

# The determination of adsorption site structures of high dispersed oxides by EXAFS spectroscopy using molecules as probe

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## Abstract

The structure of adsorption sites of highly dispersed oxides, such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{ZnO}$ , was investigated by means of  $\text{H}_2\text{Se}$  adsorption. The nanoparticles were studied with a specific surface area not less than  $50 \text{ m}^2/\text{g}$ . The oxide surface was activated either by mechanical activation or by high temperature treatment in a gas flow. Irreversible  $\text{H}_2\text{Se}$  adsorption was carried out up to saturation in  $\text{H}_2$  excess at room temperature. EXAFS spectra of the Se–K edge were measured and analyzed. The ratio between point and extended defects as a function of the activation conditions was determined for  $\text{TiO}_2$ . It was shown that oxygen, being removed from the  $\text{Fe}_2\text{O}_3$  surface during the activation, is not associated with the presence of a cation in the interstitial positions. It was shown for  $\text{ZnO}$  that a change in the ratio between cation and anion vacancies depends on the duration of the mechanical treatment. Perspectives of this approach and possibilities of using the probes are described. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

There is a lot of work devoted to the study of Klause reaction on dispersed transient metal oxides. As a rule, the main methods used for this purpose are the IR spectroscopy of molecule-probes and UV–VIS spectroscopy in the diffuse reflection mode.

In the studies of catalysis on oxides, it is considered that active centers are the defects of a surface structure and the extended defects seem to play the leading role. However, the structure of these defects is as a rule unknown so far.

IR spectroscopy allows us to determine the acidity of the surface centers by means of the selective adsorption of the molecule-probes [1]. The investigation of the surface point defects by optical spectroscopy provides information about the cation coordination, and on this basis the attempt is made to reconstruct the active sites [2]. Both of these methods cannot give direct structural information about the active sites,

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hence, new methods for studying the Klause reaction catalysis are to be worked out.

In this work, a new method is developed for determining the structure of the adsorption sites on the surface of highly dispersed oxides. This method uses adsorption of probe molecules with the subsequent study of their local arrangement by EXAFS. Taking into account a methodical limitation, we used  $\text{H}_2\text{Se}$  instead of  $\text{H}_2\text{S}$  to obtain a direct information about the analog of Klause reaction on transient metal oxides such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{ZnO}$ . The choice of these oxides was determined by various structural and catalytic properties of their surfaces. It is known from the literature that a catalytic activity for Klause reaction on the transition metal oxides decreases in a following order:  $\text{Co}_3\text{O}_4 > \text{V}_2\text{O}_5 > \text{Fe}_2\text{O}_3 > \text{Mn}_2\text{O}_3 > \text{CuO} > \text{TiO}_2 > \text{ZnO} > \text{NiO} > \text{Cr}_2\text{O}_3$ .

## 2. Experimental

The samples of  $\text{ZnO}$  and  $\alpha\text{-Fe}_2\text{O}_3$  were synthesized at the Borekov Institute of Catalysis. The samples of  $\text{TiO}_2$  are the commercial types of titanium oxide, such as Hombikat and Degussa. Preparation of  $\alpha\text{-Fe}_2\text{O}_3$  samples obtained by decomposition of oxalate and goethite at  $400^\circ\text{C}$  in air was carried out as described in Ref. [3].

The adsorption of  $\text{H}_2\text{Se}$  was made as follows. The hydrogen was purged through the metal Se at  $400^\circ\text{C}$  in the reactor with the capillary tubes length being about 6 m, then it was passed through a special trap (for Se catching). The  $\text{H}_2\text{Se}$  obtained was adsorbed on the samples at room temperature. The samples of  $\text{TiO}_2$  and  $\alpha\text{-Fe}_2\text{O}_3$  were previously treated at  $400^\circ\text{C}$  in vacuum for 3 h. The samples of  $\text{ZnO}$  were previously mechanically activated for 30 s and 1 min.

In addition, all the samples were characterized by TEM and XRD. The surface structure was investigated at 20–70% coverage of the surface by Se atoms for all the systems. The

oxides were studied with a specific surface area not less than  $50 \text{ m}^2/\text{g}$ .

