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Preparation and characterization of bulk uranium oxides for catalysis

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The physicochemical and catalytic properties of bulk uranium oxides prepared by the thermal decomposition of uranyl nitrate [$UO_2(NO_3)_2 \cdot 6H_2O$] and precipitation from an aqueous solution of this salt are reported.

Uranium (a 5*f* element) has a unique electronic structure and a variety of valence states; therefore, uranium compounds are very attractive for catalysis applications. The chemistry of uranium oxide surfaces is very complex because of many oxidation states of uranium and a great number of thermodynamically stable phases, which can exist in the uranium–oxygen system.[1] These catalysts can be applied to various chemical processes.[2] The promising use of uranium oxide catalysts in the reactions of hydrogen or syngas production,[3,4] Fischer–Tropsch process,[5] partial oxidation,[6,7] cracking,[8] motor fuel hydrotreatment[9] and purification of exhaust gases for environmental protection[10] was demonstrated. The main advantage of uranium oxide catalysts is the stability to catalyst poisons, such as sulfur, water and chlorine. Earlier, we synthesized supported[3,11] and mixed[12] uranium oxide catalysts and studied their physicochemical and catalytic properties.

This paper describes the uranium oxide structure formation depending on preparation conditions, and the physicochemical and catalytic properties of bulk uranium oxides.

The samples of uranium oxides were prepared by (1) the precipitation of ammonium polyuranate from an aqueous uranyl nitrate solution followed by calcination and (2) the thermal decomposition of uranyl nitrate under the same temperature conditions.[†] The catalysts were studied by BET, XRD, TPR and SEM methods.[‡]

The catalytic activity was studied in the reaction of butane deep oxidation.[§] Table 1 summarizes the specific surface areas (S_{BET}) and phase compositions of the samples.

The specific surface area decreases with calcination temperature due to the sintering of uranium oxide particles. The specific surface area of the samples prepared by precipitation is higher than that of the samples prepared by thermal decomposition.

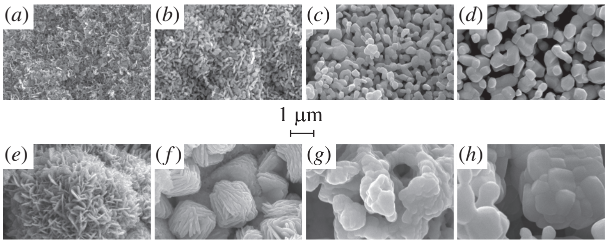

Figure 1 Micrographs of the samples of bulk uranium oxides prepared by precipitation and calcined at (*a*) 500, (*b*) 600, (*c*) 800 and (*d*) 1000 °C, or by the thermal decomposition of uranyl nitrate and calcined at (*e*) 500, (*f*) 600, (*g*) 800 and (*h*) 1000 °C.

The morphology and textural properties of uranium oxides depending on preparation conditions were studied by SEM (Figure 1).

The samples prepared by precipitation and calcined at 500 °C [Figure 1(*a*)] consist of small plates. After calcination at 600 °C, the sample consists of highly dispersed crystallites in the form of plates of 0.1–0.2 μm thickness and 1 μm in length [Figure 1(*b*)]. An increase in the calcination temperature up to 800–1000 °C leads to the sintering of the sample to form large blocks of three to five particles [Figure 1(*c*),(*d*)]. The pore size increases from 100 nm at 600 °C to 1 μm at 1000 °C.

The particles of uranium oxides prepared by thermal decomposition and calcined at 500 °C form coral-like aggregates [Figure 1(*e*)]. The micrograph of the sample calcined at 600 °C shows the presence of large layered aggregates (2×2 μm) formed from thin plates 0.1 μm in thickness [Figure 1(*f*)]. An increase in the calcination temperature to 800 °C [Figure 1(*g*)] leads to the sintering of plates into larger aggregates and the formation of a secondary pore structure with a size of ~1 μm. A further increase in the calcination temperature to 1000 °C [Figure 1(*h*)] caused the sintering of secondary pores and the growth of the aggregates to 5–7 μm. The SEM data are in a good agreement with the specific surface areas of the samples.

Analysis of XRD data (Table 1) reveals that the calcination of precipitated uranyl nitrate at 300 °C results in the decomposition of the highly dispersed complex compound $NH_3 \cdot 2UO_3 \cdot 3H_2O$.

