ESR study of paramagnetic sites in sulfated zirconia

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ESR spectroscopy was used to investigate paramagnetic sites in sulfated zirconia. Catalysts derived from zirconium oxide and zirconium hydroxide were studied. It was demonstrated that paramagnetic sites assigned to near-surface F-centers were formed during activation at temperatures above 573 K. The catalyst derived from zirconium hydroxide shows after activation at 873 K two types of paramagnetic sites: F-centers and Zr^{3+} sites. Both F-centers and Zr^{3+} sites in this catalyst form complexes with reagents upon n-butane or hydrogen adsorption at range of 423–523 K in contrast to paramagnetic sites of the oxide-derived catalyst.

Keywords: sulfated zirconia, ESR

1. Introduction

In the last years, sulfated oxides of polyvalent elements such as Fe, Zr and Ti attract significant interest as they are known to develop activity in skeletal isomerization of normal alkanes at low temperatures (20–100 °C). Their high activity was related to the superacid sites, that were characterized with the Hammett indicator technique [1]. Sulfated zirconia (SZ) was found to be the most active catalyst. Numerous studies dealing with its physical and chemical properties and catalytic activity in several reactions have appeared. It was found that the catalytic properties strongly depend on the concentration of sulfur, activation temperature and catalyst precursor [2].

However, infrared study of adsorbed weak bases showed that neither Brønsted nor Lewis superacid sites were present on SZ. Brønsted acid sites are weaker than those in acidic forms of zeolites HY and HX [3], and Lewis sites of pure and sulfated zirconia have similar strengths close to that of γ-Al_2O_3 [4]. These results indicate that the high activity of SZ may be related to another reason. Alkane activation may result from the one-electron transfer between adsorbed hydrocarbon molecules and surface sites. For example, Chen et al. found that benzene formed a radical cation when interacted with SZ, and it was claimed that the SZ contained strong oxidizing sites capable of ionizing aromatic hydrocarbons [2].

Alkanes may be activated by the paramagnetic sites formed during vacuum treatment. ESR study of ZrO_2 showed that paramagnetic sites assigned to F-centers were formed during desorption of chemisorbed molecules such as H_2O, CO, CO_2 [5]. Also, an ESR signal assigned to Zr^{3+} was observed after calcination of sulfated ZrO_2 [2]. Both Zr^{3+} and F-centers may be active in skeletal isomerization of alkanes. Moreover, paramagnetic sites were described in reports devoted to n-butane isomerization and were assigned to coke formation [6].

In the present study we try to characterize the formation and properties of paramagnetic sites in SZ.

2. Experimental

Two types of samples were investigated. Samples of the first type were prepared by impregnation of zirconium oxide by an aqeous solution of sulfuric acid (SZO). Samples of the second type were obtained by impregnation of zirconium hydroxide (SZH). The samples were dried first at room temperature, then at 383 K, after that they were calcined in a flow of dry air at 673 or 873 K. Zirconium hydroxide was precipitated by ammonia from an aqueous solution of $ZrO(NO_3)_2$ at pH 8–10 with vigorous stirring. The precipitate was washed and then dried at 383 K. Zirconium oxide was prepared by calcination of hydroxide at 773 K (ZO-773 sample).

The numbers marking the samples show the temperature of calcination in a flow of dry air.

Elemental analysis was conducted by the ICP method using a PST (Baird) spectrometer.

Phase composition was determined with X-ray powder diffraction using an HZG-4A (Carl Zeiss, Jena) diffractometer with a Cu anode.

BET surface area measurements were carried out at 77 K with a home-made equipment.

ESR measurements were carried out with Bruker ER-200D and EPR-V (Russia) spectrometers. Sample treatment and adsorption of gases were performed in the ESR ampoule. Mn^{2+}/MgO and $CuCl_2\cdot 2H_2O$ were used as standards for calculation of spectral parameters. All spectra were recorded with the microwave power of 0.5 mW, HF

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modulation of 1 G, sweep rate of 20 G/min and time constant of 200 ms. The experimental error in determining concentration of paramagnetic sites is approximately 30%, whereas the error in determination g values is below 0.001. All catalysts were activated at high temperatures in vacuum prior to experiments. The temperature of such treatment did not exceed the calcination temperature. Treatment conditions chosen were close to those preceding the catalytic experiments. To overcome the influence of hydrocarbons adsorption from the vacuum system (vacuum greese, oil), a liquid nitrogen trap was placed between the vacuum system and ESR ampoule. Some experiments were carried out in a perfectly dried system.

ESR measurements were carried out in the following order:

(0) The spectra of "as is" samples were recorded.

(1) The samples were evacuated at room temperature to 1.33 Pa.

