The Chemical Composition and Structure of Supported Sulfated Zirconia with Regulated Size Nanoparticles

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Abstract. A set of model skeletal isomerization catalysts – sulfated zirconia nanoparticles of controlled thickness anchored on different supports – was prepared using colloidal solutions of Zr salt on titania as support. The nanoparticles of zirconia (1-5 nm) are epitaxially connected to the support surface, with S/Zr ratio equals to 1.3-1.5. It was shown by EXAFS that nanoparticles of non-stoichiometric zirconium sulfate Zr(SO₄)₁₋ₓ, where x<0.5, are formed on the support surface. Its structure looks like half-period shifted counterdirected chains built-up by zirconium atoms linked by triangle pyramids of sulfate groups. Considering catalytic data of skeletal n-butane isomerisation at 150°C, one can suggest that these species behave as the active component of sulfated zirconia. They are formed in subsurface layers as zirconium hydroxide undergoes sulfation followed by thermal treatment.

Keywords: EXAFS, skeletal isomerization catalysts, sulfated zirconia supported on titania.

PACS: 00.02.70Hm; 30.32.30-r; 60.61.10Ht

INTRODUCTION

The composition and structure of the active component of sulfated zirconia remains as yet unclear even though a huge number of studies have dealt with the problem [1-9]. The bulk character of these catalysts, is not allowing one to extract reliable data about the active sulfated zirconia surface with conventional bulk physical and chemical methods. This problem may be solved by using a new type of sulfated zirconia catalysts, namely sulfated zirconia nanoparticles of controlled thickness which can be anchored on different supports. The advantages of these catalysts are: a great surface/volume value and a possibility to use all physical methods developed for studying the heterogeneous catalysts.

EXPERIMENTAL

Samples Preparation

A set of model catalysts were prepared using titania (Hombikat-100) as the support. The nanoparticles of zirconia (10-50 Å) are epitaxially grown on the support surface, and they are of similar dimensions and uniformly distributed on the support surface as it has been shown by HR-TEM [10]. Their catalytic activity to skeletal isomerization of n-butane is comparable with than for bulk sulfated zirconia [10]. At different Zr and S contents (as sulfate), their ratio S/Zr equals 1.3-1.5. As S content is less than 0.1 % after thermal treatment of titanium oxide at 600°C, all the detected sulfur should be related to the supported nanoparticles of sulfated zirconia [10].

EXAFS Experiments

EXAFS spectra at the K-edge of zirconium were taken by the standard method [11] at the EXAFS Station of the Siberian Center for Synchrotron Radiation (Novosibirsk, Russia). For this purpose, the solutions were placed into a cell, the thickness of which was chosen to obtain Δμ = 0.8.

For all the samples, the oscillating part χ(k) of the EXAFS spectra was analyzed as k²χ(k) in the wave number range k = 3-13 Å⁻¹. To isolate the oscillating part of the absorption coefficient, the program VIPER [12] was used. To determine structural data, spectra were simulated using EXCURV92 [13].
RESULTS AND DISCUSSION

For the EXAFS spectra of K-edge of zirconium absorption obtained with samples not exposed to air, there were three main maxima in the region below 4 Å on the curves of radial distribution of atoms (RDA) (Figure 1).

![FT Magnitude, a.u. vs. R - δ, Å](image)

FIGURE 1. RDA curves for the samples ZS/TiO₂, calcinated at 600ºC (a - not exposed to air, b – in air).

The second maximum was not observed in RDA curves for the samples in air. The first maximum was assigned to the Zr-O distance (2.1 Å). Note that no Zr-Ti distance was observed in the spectra acquired at Zr and Ti absorption edges. For this reason, distances Zr-O, Zr-S, Zr-Zr were considered, which allowed us to assign the next two maxima. In modeling, the model involving two Zr-O distances (ca. 2.1 and 2.5 Å), one Zr-S distance (ca. 3.5 Å) and no Zr-Zr distance shorter than 4 Å matched the best the experimental data. Hence, the active phase does not comprise zirconium atoms coordinated to one another through an oxygen bridge, Zr-O-Zr, of 3.6 Å in characteristic length. It seems most probable that zirconium atoms are coordinated through sulfate groups such as

\[
\text{SO}_2^–, \quad \text{O}^{2-} \quad \text{Zr}^{4+} \quad \text{Zr}^{4+}
\]

In terms of this model, the absence of the second maximum for the sample studied in air can be accounted for by hydrolysis of the Zr-O bond (2.5 Å) to form a shorter Zr-O bond. At distances longer than 4 Å, maxima are not more intense than noise that does not allow them to be reliably enough interpreted and modeled.

Thus, if one takes into consideration the component ratio in the synthesized particles, one can assume that nanoparticles of non-stoichiometric zirconium sulfate Zr(SO₄)₁ₓ, where x<0.5, are formed on the support surface (Figure 2). It is shown in the Figure that the structure looks like half-period shifted counterdirected chains built-up by zirconium atoms linked by triangle pyramids of sulfate groups. The occurrence of elongated Zr-O distance (ca. 2.5 Å) related to the coordination bond of zirconium with one of the oxygen atoms of the neighboring sulfate group also can be explained in terms of the suggested model. Supposedly, an identical structure is formed perpendicularly to the Figure plane to give rise to a kind of steps on the support surface. EXAFS studies did not detect any bonding of zirconium particles with the support surface.

![Suggested structure of active sulfate site (L – any ligand)](image)
One can propose that this surface sulfate species behaves as the active component of sulfated zirconia. They are formed in the surface layers as the zirconium hydroxide undergoes sulfation followed by thermal treatment.

ACKNOWLEDGMENTS

This work was supported by INTAS (grant no. 00-00863), CRDF (grant NO-008-X1) and RFBR (grant no. 05-03-32326).

REFERENCES

10. V.P. Shmachkova, N.S. Kotsarenko, V.V. Kanazhevskiy, G.N. Kryukova, D.I. Kochubey, J.C. Védrine, prepared for publication.