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## Composite Nanofibrous Materials for the Process of Hydrocarbon Oxidation

N. S. KOBOTAEVA, T. S. SKOROKHODOVA and E. E. SIROTINA

*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,  
Pr. Akademicheskiiy 4, Tomsk 634021 (Russia)*

*E-mail: see@ipc.tsc.ru*

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### Abstract

Composite material based on nanofibrous aluminium oxyhydroxide activated with metal nanoparticles (Ag, Co, Fe, Cu) was developed. Its catalytic properties in the oxidation of isopropylbenzene were studied. It was demonstrated that aluminium oxyhydroxide can be used as a support for composite materials. Isopropylbenzene oxidation in the presence of activated aluminium oxyhydroxide proceeds selectively, predominantly with the formation of isopropylbenzene hydroperoxide.

**Key words:** composite material, nanofibrous aluminium oxyhydroxide, catalytic oxidation of isopropylbenzene

### INTRODUCTION

At the present time, active searching the catalysts is performed those are designed for the selective oxidation of hydrocarbons with various structures in order to obtain primary products of hydroperoxide reactions, which is caused by the industrial value of organic compounds obtained from the hydroperoxides. In recent decades new catalytic systems or new generation catalysts were described for the oxidation of hydrocarbons by molecular oxygen and hydrogen peroxide based on nanosized, nanostructured and nanocomposite materials [1–4]. In general, the activity of a catalyst could be associated both with regular, and with defect centers on the surface. Consequently, affecting the deficiency level and the microstructure of the catalyst surface can efficiently change its reactivity and catalytic properties.

The materials those have a high deficiency level include nanosized metal powders, whose properties differ significantly from the properties of coarse metal powders and metal in the compact state. This is connected primarily with the presence of excess surface energy, which disturbs the balance and symmetry in the dis-

tribution of power and mass, results in changing the equilibrium interatomic distances as compared to their values in macrocrystals, as well as changing the length of the chemical bonds and, as a consequence, in changing the reactivity of nanoparticles [5]. One of the methods for obtaining metal nanopowders (MN) with a high deficiency level consists in the electric explosion of wire (EEW) [6]. A similar result is obtained also from the application of mechanochemical treatment of materials [7].

The authors of [8–11] considered the use of nanoscale metal powders obtained by the EEW and by mechanochemical processing as catalysts for the oxidation of isopropylbenzene (IPB) with molecular oxygen. It is demonstrated that the application of these catalytic systems allows one to perform the oxidation process at the temperature of 30–60 °C and atmospheric pressure, with a relatively high rate (without a catalyst the process is carried out at 120 °C and high pressure). These points to a high activity of nanosized metal powders in the oxidation of IPB. However, the high activity of MN represents also their disadvantage, since in the oxidation process they are easily aggregated and eventually lose their activity. In ca-

talysis, in order to solve the problem one uses fixing nanosize particles on different carriers.

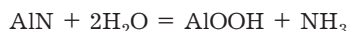
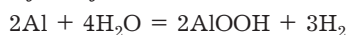
In choosing a carrier, its physical and chemical properties are crucial [12]. Taking into account requirements for the carriers of the active phase of a catalyst, matrices could be presented by a variety of disperse inorganic material (*e. g.*, metal oxides). Among oxide supports, silicon oxide (SiO<sub>2</sub>) and alumina (γ-Al<sub>2</sub>O<sub>3</sub>) are most widely used [13]. The reactivity of the surface groups of silica and alumina is well established. Taking into account the diversity of the reaction, where they could participate, one can use different methods for fixing agents on the surface. In recent years, new nanosized oxides and oxyhydroxides produced using modern technology and having a set of physical and chemical properties, so that they can be used as carriers of the active phase of the catalyst. One of these carriers – nanofibrous (nanolayered) aluminium oxyhydroxide (AlOOH) [14].

This paper presents the results of studying the possibility of fixing nanosized metal particles on aluminium oxyhydroxide, physical and chemical properties of the composites and their catalytic activity in the oxidation of alkylaromatic hydrocarbons.

## EXPERIMENTAL

We used in the work of Co, Cu, Fe and Ag nanopowders (NP) with specific surface area 11.7, 13.7, 10.5 and 10.5 m<sup>2</sup>/g, respectively, obtained *via* the method of EEC under nitrogen atmosphere.

