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The use of RDF analysis in the study of powder samples: Zirconia complex supported by clay and pseudoboehmite

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Abstract. Two examples illustrating the use of radial distribution functions of electronic density to determine the structure of supported zirconia complex and particularities of the pseudoboehmite structure are reported.

Introduction

Complete diffraction patterns of X-rays, neutrons or electrons from single crystals are known to make it possible to resolve their structure, i.e. spatial distribution of atoms. However, for highly dispersed materials, especially for substances in the amorphous state, this problem is not solved completely. Still it is possible to construct a real-space one-dimensional description of the order as radial electron distribution (RED) [1], or wide angle x-ray scattering radial distribution function (WAXS RDF, RDF), or pair distribution function (PDF). This technique is often used to study the structure of catalysts and supports. Such materials are characterized by crystalline sizes from 1 to 100 nm or more, and their diffraction patterns sometimes contain diffuse scattering and broadened Bragg peaks as well as sharpened ones.

RDF contains data on interatomic distances and coordination numbers of investigated materials. However, these materials can have some particularities in their structure in comparison with their single crystal analogues. In this case it is necessary to compare the experimental RDF with a model one constructed for the assumed phase composition of the sample. Such comparison can not only help to determine exactly the phase composition, but also reveal the local structure of the material.

The aim of this work was to demonstrate two approaches for application of the RDF analysis: 1) to display differences in the local structures of boehmite and pseudoboehmite, which are common materials for use as precursors of catalyst supports; 2) to determine the structure of the active component in the supported catalyst (zirconia on montmorillonite clay).

Method

The RDF analysis of electronic density is based on the relation between the radial distribution function of electronic density $4\pi r^2\rho(r)$ and the normalized intensity of coherent scattering in X-ray diffraction. The RDF calculation technique used by our group has been described in detail elsewhere [1-3]. It is somewhat different from the one used by Billinge and Egami, et al. [4]. We circumvent a significant influence of termination ripples by using a buffer factor $exp(-bQ^2)$ in the Fourier transform integrand. Using our technique, one can directly define interatomic distance and coordination number Z (the number of atoms at this distance) from the position and peak area in the RDF curve, with no regard to unit cell parameters, coordinates of atoms, etc. It can be very important in the case of amorphous or nano-material. Moreover, it is possible to construct a differential RDF when one needs to determine the structure of a certain component in a composite material, such as an active component in a supported catalyst.

To determine particularities in the local structure of nanomaterials in comparison with well crystallized analogues, we construct a model RDF using relation (1) somewhat similar to that described by Proffen and Billinge [5]:

$$4\pi \cdot r^2\rho(r) = \sum_i \frac{S_i}{\sqrt{2\pi \cdot b_i^2} \cdot \left(1+\frac{b_i^2}{r_i^2}\right)} \cdot \exp\left[\frac{(r-r_i)^2}{2b_i^2}\right] \cdot \left(\frac{r}{r_i}\right)^2, \tag{1}$$

where r_i - equilibrium interatomic distance in the crystal structure, b_i – width and S_i - area of the RDF maximum. S_i is defined as

$$S=c_aK_a^2Z_{aa}. \tag{2}$$

in the case of identical atom types and

$$S=c_aK_aK_bZ_{ab}. \tag{3}$$

in the case of different atom types, where c_a is the concentration of a-type atoms, Z_{ab} - coordination number, K_a – effective scattering power or "number of electrons" in a-type atom. K_a is defined by relation (4):

$$K_a^2 = \frac{\int_0^{s_{\max}} f_a^2(s)\cdot s^2 ds}{\int_0^{s_{\max}} f_L^2(s)\cdot s^2 ds}, \tag{4}$$

where f_L is the atomic scattering factor of the atom with the lowest atomic number in the investigated system.

The calculation of interatomic distances r_i and coordination numbers Z is carried out for all separated phases in the investigated material from the known structural data: unit cell parameters, space group, coordinates of atoms and occupation of positions. In the present work structural data from the ICSD/Retrieve database and "*Pearson's Handbook of Crystallographic Data of Intermetallic Phases*" [6] were used. Interatomic distances and coordination numbers were calculated by the ICSD/Retrieve program and the original IK program designed at Boreskov Institute of Catalysis. Comparison of the experimental RDF and the model one constructed by this way can both reveal changes in the structure at the short-range order and detect highly dispersed X-ray amorphous phases, which are usually not detected in the diffraction pattern. The approbation of the model RDF construction procedure was carried out for the reference SRM-676 α-Al_2O_3 sample supplied by the International Centre on Diffraction Data (ICDD). The model and experimental RDF for this structure shown in the Figure 1 are in close agreement with each other with the R-factor equal to 6 %.

