

# NOVEL REACTIONS OF OXIDES WITH SCF-ISOPROPANOL AS A REAGENT.

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The goal of the given activity is study and development of the possibility of supercritical fluid as specific reactant. We report on the first evidence of 100% reactivity of some oxides (as powders or pattern) with supercritical isopropanol.

We developed two autoclave methods for performance of experiments: in sealed ampoules and in opened glass containers. The transition in supercritical state has been conducted by increasing of reaction temperature and the inner pressure respectively. The standard experiments have been carried out at temperatures and pressures, which were higher (on 50-70<sup>0</sup>C and more) than critical ones of isopropanol to go out of the field of instability, which usually occurred in the field of phase transition. After the reaction the solid phase has been studied by X-ray analysis, DTA, TGA and the liquid one—by GC and GC-MS. We were the first to notice heterogeneous chemical reaction, the reactants of which were supercritical fluid and metal oxide.

The study of the reactions of the various oxides of I-VIII with SCF-isopropanol has been conducted. It was established that the oxides could be divided in 4 groups:

- 1) oxides, that were reduced up to metal (CuO, CdO, PbO, Pb<sub>2</sub>O<sub>3</sub>, Sb<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub>, Co<sub>2</sub>O<sub>3</sub>, ReO<sub>3</sub>, TeO<sub>2</sub>, PtO<sub>2</sub>);
- 2) oxides of metal with the variable valences, which were reduced up to low oxidation levels (V<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>);
- 3) oxides, that reacted with addition of hydrogen (M<sub>2</sub>O<sub>3</sub>, where M=La, Nd, Sm, Eu, Gd, Dy, Yb)
- 4) oxides, that were not reduced by SCF-isopropanol at all (UO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, WO<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, SiO<sub>2</sub>, GeO<sub>2</sub>, TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>).

## INTRODUCTION

Binary and mixed metal oxides form a vast class of inorganic compounds. Their unique physical characteristics (magnetic, optical, electrical, and others) stimulated researchers to study their structure and reactivity. Among the numerous problems existing in this field of chemical materials science, the following are the most attractive:

- (1) to develop the synthetic methods for suboxides, their structural characterization, and the production of cluster structures;
- (2) to control over oxygen stoichiometry in phases of variable composition;
- (3) to control over the composition and structure of near-surface layers of mixed oxide single crystals;
- (4) to introduce into an oxide host the organic compounds, hydrogen, and other reactants;

(5) to control the reduction of mixed oxides targeted at preparing compounds with a desired ratio of *d* elements with various oxidation numbers; and so on.

Varying of oxygen stoichiometry of oxides under mild conditions without introducing impurities is challenging problem of materials chemistry. There are many oxides, whose properties change dramatically as a result of slight variations in oxygen stoichiometry (dielectric ↔ semiconductor ↔ semimetal ↔ metal)

The purpose of this work was to find out whether it was possible to conduct reactions of supercritical isopropanol with different oxides – the reactions that are infeasible under ordinary conditions. Supercritical fluids (SFs) have been studied extensively in recent years. Traditionally, they have been tested as solvents. At present, there is increasing interest in SFs as reaction media and reagents. As a rule the pairs liquid-liquid and liquid-gas have been studied and the initially solid substrates were usually dissolved in one of the components of mixture. The systems, where the state SCF-solid phase was saved during the whole process, have been performed in two cases: numerous examples of extraction (predominantly by SCF-CO<sub>2</sub>.) and a few examples of heterogeneous catalysis with participation of substrate, dissolved in fluid phase [1, 2]. There are a few processes in which an SF is used as reagents. For example, treating dry coal with supercritical alcohols yields considerable amounts of liquid product substantially enriched in hydrogen as compared to the original coal [3]. The corresponding amounts of carbonyl products of alcohol dehydrogenation are found among light fractions. Experiments with model compounds demonstrated [4], that hydrogenation (and alkylation) of organic compounds with multiple bonds with alcohols under supercritical conditions occurred without catalysts [5]. Isopropanol is always converted to acetone in an amount proportional to the amount of hydrogenation product. Hydrogenating capacity decreases in the following order: (CH<sub>3</sub>)<sub>2</sub>CHOH >> C<sub>2</sub>H<sub>5</sub>OH > CH<sub>3</sub>OH [6]. It is well known, that under subcritical conditions the alcohols do not exhibit hydrogenating properties in absence of a catalyst. We believe that the aforementioned unique properties of SCF alcohols are applied to approach some problems from the above list of oxides.