Iron oxides were prepared in two ways, namely, by oxalate and goethite decomposition. The oxides obtained in various ways can differ with respect to the presence of defects of the surface structure. Preliminary studies of the  $\text{H}_2\text{Se}$  adsorption on iron oxides have shown a strong selective interaction with surface defects [4]. Thus, it is possible that there took place both  $\text{H}_2\text{Se}$  adsorption and its transformation, similar to Klause reaction. It allows both to characterize a surface state and to study the course of Klause reaction on these systems using  $\text{H}_2\text{Se}$  instead of  $\text{H}_2\text{S}$  as a reactant. The samples obtained by goethite decomposition consist mainly of thin platelets  $300 \text{ \AA}$  wide and  $1 \text{ }\mu\text{m}$  long, with the most developed planes (01–10) [3]. The samples obtained by oxalate decomposition have the most developed planes (0001) [3].

The EXAFS spectra of the Ti–K, Zn–K, Fe–K, and Se–K edges for all the samples were obtained at the EXAFS Station of Siberian Synchrotron Radiation Center. The storage ring VEPP-3 with an electron beam energy of 2 GeV and an average stored current of 80 mA was used as the source of radiation. The X-ray energy was monitored with a channel cut Si(111) monochromator. All the spectra were recorded under transmission mode using two ionization chambers as detectors. The harmonics rejection was performed by using a gold mirror for Ti–K edge. For the EXAFS measurements, the samples were prepared as pellets with a 0.5 absorption jump at the absorption edges. The EXAFS spectra were treated using the standard procedures [5]. The background was removed by extrapolating the pre-edge region onto the EXAFS region in the forms of Victoreen's polynomials. Three cubic splines were used to construct the smooth part of the adsorption coefficient. The inflection point of the edge of the X-ray absorption spectrum was used as initial point ( $k = 0$ ) of the EXAFS spectrum. The function of the radial distribution of the atoms

(RDA) was calculated from the EXAFS spectra in  $k^3\chi(k)$  using Fourier analysis at the wave number interval 4.0–12.0  $\text{\AA}^{-1}$ .

### 3. Results and discussion

In all the spectra, the first peak of various intensity was observed at the distance 1.4–1.6  $\text{\AA}$ . It was ascribed to the Se–O chemical bond. It should be noted that great distortions of the amplitude of this peak are caused by EXAFS spectra procedure. This is a technique limitation which cannot be eliminated. So, it is impossible to estimate precisely the amplitude for this peak and Se–O coordination number.

There are few possibilities of  $\text{H}_2\text{Se}$  interaction with the surface centers. In the case of a point surface center (active oxygen ion), they are the replacement of oxygen by Se and the formation of water on the surface. Thus,  $\text{Se}^{2-}$  chemically interacts with Me ions, being placed

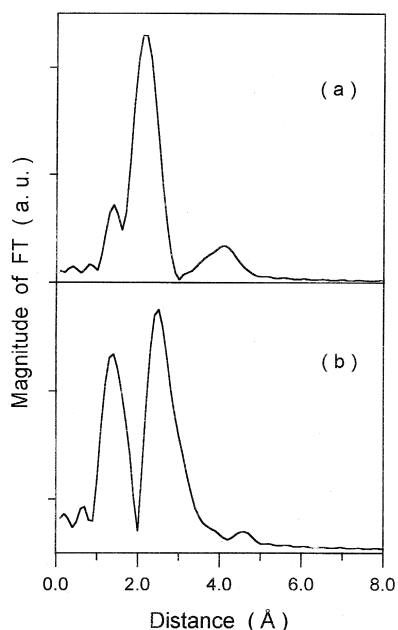


Fig. 1. Curves of RDA for selenium local arrangement of Se-marked  $\alpha\text{-Fe}_2\text{O}_3$  samples prepared from oxalate (a) and goethite (b).

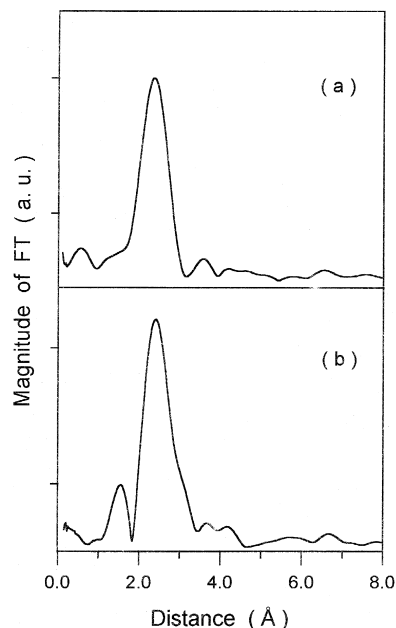


Fig. 2. Curves of RDA for selenium local arrangement of Se-marked  $\text{TiO}_2$  samples; Hombikat (a) and Degussa (b).

approximately in the oxygen position. The formation of molecules of the selenium oxide is possible in the case of the extended surface active center. In this case, Se forms the adsorbed molecules, such as  $\text{SeO}_2$  or  $\text{SeO}_3$ , on the surface and is not bound structurally to the defects. In addition, the formation of elementary selenium in various modifications on oxide surface is quite possible in all cases according to the analog of Klause reaction. The short results for these three cases are discussed below.