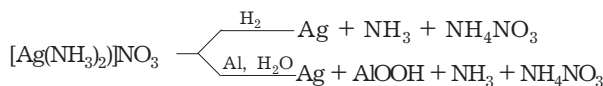
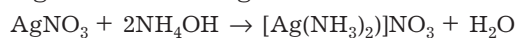
Aluminium oxyhydroxide was obtained *via* the hydrolysis and oxidation of aluminonitride composition nanopowder (EEC, under nitrogen) with water as described in [14, 15]. The specific surface area of the oxyhydroxide was more than 200 m<sup>2</sup>/g at 60 °C, the reactions of oxidation and hydrolysis of aluminium nitride are they:



The composition of aluminium oxyhydroxide activated by Cu, Co, Fe nanoparticles was prepared as it follows. To an aqueous suspension of aluminonitride composition (Al/AlN = 40–60) was added a suspension of NM at 60 °C and continuous stirring at the beginning of the formation of oxyhydroxide aluminium fibres.

The latter were preliminary dispersed in water using an ultrasonic disperser. After the reaction ending registered by ceasing the evolution of gas, the precipitate formed was filtered, washed with water to obtain neutral wash water pH and dried at 100 °C during 2 h.

The composite material with silver nanoparticles was obtained *via* the introduction of alkaline solution of silver salt into the suspension of aluminonitride composition nanopowder in water heated up to 80 °C under beginning the formation of AlOOH. The formation of silver nanoparticles on AlOOH occurred according to the following reactions



The specific surface area of MN, aluminium oxyhydroxide and composite materials based on them we measured using nitrogen thermal desorption technique by means of Sorbtometr M with the calculation *via* multipoint BET method in an automatic mode.

Studying the size and shape of particles in the compositions under investigation was performed using transmission electron microscopy (TEM) on a JEM-100 CX II JEOL electron microscope.

Determining the phase composition of aluminium oxyhydroxide and MN were performed using XRD technique (Shimadzu XRD-6000 diffractometer, CuK<sub>α</sub> radiation database RSRDFWIN).

The catalytic activity of the obtained composite material was evaluated from oxygen absorption rate (*dv/dt*) and total oxygen absorption (*V*<sub>O<sub>2</sub></sub>) in the IPB composite system. The reaction was stopped at a constant rate of oxygen absorption in 15–20 min.

The investigation on the IPB oxidation process was performed using manual gasometrical installation [16] at 60, 50 and 40 °C and atmospheric pressure with no initiator. The scale of the glass manometer of the instrument reflects the partial absorption of gaseous oxygen. To the reactor, was placed 8.6 g of IPB and 0.0107 g of MN or composite material (calculated for its active phase). The scatter of the results for the five measurements was equal to 10 %.

For the oxidation we used 1st grade industrial oxygen (State Standard GOST 5583–78). The oxygen content amounted to 99.7 %.

In the work, we used Fluka commercial IPB with a purity of 99.8 %. Isopropylbenzene hydroperoxide (IBP HP) content was determined iodometrically by means of a method described

in [17]. The oxidation products such as acetophenone (AP) and dimethylphenylcarbinol (DMPC) were analyzed using a gas chromatography method by means of a PerkinElmer Sigma 2B chromatograph with a plasma ionization detector (column SE-52, column length 33 m) in a temperature programming mode.