In this work we focus on the reactivity of supercritical isopropanol toward metal oxides in the form of powders or plates. The interaction of the oxides of different elements of I-VIII groups with SCF isopropanol has been studied as in subcritical and also in supercritical areas. The oxides of transition and non-transition elements have been used for the research. Study of reaction of metal oxides with isopropanol has been conducted in the field of supercritical and also in subcritical field of isopropanol.

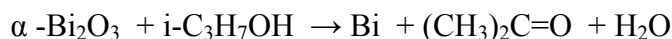
## **MATERIALS AND METHODS.**

All commercial chemicals were reagent grade. For high-pressure experiments, we developed two autoclave procedures: one using sealed ampoules and the other using open tubes. The system was brought to a supercritical state by raising the temperature and, accordingly, pressure. Standard experiments were performed 50-70<sup>0</sup>C above the critical temperature of isopropanol or at even higher temperature, outside the instability region, which generally lies near the transition point [7]. After ampoule was cooled and unsealed, the solid phase was characterized by X-ray diffraction (Geigerflex diffractometer, Ni - filtered, Cu K $\alpha$  – radiation) and thermal analysis (DTA and TG) in air (STA- 409 Netzsch thermoanalyser, platinum or Al<sub>2</sub>O<sub>3</sub> crucibles). The samples were heated and cooled at the rate of 5<sup>0</sup>C/ min. Liquid phases were studied by GC and GC-MS.

## RESULTS

At first we studied the reaction of metal oxide and SCF-isopropanol on the example of  $\alpha$ - $\text{Bi}_2\text{O}_3$  as representative of oxides of nontransition elements in detail.

We have found, that the interaction of  $\alpha$ - $\text{Bi}_2\text{O}_3$  with i-PrOH above critical point of alcohol (235 $^\circ\text{C}$ ) proceeded as following:



The analysis of a fluid phase has shown that alongside with initial isopropanol acetone was found in it in stoichiometric amounts. The experiment in the special set up, permitting visual observation of the reaction, has shown, that the achievement of critical temperature for isopropanol was accompanied by disappearance of a meniscus; during the whole reaction any phase separation in a system was absent. Thus the solid phase at the bottom ampoules was saved during all time of experiment, only changing the color and form. **By this means, the found reaction represents solid-phase reduction of bismuth oxide up to bismuth-metal under SCF-isopropanol.**

After opening of ampoules and eliminating of a liquid phase, Bi-metal represents either regular, or spherical particles of different sizes (with the diameters from 1 mm up to 0.001 mm). It is necessary to mark, that some chemical interaction of i- $\text{C}_3\text{H}_7\text{OH}$  with bismuth oxide starts at temperatures 160-180 $^\circ\text{C}$  (i.e. below critical). After heat time during 2 hours the initial yellow color of  $\alpha$ - $\text{Bi}_2\text{O}_3$  powder changed on light grey at 160 $^\circ\text{C}$ , dark - grey at 180 $^\circ\text{C}$  and black – grey at 200 $^\circ\text{C}$ . However after the X-ray data all samples represented the presence  $\alpha$ - $\text{Bi}_2\text{O}_3$ . Bi-metal or other phases by this method were not detected. GC also did not detected acetone in liquid phase at the mentioned temperatures. DTA and TGA methods have been used for the detection of small amounts of metallic bismuth. On the heating curve of DTA of the sample treated at 160 $^\circ\text{C}$  the only effect  $\alpha \leftrightarrow \delta$  of polymorphic transformation of bismuth oxide has been noticed. On the corresponding curve of TG the changes of sample masses were not established. However for the samples, treated at 200 and 220 $^\circ\text{C}$ , the exothermal effect with a maximum at 245-265 $^\circ\text{C}$  has been noticed on the DTA heating curves. On TG curves there were the increases of weight 0.24 and 0.38 % accordingly, probably owing to oxidation of Bi-metal, derivatives on a surface [8].

On the basis of these experiments it is possible to suggest, that the interaction of isopropanol with bismuth oxide started long before achievement of phase change, but underwent with a low rate. In such case the increase of reaction time should result to more complete reduction. Really, the heat time of bismuth oxide in alcohol during 90 hours at 200 $^\circ\text{C}$  resulted to complete reduction of  $\alpha$ - $\text{Bi}_2\text{O}_3$  into metal.

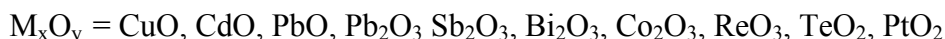
Thus, in the temperature range 200-250 $^\circ\text{C}$  the time of 100% interaction of  $\alpha$ - $\text{Bi}_2\text{O}_3$  with isopropanol decreases from 90 hours to 30 minutes. Therefore, the given reaction was sharply accelerated at transition of a reactant in SCF.