(1)  $\alpha\text{-Fe}_2\text{O}_3$ . RDA curves of the local selenium arrangement for the samples obtained by oxalate and goethite decomposition are shown in Fig. 1a and b, respectively. The curves differ rather strongly, which is determined by different structures formed by the surface complexes in both cases [4].

(2)  $\text{TiO}_2$ . RDA functions for the selenium local arrangement of Se-marked  $\text{TiO}_2$  samples; Hombikat and Degussa are shown in Fig. 2a and b, respectively. Some differences of the curves correspond to the difference in the ratio

of the elemental Se and  $\text{SeO}_x$  species, which are formed on various type of  $\text{TiO}_2$  after  $\text{H}_2\text{Se}$  adsorption.

(3) ZnO. RDA functions for the selenium local arrangement of Se-marked ZnO samples after 30 s and 1 min mechanical activation are shown in Fig. 3a and b, respectively. These RDA functions differ rather strongly, that is determined by the differences in the structures formed by the surface complexes in both cases. It seems that various type surface defects are formed at various activation time.

From the analysis of the data for all the three oxides, we may conclude that the adsorbed selenium is present in two forms. As the first form, selenium is adsorbed on the Brönsted centers through Se–O bonds. As the second form, selenium is adsorbed on the Lewis centers with a direct bond Se–Me. Elemental selenium is absent in that samples, as the Se–Se distance  $\sim 2.3\text{--}2.4 \text{ \AA}$  was not observed. The proportions of these two types of selenium adsorption forms

depend on the type of oxide and method of activation. Determination of specific forms of all the adsorption centers is the subject of further publications. For Fe and Zn oxides, we observed the next coordination sphere which makes it possible to determine the structures of the adsorption sites. The absence of the next interatomic distances for  $\text{TiO}_2$  oxides may be interpreted through adsorption on the edges of (110) plane that commonly forms the surface of highly dispersed  $\text{TiO}_2$ . The first Se–Fe distance was different for iron oxides obtained from different precursors. It may be supposed that different surface structures of these oxides result from the differences in their morphology. Zn oxides easily interact with  $\text{H}_2\text{S}$  even at room temperature. The RDA functions of mechanically activated Zn oxides contain peaks up to  $5 \text{ \AA}$ . This fact is explained by a strong interaction of Se with the oxide and the formation of a hard structure.

It could be seen that the application of EX-AFS spectroscopy in the variant of the molecule-probes gives some information about the catalyst surface and the reaction mechanism. The detailed analysis of the surface compound is very difficult, but anyway, the obtained data may be used as a «fingerprint» for the testing of catalysts.

#### 4. Conclusions

A new method for testing the surface structure is developed by the use of molecule-probes. Perspectives of this approach in the surface testing of catalysts and in studying the reaction courses are shown.

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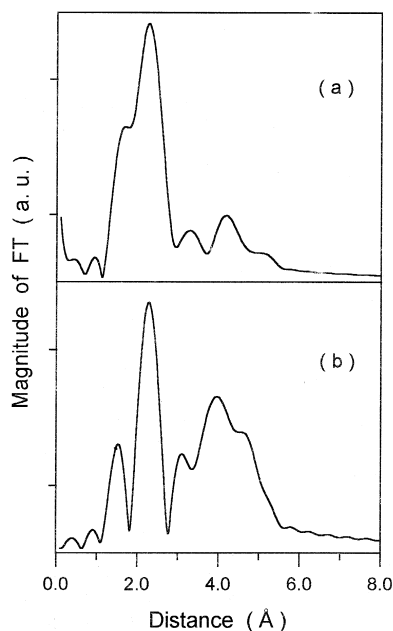


Fig. 3. Curves of RDA for selenium local arrangement of Se-marked ZnO samples after various time of mechanical activation; 30 s (a) and 1 min (b).

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