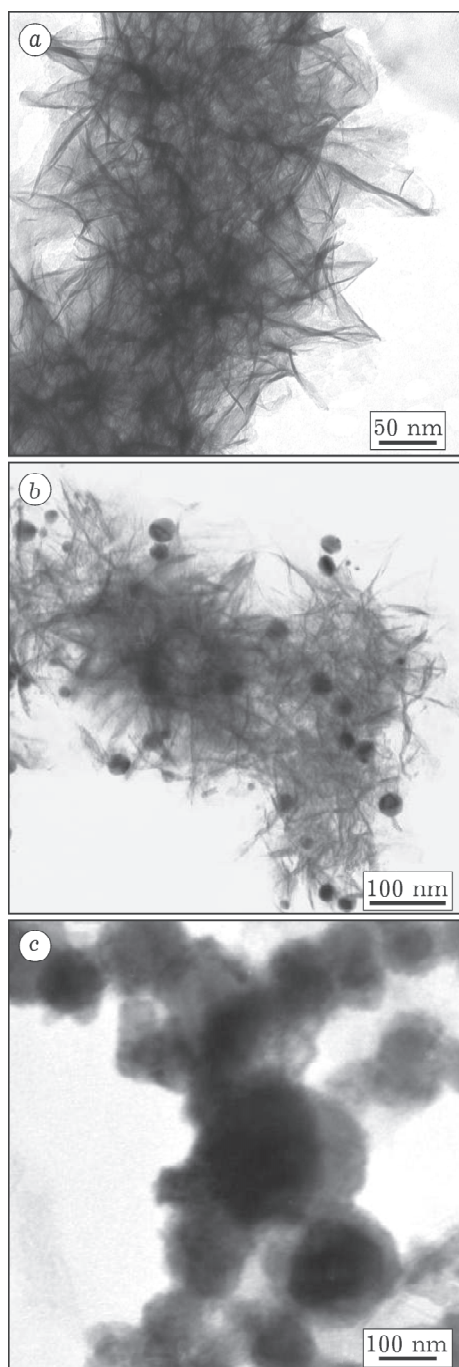


Fig. 1. TEM micrographs of aluminium oxyhydroxide (a), composite materials based on aluminium oxyhydroxide and silver (b) and cobalt (c) nanoparticles.

## RESULTS AND DISCUSSION

As a carrier of the active phase in making composite materials in catalysis, as a rule, one uses an industrial thermostable  $\gamma\text{-Al}_2\text{O}_3$  sample. For such purposes we have chosen nanofibrous aluminium oxyhydroxide not studied earlier produced *via* the oxidation and hydrolysis of an aluminonitride composition with water. The phase composition of aluminium oxyhydroxide represented pseudoboehmite ( $\text{AlOOH}$ ) with the admixtures of gibbsite ( $\text{Al}(\text{OH})_3$ ) and  $\gamma\text{-Al}_2\text{O}_3$ .

The TEM image of aluminium oxyhydroxide (Fig. 1, a) demonstrates that the particles are shaped to be curved nanosheets with a thickness of less than 8 nm and a length of 100–200 nm. The aluminium oxyhydroxide has a good mechanical and thermal stability. Preliminary studies of IPB oxidation reaction in the presence of unactivated aluminium oxyhydroxide demonstrated that the latter is resistant with respect to oxygen (the phase composition remains unchanged) and inert with respect to the oxidation of IPB (the IPB oxidation reaction in the presence of aluminium oxyhydroxide does not occur at 30–60 °C). Basing on aluminium oxyhydroxide we obtained compositions with an active MN (Fe, Cu, Co, Ag) phase.

The images of these composite material based on aluminium oxyhydroxide and silver nanoparticles, and cobalt (see Fig. 1, b and c) demonstrate that the average size of the silver nanoparticles on aluminium oxyhydroxide (the content of the active phase being of 15 mass %) ranges within 10–20 nm (see Fig. 1, b), whereas the shape of the particles is nearly spherical.

Cobalt nanopowders on aluminium oxyhydroxide (the content of the active phase being 60 mass %) represent particles with the diameter ranging mostly within 80–100 nm, but there are particles with a larger diameter (see Fig. 1, c). The shape of the particles, just as in the case of silver nanoparticles, is nearly spherical;