It is known, that SCF have high penetrating power permitting to extract dissoluble products from different solid materials; as a rule natural polymer materials (coals, biomass, coffee, etc.) have been used. The last ones have a definite degree of porosity. It was interesting to study, as far SCF can "permeate" into the structure of perfect monocrystals and "to extract" oxygen from internal layers of crystal lattice of oxides. With this purpose the interaction of the monocrystal  $\alpha$ - $\text{Bi}_2\text{O}_3$  by the sizes 5x10x2 mm with SCF-isopropanol has been investigated in sealed ampoules. It has been shown, that there was formation of the bismuth-metal layer on the surface of monocrystal pattern, the thickness of which was defined

by time and temperature of experiment. The analysis of polished sections of monocrystal after removing of the reduced layer demonstrated, that during interaction with SCF the defects of crystal structure of pattern (location, sector boundary etc.) have been emerged.

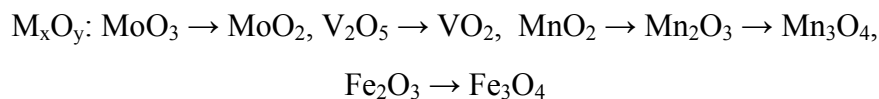
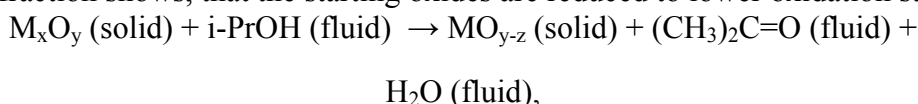
The experiments showed that, with respect to character of reaction products yielded by the  $M_xO_y$ -i-PrOH (SCF) system, four groups are distinguished among the binary oxides of I-VIII Groups of Periodic System:

1) Oxides that readily react with SCF-i-PrOH. The major reaction route in this case is the reduction to the metal:



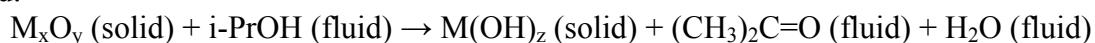
Analysis of the solid reaction products in some cases shows the unreacted starting oxides (alongside with the metal phase); nonstoichiometric oxides of variable composition also appeared. The liquid phase, in addition to acetone, contains the products of catalytic conversions of the alcohol and acetone.

2) Polyvalent metal oxides. Judging from the composition of the liquid phase, these oxides intensely react with SCF-i-PrOH (significant amounts of acetone were found). X-ray powder diffraction shows, that the starting oxides are reduced to lower oxidation states:



Probably, these metal oxides could be further reduced under more severe conditions.

3) The novel reaction of hydrogen addition with the formation of hydroxides has been found:



This reaction is typical for the rare-earth element oxides  $Ln_2O_3$  ( $Ln=La, Nd, Sm,$

$Eu, Gd, Dy, Yb$ ). The reaction of hydrogenation of the oxides (except  $CeO_2$ ) proceeded with the formation of corresponding hydroxides. It is necessary to note, that in the same conditions of the experiments, the yield of the reaction between oxide and SCF-isopropanol depends on the rare-earth element. Complete transformation (yield 100% of the oxide into hydroxide was found for lanthanum and neodymium.

This type of interaction was first discovered upon an analysis of the reaction products of amorphous  $MnO_2$ ; X-ray powder diffraction showed that the reaction product was 80% pyrochroite  $Mn(OH)_2$  and 20%  $\beta$ -kurnakite  $Mn_2O_3$ .

4) There are some oxides, that did not interact with SCF-isopropanol ( $UO_2, Ga_2O_3, In_2O_3, WO_3, ZrO_2, CeO_2, SiO_2, GeO_2, TiO_2, Cr_2O_3, SnO_2$ ) in the examined conditions.

## CONCLUSION

It was found, that:

- 1) reactions of the different oxides and SCF-isopropanol proceed at mild conditions;
- 2) reactions of oxides and SCF-isopropanol are heterogeneous;
- 3) interesting reaction of hydrogen addition to the oxides in SCF-isopropanol has been found;
- 4) our experiments have shown a diversity of reaction routes of metal oxides with SCF-i-PrOH;
- 5) original lines of research have been found. Their development will highlight the role of the supercritical state as a reactant in defining the route of heterogeneous reactions.

## ACKNOWLEDGEMENT

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