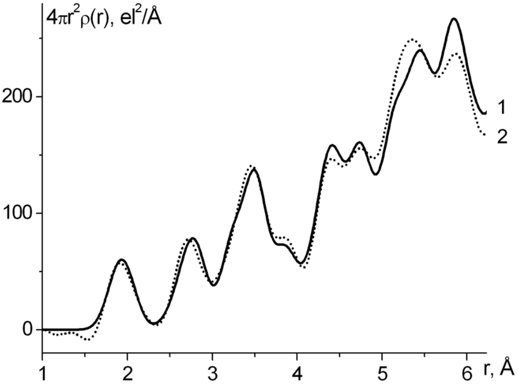

Figure 1. Model (1) and experimental (2) RDF of α-Al_2O_3.

One can see that using equation (1) it is possible to find partial components of RDF, which correspond to the distribution between certain types of atoms. The application of such model by comparison of the obtained experimental RDF with the model ones makes it possible to study in more detail both the phase composition and the local structure of highly dispersed substances, such as catalysts.

Experiment

The diffraction patterns required for the RDF calculations were obtained at the high resolution diffractometer in the Siberian Synchrotron and Terahertz Radiation Centre (Budker Institute of Nuclear Physics, Novosibirsk, Russia). The used wavelength was 0.703Å. A diffracted-beam Si monochromator was used. The scanning was performed in the 2θ range 3-145° with the step of 0.1°.

Results

Local structure of pseudoboehmite

It is usually considered that the pseudoboehmite structure differs from the boehmite one only by number of water molecules located in the interlayer space. Otherwise, the structure of the layers is assumed to be identical. In contrast to the reference data, we have found that modifications occur in the structure of the pseudoboehmite layer after insertion of additional water molecules. To determine the differences between the boehmite and pseudoboehmite structures, partial model RDF functions shown in the Figures 2 and 3 were calculated. They display the contributions of the interatomic distances within and between the layers of octahedrons (Figure 2) and the contribution of Al^{3+}-Al^{3+}, Al^{3+}-O^{2-} and Al^{3+}-OH^{1-} distances in the general model RDF (Figure 3).

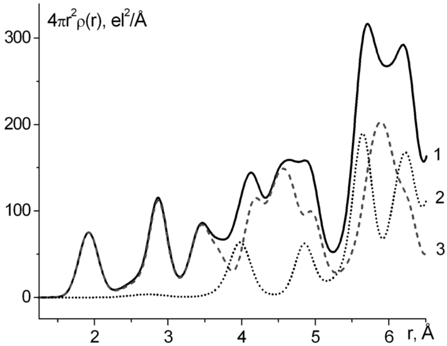

Figure 2. Overall model RDF of boehmite (1) and partial RDF for interlayer (2) and intralayer (3) distances.

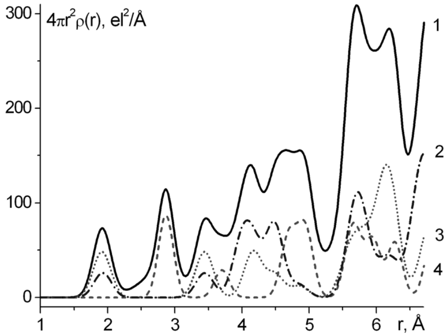

Figure 3. Overall model RDF of boehmite (1) and partial RDF for Al^{3+}–OH^{-} (2), Al^{3+}–O^{2-} (3) and Al^{3+}-Al^{3+} (4) distances.