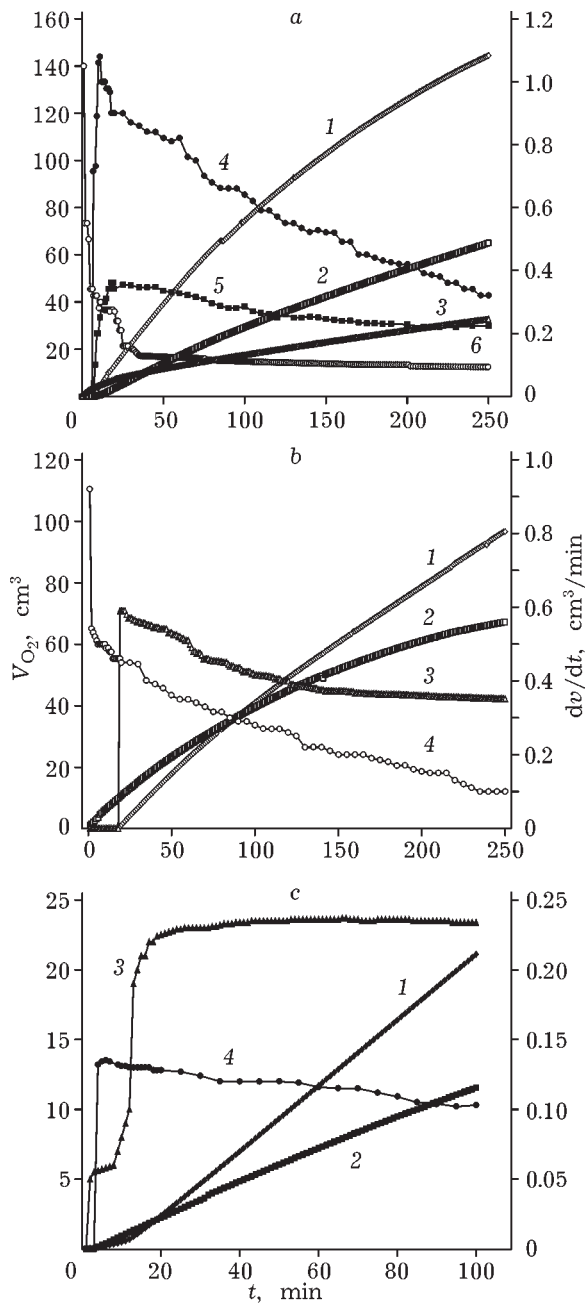


Fig. 2. Kinetic curves for IPB oxidation by molecular oxygen in the presence of composite materials: *a* – the amount of oxygen absorption  $V_{O_2}$  (1–3) and the rate of  $O_2$  absorption  $dv/dt$  (4–6) in the presence of Ag on AlOOH at  $T = 60$  (1, 4),  $40$  °C (2, 5) and Ag NP (WEE) (3, 6); *b* –  $V_{O_2}$  (1, 2) and  $dv/dt$  (3, 4) in the presence of Co (EEW) on AlOOH (1, 3) and Co NP (EEW) (2, 4) at  $T = 60$  °C; *c* –  $V_{O_2}$  (1, 2) and  $dv/dt$  (3, 4) in the presence of Fe (EEC) on the AlOOH (1, 3) and Fe NP (WEE) (2, 4) at  $T = 60$  °C.

there are also separate agglomerates. Metal nanopowders consist of only one phase such as metal, the oxide shell could represent, to all appearance, XRD amorphous phase, the reflexes of the latter are absent on the XRD patterns.

The obtained compositions of activated aluminium oxyhydroxide were investigated as catalysts for the reaction of IPB oxidation by molecular oxygen. Kinetic curves for the oxidation of IPB by molecular oxygen in the presence of composite materials are demonstrated in Fig. 2. For comparison, there are kinetic curves presented for IPB oxidation in the presence of MN obtained EEW in a nitrogen atmosphere.

According to the results obtained it was demonstrated that the oxidation of IPB occurring in the presence of Co, Ag, Fe and Cu (EEW) nanopowders, characterized by a small induction period, by maximal (with a very high value) rate of oxygen consumption at the beginning of the reaction and an abrupt decrease in the rate to a minimal, almost constant value within about 10 min of oxidation time. As noted in [8, 10], a high rate of oxygen absorption in the beginning of the reaction could be caused by a high deficiency level of the crystal structure MN obtained *via* EEW. In the same studies it was demonstrated that at the first stage of the reaction the amount of oxygen absorbed was not equivalent to the amount of the reaction products formed (oxygen was not absorbed more). We can assume that absorbed oxygen not involved in the formation of the reaction products is either consumed for MN oxidation and the formation of metal oxides, or it is irreversibly adsorbed on the surface of the nanopowder. The XRD investigation of MN obtained *via* EEW in an inert atmosphere before and after the oxidation reaction demonstrated that there is no formation of additional metal oxides. For example, the authors of [8] presented XRD data for copper nanopowders (EEW under nitrogen) before and after the oxidation of IPB. Basing on this, it was suggested that a part of oxygen absorbed at the early stage of the reaction is irreversibly adsorbed on the surface of MN, with participation in the oxidation of IPB, but with no oxidizing the nanopowders. Oxygen adsorbed onto metal surface, to all appearance, could be quite strongly retained on the surface in areas of a maximum concentrations of defects, thereby blocking some active (reactive) centres of the surface, as indicated by reduced rate (and volume) of oxygen absorption over time.

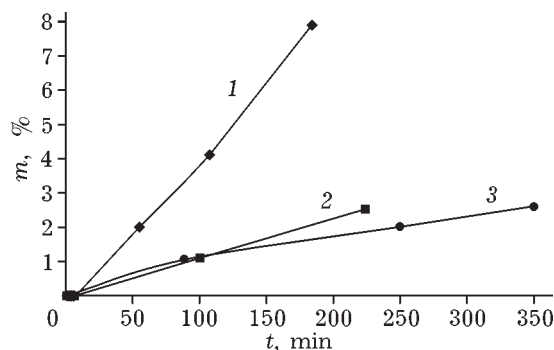


Fig. 3. Kinetic curves for IPB HP accumulation ( $m$ ) in the reaction of IPB oxidation by molecular oxygen catalyzed by Ag-AlOOH composite material (1, 2) and Ag NP (WEE) (3).  $T$ , °C: 40 (2), 60 (1, 3).