(2) The samples were calcined in static air in the ESR ampoule for 60 min at various temperatures. As stated above, the temperature of treatment did not exceed the calcination temperature. The only exception was ZO-773 with treatment temperatures of 573 and 873 K.

(3) The samples were evacuated for 60 min at the treatment temperature and pressure of 0.01 Pa.

(4) The samples were cooled to recording temperature for 30 min. ESR spectra were recorded at room temperature or at 77 K.

The interactions of the samples with oxygen, hydrogen and n-butane were investigated.

Interaction of paramagnetic sites with oxygen makes it possible to distinguish between surface and bulk sites [7]. The dry air was injected into the ampoule at room temperature up to atmospheric pressure. The ESR signal of surface and near-surface sites dissappears after oxygen absorption. The signal vanishes while the paramagnetic site interacts with oxygen when the distance between paramagnetic site and oxygen molecule is 20 Å or less.

The samples were exposed to hydrogen at 1.2×10^4 Pa and 523 K for 60 min. It is well known that hydrogen slows down the deactivation of catalysts in skeletal isomerization of n-butane under these conditions [8]. The samples were evacuated at 523 K to 0.01 Pa prior to ESR measurements.

The influence of treatment by n-butane at 423 and 473 K on ESR spectra of the SZH-873 sample prepared in the above way was studied.

3. Results and discussion

The chemical and phase composition as well as BET surface areas of the prepared samples are shown in table 1. The calcination temperature strongly influences the sulfur content in the samples. Samples calcined at 673 K show nearly initial SO_3 content, while the calcination at 873 K leads to partial removal of sulfur.

Table 1
Phase and chemical composition, catalyst precusor and S_{BET} of the samples studied.

Sample	Catalyst precursor	SO_3 (wt%)	S_{BET} (m^2/g)	Crystalline modification
SZH-673	hydroxide	4.2	170	amorphous
SZH-873	hydroxide	3.9	110	tetragonal ZrO_2
SZO-673	oxide	2.8	70	monoclinic ZrO_2
SZO-873	oxide	1.9	80	monoclinic ZrO_2

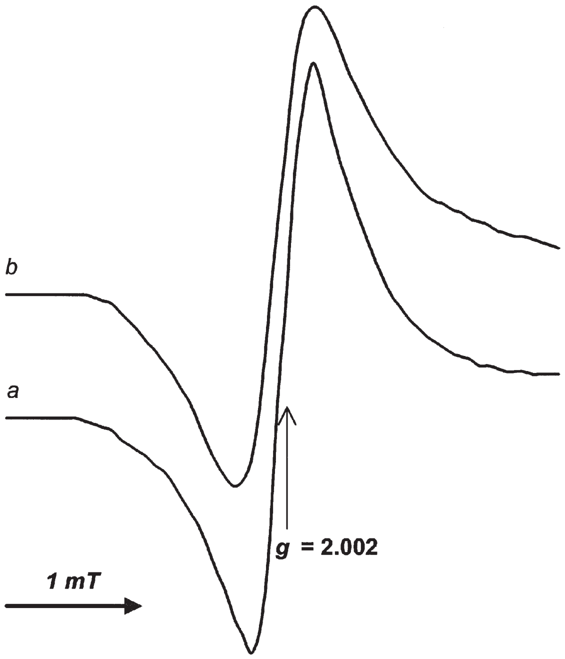

Figure 1. ESR spectra of SZH-873 after activation at 673 K (a) and after exposure to hydrogen at 523 K (b).

The XRD patterns show only ZrO_2 reflections (monoclinic for the SZO series and tetragonal for SZH-873) in the whole range of sulfur contents and calcination temperatures. The formation of crystalline zirconium sulfate does not occur. The SZH-673 sample is found to be X-ray amorphous.

As-prepared samples as well as those evacuated at room temperature (steps 0–1) show absence of paramagnetic sites. All samples change color after vacuum treatment (steps 3–4). Originally white samples became gray and ESR signals appeared. All signals vanished when dry air was introduced at room temperature, indicating the localization of these sites on the surface or in the near-surface layer about 20 Å thick. Therefore, the concentration of paramagnetic sites was referred to unit of the surface area.

ESR spectra of all samples studied show a symmetrical singlet with $g = 2.002$–2.003 after treatment step 4 (see figure 1). ESR spectral parameters and the concentrations

Table 2
Parameters and concentrations of paramagnetic sites formed during various treatments.

