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Preparation of Nb_3O_8/MgO monoslab nanoparticles as a model of niobate oxide surfaces

Dmitrii I. Kochubey* and Vera P. Babenko

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 330 8056; e-mail: kochubey@catalysis.ru

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Monoslab HNb_3O_8 supported on MgO was obtained; the changes of the structure of HNb_3O_8 after exfoliation and after aniline adsorption were detected.

Studying the mechanism of catalytic reactions, one always faces the problem of the nature and structure of catalyst active centers. For oxide catalysts, studies of the active centers on the surface of transition metal oxides have been carried out for several decades.[1–3] Such studies are usually performed by spectral methods, because for highly dispersed oxides, the structural methods give information about volume of oxide. However, it is common knowledge that the structure of the transition metal oxides surface can significantly differ from that of the volume due to a non-stoichiometric composition, interactions with hydroxyls *etc*. Therefore, the use of structural methods for direct studying surface structures of oxide catalysts is of chief interest today.

The contribution of volume of a catalyst active component to structural data is partially removed by using supported catalysts characterized by a high surface/volume ratio. For the standard preparation of a supported catalyst, an active component is directly synthesized on the support surface. A new problem arising in this case is associated with the formation of a set of structures resulting from the interaction with a support which do not exist as massive compounds. One can solve the problem using preliminary prepared and thoroughly characterized bulk compounds, which following their splitting-up to mono-layered or monoslab forms are anchored to the surface of a support which weakly interacts with them.

Previously,[4–6] we prepared massive layered compounds which were exfoliated to a monoslab state as colloids to study the structure of an active component in the MoS_2-based hydrodesulfurization catalysts. Monoslab particles differ from the massive particles of MoS_2 in structure and electron properties. Similarly, the colloids of layered oxide complexes, primarily, clays and layered titanates and niobates, were prepared.[7–9] Such colloids are widely used for performing catalytic reactions in solutions. To study structural changes on the surface of heterogeneous oxide catalysts in detail, it is necessary to prepare stable monoslab catalysts with a known structure.

Here, we describe the synthesis and characterization of two-dimensional layered KNb_3O_8 prepared by exfoliation and supported on the oxide with a developed surface with the use of methylamine as an exfoliation agent.

The above oxide features a layered structure formed by three layers of niobium cations. Cations Nb(1) are supported on the slab surface and cations Nb(2) are in the oxide core (Figure 1). This permits easy modifications of electronic properties of the oxides to be performed by replacing K^+ with H^+ or metal cations.[10] Such oxides are used as partial oxidation catalysts, possessing strong acid sites,[11] and photocatalysts for decomposition of organics by visible light,[12] which is impossible for TiO_2 (anatase) photocatalysts. Traditionally, such catalysts are prepared from massive oxides, which limit their widespread application due to high costs. Deposition of the Nb_3O_8 monoslabs on the support surface allows one to study the mechanism of interaction between the reagents and the catalyst surface and to prepare catalysts with the developed surface and low consumption of niobium.

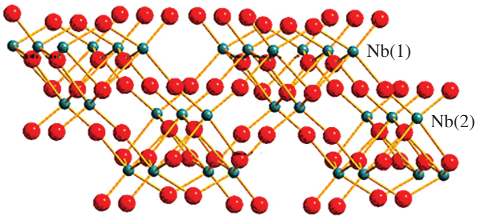

Figure 1 The structure of HNb_3O_8 slab.

The niobate supported catalysts were prepared from KNb_3O_8, synthesized from Nb_2O_5 and KCl[13] at 800 °C for 3 h.

Potassium was replaced by hydrogen according to a published procedure.[14] Protonation was carried out in a 6 N solution of HNO_3 for five days under reflux. The exfoliation of HNb_3O_8[14] was performed in an aqueous solution of $MeNH_2$. The resulting suspension was centrifuged, and the liquid part with the exfoliated HNb_3O_8 nanoparticles was mixed with MgO as a support and stirred for 3 h. The concentration of Nb_3O_8 in the catalysts was 0.3 wt%.

EXAFS was used to determine the local structures of the surrounding of massive HNb_3O_8 and Nb_3O_8 supported on MgO.

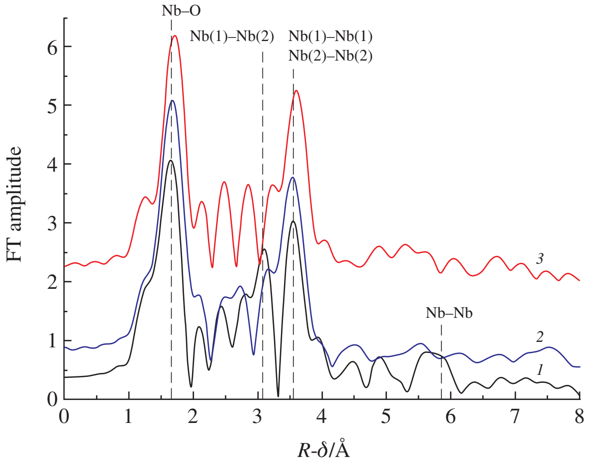

Figure 2 Radial distribution functions around Nb for (*1*) bulk HNb_3O_8, (*2*) monoslab Nb_3O_8 and (*3*) monoslab Nb_3O_8 after aniline adsorption.

Figure 2 shows that the exfoliation of the massive oxide is accompanied by significant changes in the niobium surrounding, primarily ions Nb(1) situated in the upper oxide layer. Thus, the peak intensity responsible for distances between atoms in inner and outer layers in one slab at 3.4 Å decreases, which suggests deformations in the structure of the slab and the disappearance of a peak at 6.1 Å responsible for distances between slabs in the massive oxide. Preliminary experiments on the chemisorption of aniline showed that chemisorption manifested itself as changes in the slab structure. These changes imply an increase in the Nb–O and Nb–Nb interatomic distances and a further decrease in the peak intensity responsible for the Nb(1)–Nb(2) distance. TEM or AFM cannot be used in this case because the amounts of nanoparticles are small. However, the adsorption of aniline influenced the structure of the entire volume of nanoparticles. This can be in the case when the thickness of these nanoparticles is close to that of a monoslab.

Thus, this work resulted in the the preparation of monoslab Nb_3O_8 nanoparticles supported on MgO and showed the possibility of studying changes in the surface structures upon the chemisorption of a reagent.

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