Finally, two model RDF functions were calculated for pseudoboehmite. *Model 1* assumed it to have the boehmite structure with increased ***b*** parameter, as it was revealed by the x-ray phase diffraction analysis, and invariable intralayer distances. *Model 2* had the boehmite structure with uniform stretching along the ***b*** axis. The comparison of the experimental and calculated curves (Figure 4) shows that none of the suggested models describe changes taking place in the structure of pseudoboehmite in general. It is necessary to note that it is impossible to define a full structural model of a substance using its one-dimensional description, as RDF or PDF. We suppose that the changes in the local structure of the layers are caused by the formation of new bonds between the water molecules and the layers.

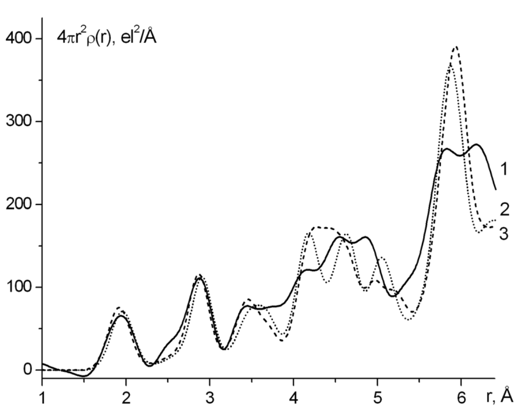

Figure 4. Experimental RDF of pseudoboehmite (1) and calculated RDF for models 1 (2) and 2 (3).

The structure of supported complex in zirconia-pillared interlayered clays (Zr-PILC)

There are a number of papers [7-9] describing the structure of zirconium polynuclear particles in solutions. It is known that the zirconyl ion in the structure of zirconium oxide chloride hydrate is present as a tetramer $[(Zr(OH)_2 \cdot 4H_2O)_4]^{8+}$ [7]. The tetramer complex is preserved, i.e. its configuration is stable, after dissolution in water [8]. At the same time, the structure of pillars in Zr-PILC is poorly investigated.

We have characterized the structure of this complex using the RDF analysis. Details of the synthesis procedure and properties of Zr-PILC are reported elsewhere [10]. Since the "general" RDF gave the information about both the support and zirconia pillars, differential RDF, shown in Figure 5, was used for the analysis.

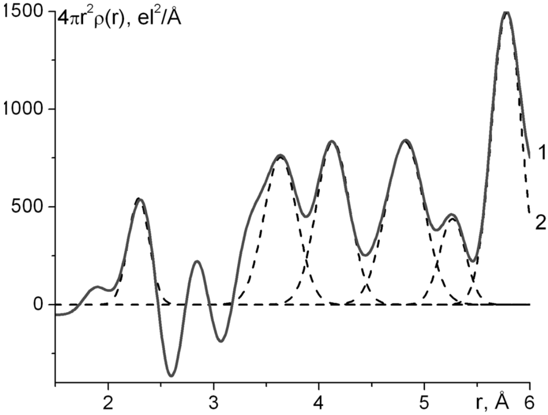

Figure 5. Differential RDF of deposited zirconia complex (1) and its decomposition to coordination peaks (2).

Derived interatomic distances and coordination numbers, and the corresponding values calculated for zirconium tetramer using structural data presented by Clearfield and Vaughan [7] are reported in Table 1.

Table 1. Interatomic distances and coordination numbers in deposited zirconia complex and zirconium tetramer (given in parenthesis).

	Zr-O	Zr-Zr	Zr-Zr	Zr-(Si, Al)	Zr-O
Assignment	Tetramer			Tetramer - Clay	
Interatomic distance, Å	2.28 (2.11-2.22)*	3.62 (3.56)	5.26 (5.03)	4.12	4.79
Coordination number	4.5 (8)	2.1 (2)	1.0 (1)	5.1	9.5

It was found that: 1) zirconium polynuclear complex is fixed in the interlayer space of the clay; 2) the structure of the complex is similar to that of the zirconium tetramer that is a characteristic structural unit for zirconium oxide chloride hydrate $ZrOCl_2 \cdot 8H_2O$; 3) chemical bonds and interatomic distances appear due to interaction between the tetramer and the clay.

Summary

The local structures of two nanomaterials are investigated by WAXS RDF. It has been found that the pseudoboehmite local structure is substantially different from the boehmite one. The structure of the zirconia complex supported by montmorillonite clay has been determined. The structure of the complex has been shown to be similar to that of the tetramer unit in $ZrOCl_2 \cdot 8H_2O$.

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