Sample	ZO-773				SZO-673		SZO-873				SZH-673		SZH-873	
Treatment[a]	v.t. 573 K	h.t.	v.t. 873 K	h.t.	v.t. 673 K	h.t.	v.t. 673 K	h.t.	v.t. 873 K	h.t.	v.t. 673 K	h.t.	v.t. 673 K	h.t.
Concentration of paramagnetic sites ($\times 10^{15}$ g^{-1})	1.5	0.8	0.17	0.22	10	14	50	18	65	75	86	22	7.8	6.6
Concentration of paramagnetic sites ($\times 10^{13}$ m^{-2})	1.36	0.72	0.15	0.2	14.3	20.0	62.5	22.5	81.3	93.8	50.5	12.9	7.1	6.0
Spectral parameters														
Width (G)	6.8	6.8	0.7	0.7	4.6	4.6	5.4	5.7	8.7	8.3	5.5	5.8	5.0	5.0
g	2.003	2.003	2.003	2.003	2.002	2.002	2.002	2.002	2.002	2.003	2.003	2.003	2.002	2.002

[a] v.t.: vacuum treatment, h.t.: hydrogen treatment.

Table 3
Parameters and concentrations of paramagnetic sites formed during various treatments of the ZSH-873-873 sample.

Treatment[a]	v.t. 873 K		h.t. 523 K		b.t. 473 K	b.t. 423 K	
Signal		B_1	B_2	B_1	B_3	B_3	B_1
Concentration of paramagnetic sites ($\times 10^{15}$ g^{-1})	10.0	5.0	13.1	1.2	14.8	13.6	0.8
Concentration of paramagnetic sites ($\times 10^{13}$ m^{-2})	9.1	4.6	11.9	1.1	13.5	12.7	0.7
Spectral parameters							
Width (G)	3.9	3.3	4.0				
g	2.002	$g_\perp = 1.980$ $g_\parallel = 1.976$	$g_\perp = 2.001$ $g_\parallel = 2.003$	$g_\perp = 1.980$ $g_\parallel = 1.976$	$g_\perp = 2.000$ $g_\parallel = 2.005$	$g_\perp = 2.000$ $g_\parallel = 2.005$	$g_\perp = 1.980$ $g_\parallel = 1.976$

[a] v.t.: vacuum treatment, h.t.: hydrogen treatment, b.t.: n-butane treatment.

of paramagnetic sites formed are shown in table 2. The intensity of the singlet changes after exposure to hydrogen, while its g value does not change.

The SZH-873 sample activated at 873 K (SZH-873-873) shows an additional signal with axial symmetry with $g_\perp = 1.980$, $g_\parallel = 1.976$ (signal B_1) besides the singlet (figure 2). After exposure to hydrogen, the singlet vanishes, the intensity of B_1 decreases and a new anisotropic signal with $g_\perp = 2.001$ and $g_\parallel = 2.003$ appears (figure 2, signal B_2).

The spectra of the SZH-873-873 sample exposed to n-butane depend on temperature of exposure. At 423 K, the singlet vanishes, the intensity of B_1 drastically decreases and a new signal with $g_\perp = 2.000$ and $g_\parallel = 2.005$ appears (signal B_3). At 473 K, both signals disappear and the intensity of B_3 does not change (figure 2).

It is necessary to discuss each group of signals described above since they correspond to different paramagnetic sites.

3.1. Singlets with g values close to g_e

Our experimental conditions prevent formation of coke due to hydrocarbons from the vacuum system. ESR signals with $g = 2.003$ were observed also after calcination of different oxides with preadsorbed organic molecules.

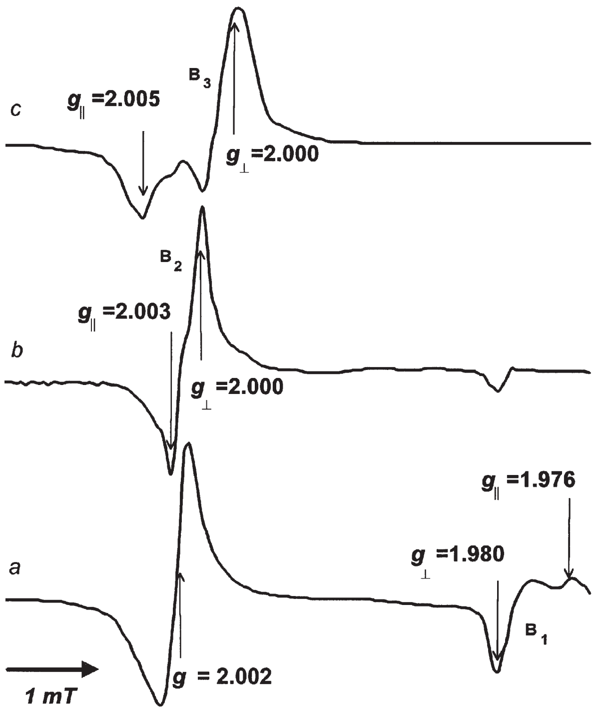

Figure 2. ESR spectra of SZH-873 after activation at 873 K (a), after exposure to hydrogen at 523 K (b) and to n-butane at 473 K (c).