[†] An ammonia solution was added dropwise to the uranyl nitrate solution with stirring to pH 10–11. The resulting yellow precipitate of $NH_3 \cdot 2UO_3 \cdot 3H_2O$ was allowed to stay overnight, filtered off, washed with water to remove ammonia, and dried under an IR lamp at 100 °C. The samples were calcined at 300, 500, 600, 800 and 1000 °C in air.

[‡] The specific surface areas of the catalysts were measured using the argon desorption (BET) method on a SORBI N.4.1 instrument. The morphology of catalyst samples was studied using a JEOL JSM-6460LV scanning electron microscope. Phase composition was determined by XRD on an HZG-4C diffractometer using CoKα radiation in the 2θ range of 20–80° with a sweep rate of 1 degree per minute. The samples were identified using the JCPDS X-ray database.

Temperature-programmed reduction by hydrogen (TPR-H_2) was performed in a fixed-bed reactor. Before the experiments, catalyst samples were treated in an oxygen flow at 500 °C. During TPR-H_2, the temperature was raised from 40 to 900 °C at a rate of 10 K min^{-1}. The composition of the gas mixture was 10% H_2 in Ar.

[§] Catalytic activity was measured in a tubular quartz flow reactor at temperatures from 200 to 700 °C. The catalyst loading in the reactor was 1 cm^3. The initial reaction mixture containing 1 vol% C_4H_{10} in air was supplied to the reactor at a flow rate of 16.7 cm^3 min^{-1}, which corresponded to GHSV = 1000 h^{-1}. The analysis of the initial reaction mixture and the products at the reactor outlet was performed with a LKhM-8D gas chromatograph with a TCD. The separation of the mixture components was conducted on a Porapak Q column.

Table 1 Phase composition and specific surface area of uranium oxides *versus* conditions of thermal treatment.

T_{calc}/°C	Precipitation		Thermal decomposition	
	S_{BET}/ $m^2\ g^{-1}$	Phase composition	S_{BET}/ $m^2\ g^{-1}$	Phase composition
300	8.7	High-dispersed (<60 Å) unidentified phase, probably a mixture of products of thermal decomposition of $NH_3 \cdot 2UO_3 \cdot 3H_2O$	3	γ-UO_3 and/or γ'-UO_3,[a] traces of α-$UO_{2.92}$
500	12.5	β-UO_3	7	γ-UO_3 and/or γ'-UO_3, traces of β-UO_3
600	11	α-U_3O_8	1.7	α-U_3O_8, γ-UO_3 and/or γ'-UO_3
800	3.4	α-U_3O_8	1.1	α-U_3O_8
1000	1.2	α-U_3O_8	0.18	α-U_3O_8, traces of γ-U_3O_8

[a] Orthorhombic γ-UO_3 and γ'-UO_3 have close crystalline parameters. The line position precision does not allow identifying exactly these phases at crystalline size lower than 300 Å.

A further temperature increase leads to the crystallization of β-UO_3 at 500 °C and the formation of α-U_3O_8 at 600 °C. Phase composition of the sample prepared by thermal decomposition changes from γ-UO_3 at 300 °C to α-U_3O_8 at 600 °C or higher.

The results of the TPR-H_2 of bulk uranium oxides prepared by precipitation and thermal decomposition and calcined at 500–1000 °C are presented in Figure 2(*a*),(*b*). An increase in the reduction temperature of the samples having similar phase composition at a rise of the calcination temperature is likely due to a decrease of uranium oxide dispersion. This was shown by the morphology and specific surface area study. Reduction of the samples prepared by the thermal decomposition method proceeds at higher temperatures in comparison with the samples prepared by the precipitation method and calcined at the same temperatures. It can be described by the lower dispersion of uranium oxides prepared by thermal decomposition.

