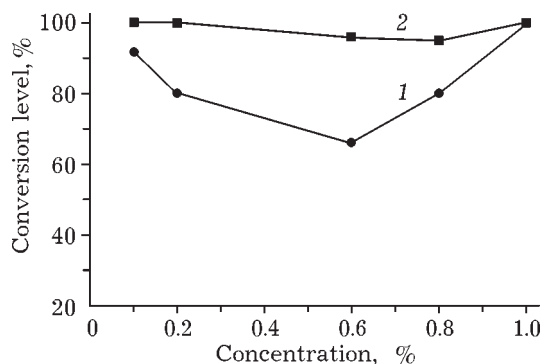


Fig. 9. Influence of chlorobenzene concentration upon the total efficiency of U_3O_8 catalyst at the volume flow rate of $70\,000\text{ h}^{-1}$ and the temperature values of 350 (1) and 400 °C (2).

The authors of [160] have considered the influence of chlorobenzene concentration upon the activity of U_3O_8 catalyst. Decreasing chlorobenzene concentration at the temperature of 350 °C was accompanied by a decrease in the conversion level. So, at the concentration of chlorobenzene equal to 1.04 %, the conversion level amounted to 99.7 %, whereas at 0.12 % (1200 ppm) this value was equal to 92.5 %. Increasing the reaction temperature up to 400 °C the conversion level exceeded 96 % and remained high for almost all the values of concentration (Fig. 9). With changing in chlorobenzene concentration the CO/CO_2 selectivity did not change, which indicates the formation of CO_2 immediately on the catalyst, rather than owing to the further CO oxidation.

From Fig. 10 it is seen that with the use of benzene and chlorobenzene mixture at a ratio $1 : 1.29$ the conversion level sharply increases starting from the temperature of 300 °C and up to 350 °C. Under the further rise in temperature the growth of the conversion level becomes slower, and at 550 °C this value attains 97 and 96 % for benzene and chlorobenzene, respectively. Obviously, it could be caused by the effect of mass transfer, and the problem can be solved at the expense of designing a special reactor. The starting temperature of benzene oxidation on the catalyst under consideration amounts to 400 °C, but in a mixture with chlorobenzene due to adiabatic heating this value became 50 °C lower. The conversion level of chlorobenzene amounted to 99.9 % at the time of testing which lasted for 400 h. Though

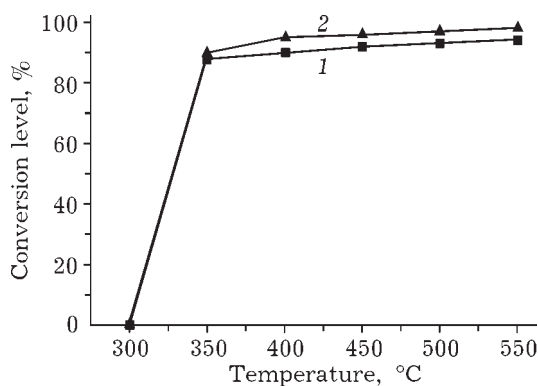


Fig. 10. Oxidation of 1.16 % mixture of benzene and chlorobenzene ($1 : 1.29$) on U_3O_8 catalyst at the volume flow rate of $70\,000\text{ h}^{-1}$: 1 - benzene conversion level, 2 - chlorobenzene conversion level.

this time is low as compared to the operating time of industrial catalysts, the testing has demonstrated that the uranium oxide catalyst is stable with respect to deactivation during sufficiently long time in the presence of chlorine-containing products (Fig. 11).

Four kinds of uranium oxide catalysts used in the reactions of benzene and chlorobenzene oxidation are presented: 1) bulk (U_3O_8 , UO_3 , Co_3O_4); 2) applied onto SiO_2 (10 mol. % U/SiO_2); 3) applied, promoted Cu , Cr , Co , Mn ; 4) mixed oxide catalysts (Co_3O_4/U_3O_8 , CuO/U_3O_8). These catalysts are also active in the reactions of butane, cyclohexanone and butylacetate oxidation [168].

The process of obtaining chloro derivatives of ethylene with catalytic combustion of chlorine-containing by-products on the catalyst con-

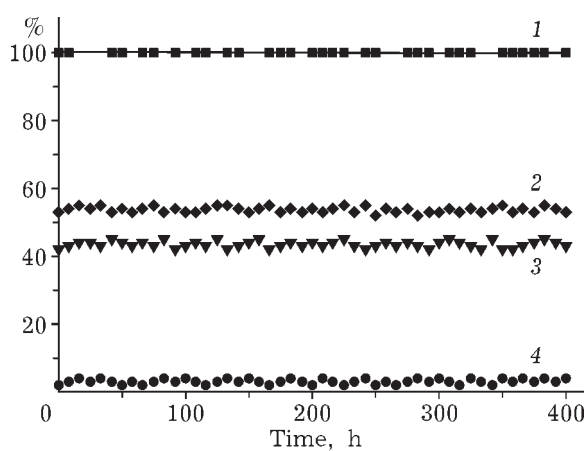


Fig. 11. Long-term testing of the oxidation of 0.12 % chlorobenzene on U_3O_8 catalyst at 450 °C and at the volume flow rate of $70\,000\text{ h}^{-1}$: 1 - conversion level of chlorobenzene, 2, 3 - selectivity level for CO (2) and CO_2 (3), 4 - conversion level of oxygen.