The IPB oxidation in the presence of composite materials is realized in a different manner: the process is characterized by a high rate of oxidation for a long time, and in some cases the oxidation kinetic curves exhibit saturation. Thus, the oxidation in the presence of composite materials occurs in a more stable manner, with a constant rate in some cases (see Fig. 2, b and c).

Basing on data concerning the high rate of oxygen absorption it could be assumed that the oxidation can proceed also at a lower temperature value such as 50 and 40 °C (Fig. 4, curves 2 and 3). It can be seen that the rate of oxygen consumption is high enough in the case of the reaction at 40 °C.

The IPB oxidation results in forming the isopropylbenzene hydroxide (IPB HP):

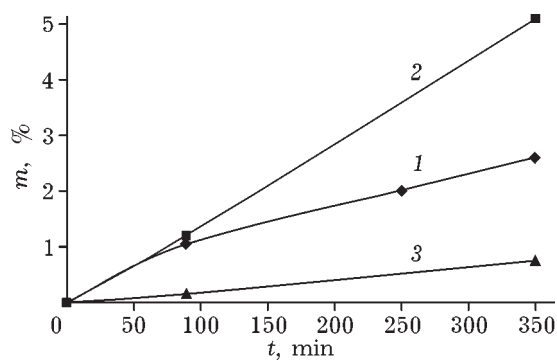
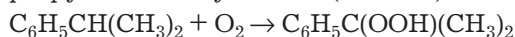


Fig. 4. Kinetic curves for the accumulation of IPB HP (1), DMPC (2) and AP (3) in the reaction of IPB oxidation by molecular oxygen catalyzed by Ag NP (EEW).  $T = 60$  °C.

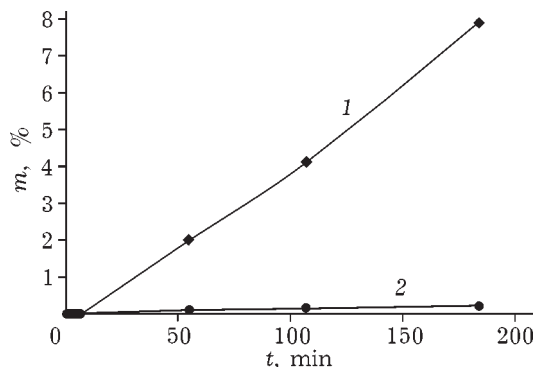
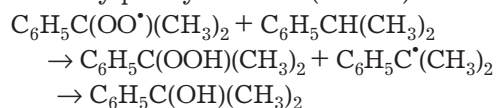
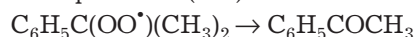


Fig. 5. Kinetic curves for the accumulation of IPB HP (1) and DMPC (2) in the reaction of IPB oxidation by molecular oxygen catalyzed by Ag-AlOOH composite material.  $T = 60$  °C.

dimethylphenylcarbinol (DMPC):



acetophenone (AP):



The kinetics of reaction product accumulation is demonstrated Figs. 3–5. The formation of IPB HP starts simultaneously with the absorption of oxygen, so the kinetic curves of IPB HP accumulation exhibit certain induction period values. The accumulation of HP due to the oxidation in the presence of IPB MN (EEW) is linear only at low concentrations of HP (see Fig. 3, curve 3). Further, as the accumulation progresses, the dependence represents a saturation curve, which indicates either the complexation between the components of the system, or the decomposition of the HP. The second assumption is more likely; since in the reaction mixture there were revealed the AP and DMPA (see Fig. 4, curves 2 and 3). The IPB oxidation in the presence of composites results in the formation mainly IPB HP (see Fig. 3, curves 1 and 2) and trace amounts of DMPA and AP (see Fig. 5, curve 2).

Thus, binding the MN on aluminium oxyhydroxide alters the catalytic activity of the composite material in the oxidation of IPB, which could be caused by changing the type and location of reaction sites on the catalyst surface.

## CONCLUSION

1. Composite materials were obtained based on nanofibrous aluminium oxyhydroxide acti-

vated by the nanoparticles of metals (cobalt, copper, silver, iron); their catalytic activity in the oxidation of isopropylbenzene with molecular oxygen was studied.

2. The oxidation of IPB by molecular oxygen with the use of composite materials occurs at a higher rate for a long time compared to the process of IPB oxidation in the presence of metal nanopowders to be accompanied by the formation of predominantly the main product such as isopropylbenzene hydroperoxide.

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