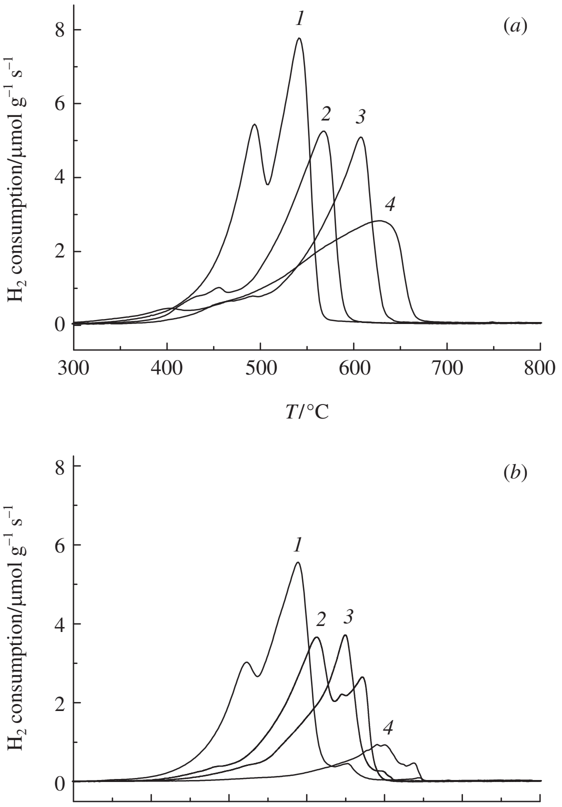

Figure 2 TPR curves of bulk uranium oxides prepared by the (*a*) precipitation and (*b*) thermal decomposition of uranyl nitrate and calcined at (*1*) 500, (*2*) 600, (*3*) 800 and (*4*) 1000 °C.

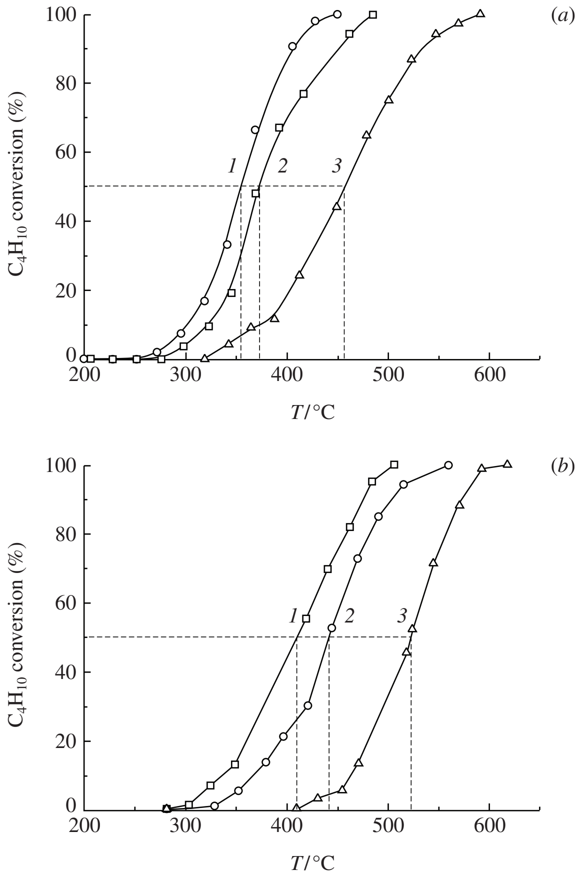

Figure 3 Temperature dependences of butane conversion on bulk uranium oxides prepared by the (*a*) precipitation and (*b*) thermal decomposition of uranyl nitrate and calcined at (*1*) 600, (*2*) 800 and (*3*) 1000 °C.

Butane conversion *versus* temperature curves for both series of catalysts depend on catalyst preparation calcination temperature; *e.g.*, catalytic activity decreased with calcination temperature (Figure 3). The comparison of two types of the catalysts shows that uranium oxides prepared by the precipitation method [Figure 3(*a*)] are more active than the catalysts prepared by the thermal decomposition of uranyl nitrate [Figure 3(*b*)]. These data, as well as the TPR data, demonstrate a direct correlation of the catalytic activity with the specific surface area of the oxides. The initial reaction rate of butane oxidation at 450 °C on U_3O_8 prepared by the thermal decomposition of uranyl nitrate and calcined at 800 °C was found[13] to be 7.68×10^{-8} mol g^{-1} s^{-1}. In our case, the initial reaction rate on a similar catalyst is 7.8×10^{-8} mol g^{-1} s^{-1}. The initial reaction rate of U_3O_8 catalyst prepared by precipitation and calcined at 800 °C is 4.51×10^{-7} mol g^{-1} s^{-1}, which is higher than the reaction rate of the catalyst prepared by thermal decomposition and calcined at the same temperature. Thus, the reaction rate of butane oxidation and the reactivity in TPR-H_2 rise with an increase in the specific surface area of catalysts having the same phase composition (U_3O_8).

In conclusion, the physicochemical (phase composition, specific surface area and morphology) and catalytic properties of bulk uranium oxides depend on preparation methods and thermal treatment; thus, they can be controlled by preparation conditions. Catalytic activity in the deep butane oxidation decreases with the catalyst calcination temperature. The catalysts prepared by precipitation are more active than those prepared by thermal decomposition of uranyl nitrate.

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