taining 5–20 % of UO_3 applied onto 80–95 % Al_2O_3 , SiO_2 or the combination of $\text{Al}_2\text{O}_3 + \text{SiO}_2$ is presented in the patent [169]. Heat generated due to catalytic combustion is consumed for preliminary heating of reagents. The specific surface of the catalyst amounts to 175–600 m^2/g . The combustion occurs within the temperature range of 350–450 °C. The reaction products are presented by HCl and chlorinated hydrocarbons, the further ethylene interaction with those results in the formation of dichloroethylene. Elemental chlorine does not evolve. The contact time between gas flow and the catalyst amounts to 10–50 s. In order to prepare this catalyst, uranyl acetate is used which is dissolved in water to impregnate a carrier with the solution. Then the catalyst is dried and calcinated at 540 °C during 16 h. The disadvantage consists in a low selectivity with respect to CO_2 . The reaction proceeds within a fluidized bed reactor.

The process purposed for the oxidation of organic pollutants contained in liquid industrial wastes with the use of uranium oxide catalysts at a low temperature including a room temperature is presented in the patent [170]. Besides uranium oxide, the catalyst can contain the oxides of such metals as vanadium, iron, copper or platinum. The catalyst can be applied onto SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , CeO_2 , zeolites or activated coal. According to this invention, the use of these catalysts could result in decomposing a number of organic compounds, such as alkanes, alkenes, alkyne, aromatic compounds, alcohols, aldehydes, ketones, acids, ethers, esters, amines, surfactants and organophosphoric compounds. It has been demonstrated that tributylphosphate, sodium dibutylphosphate and hydrogen monobutylphosphate can be readily oxidized by hydrogen peroxide.

The composition of multifunctional catalysts consisting of SiO_2 , Al_2O_3 , ThO_2 , U_3O_8 , REE, Fe_2O_3 , TiO_2 , MgO , Na_2O , K_2O , and P_2O_5 is claimed in patents [171, 172]. Such catalysts are used in the process of liquid fuel combustion. The catalysts are prepared via mixing powders with water and further calcination at 1250–1300 °C.

CONCLUSIONS

In the review, data are presented concerning physicochemical properties of several, the

most stable, uranium oxides and of some compounds used in the preparation of uranium oxide catalysts. Publications are considered those reflect the complexity as well as a great variety of compounds in the uranium–oxygen system.

Uranium oxide catalysts have found application in the processes of obtaining synthesis gas, Fisher–Tropsch reactions, the processes of partial oxidation, hydrocracking, hydrotreating, CO oxidation. A high efficiency of catalysts in the reaction of low-temperature catalytic oxidation of volatile organic compounds including chlorine-containing ones is demonstrated. The analysis of the works published indicates a great variety of chemical processes those efficiently proceed with the participation of catalysts containing uranium compounds. The further studies on these catalytic systems open new prospects in catalysis.

There is no doubt, a question arises with respect to recycling catalysts containing uranium compounds. One of the methods for recycling the spent catalyst containing depleted uranium is presented in the patent [173].

We have reviewed scientific publications concerning studies on the properties of uranium-containing catalysts as well as patents concerning the use of uranium compounds in catalysis. The frameworks of the present review do not allow us to elucidate comprehensively the problems of manufacturing application of industrial catalysts containing uranium compounds, since they require for accomplishing entire complex of technological, engineering and designing tasks. Considering these problems with respect to Russia one should take into account the questions concerning toxicity [174] and radiation safety [175, 176]. Manufacture of catalysts based on depleted uranium should be organized according to the requirements of “Basic Sanitary Rules for Radiation Safety”, first of all, at the enterprises of nuclear fuel cycle with established infrastructure for safe handling of radioactive substances. Besides, federal norms and rules for accounting and checking nuclear materials [177] should be distributed to commercial production of catalysts based on depleted uranium, which would also require for organizing or using already established infrastructure of the enterprises of this branch.

At the same time, it should be noted that the maximum permissible concentration (MPC) for uranium-238 are determined only by its chemical toxicity amounting to 0.075 mg/m³ in air of working zone and 15 mg/L in the form of soluble compounds [174]. For the comparison, the MPC for an active component of many industrial catalysts such as nickel and its compounds in air of working zone are much lower amounting to 0.05 mg/m³, whereas the MPC for Ni, Cu, Zn as soluble compounds is equal to 0.1 mg/L.

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