These signals were assigned to coke formation. In the case of sulfated zirconia such signals were found to disappear after calcination at 675–823 K. In the samples studied these signals do not disappear after calcination at 875 K. Therefore, symmetrical singlets with $g = 2.002$–2.004 in the spectra of sulfated zirconia should not be assigned to coke.

Similar signals were observed earlier in ESR spectra of ZrO_2 prepared by calcination of zirconium hydroxide in vacuum [5] and in nanoparticles of ZrO_2 after thermal treatment [9]. They were attributed to F-centers, i.e., electrons stabilized in oxygen vacancies. The color change due to formation of F-centers was also observed [5].

The tetragonal-to-monoclinic phase transition in ZrO_2 samples under study accompanied by a decrease in the concentration of F-centers occurs at a lower temperature compared to literature data. This transition was reported to take place at 973 K [5]. In our case, concentration of F-centers diminishes at calcination temperatures below 873 K, and the samples calcined at 873 K are mainly monoclinic. This difference may be explained by the strong influence of catalyst genesis on the phase transition [5].

In the sulfated zirconia, the signals with $g = g_e$ may be attributed to F-centers as well as to SO_3^- groups. The ESR spectrum of SO_3^- represents a symmetric line with $g = 2.0036$ [10]. It is possible, however, to distinguish between F-centers and SO_3^- groups. After exposure of the samples to oxygen at the calcination temperature, the signal vanishes and a new signal assigned to O_2^- ($g_1 = 2.003$, $g_2 = 2.01$ and $g_3 = 2.03$) appears after evacuation at room temperature. O_2^- is formed via the reaction of oxygen with surface paramagnetic sites. Electron affinity of the oxygen molecule (less than 0.44 eV) is much lower than that of sulfur oxides (more than 1.2 eV) [11]. Therefore, electron transfer from SO_3^- to O_2 is not possible. This fact confirms that the singlet with $g = 2.002$–2.004 belongs to F-centers.

The most probable way of formation of F-centers is desorption of various surface groups, mainly sulfate and hydroxyl groups, during vacuum treatment. Another possible way is the removal of lattice oxygen accompanied by reduction of sulfated zirconia.

As shown in table 2, modification of zirconia with sulfate anions results in an increase in the concentration of F-centers. This concentration depends on the preparation method and calcination temperature. An increase in the calcination temperature for the samples derived from zirconium oxide (SZO series) leads to an increase in the concentration of F-centers at the same temperatures of activation (673 K). In contrast, the SZH-873 sample activated at 673 K is characterized with a lower concentration of F-centers than SZH-673, after activation at the same temperature. Such a difference may be explained by the difference in the concentration of point defects stabilizing a free electron.

3.2. Anisotropic signals with $g < g_e$

The peculiar feature of the SZH-873-873 sample is the formation of paramagnetic sites with $g_{\|} = 1.976$ and $g_{\perp} = 1.980$ after vacuum treatment (signal B_1). A similar signal in ESR spectra of sulfated zirconia-based catalysts showing activity in the skeletal isomerization of n-butane was reported earlier and was assigned to Zr^{3+} [2,6].

Exposure of the SZH-873-873 sample to hydrogen or n-butane results in an interaction of paramagnetic sites with reagents and appearance of the new asymmetric signal with $g_{\perp} = 2.001$ and $g_{\|} = 2.003$ (hydrogen) and $g_{\perp} = 2.000$ and $g_{\|} = 2.005$ (n-butane). Thus, both types of paramagnetic sites form complexes with adsorbed molecules. According to literature data, the relation between $g_{\perp}$ and $g_{\|}$ of Zr^{3+} ($g_{\perp} > g_{\|}$) is typical for a d^1 ion in the cubic crystalline field with tetragonal distortion. This relation for B_2 and B_3 signals was found to be inverse ($g_{\perp} < g_{\|}$), which may be related to significant contribution of the covalent bond to complexes formed.

4. Conclusions

This study showed that paramagnetic sites formed on the surface of sulfated zirconia during vacuum treatment are not related to coke formation. Modification of zirconia with sulfate anions increases the number of paramagnetic sites formed, the extent of this increase being determined by the preparation method. These paramagnetic sites are located on the surface or in the near-surface layer and are accessible for reagents and interact with hydrogen and n-butane.

The highest concentration of F-centers formed during vacuum treatment was observed in the SZO series. Formation of Zr^{3+} occurs in the SZH-873-873 sample only. While interacting with hygrogen and n-butane, these species are converted into paramagnetic complexes of Zr^{3+} with reagent molecules. It is known that only hydroxide-derived catalysts (SZH series) exhibit activity in skeletal isomerization of n-butane [12]. These facts lead to the hypothesis that the first step of isomerization is the interaction of Zr^{3+} with the n-butane molecule, so Zr^{3+} plays the key role in the reaction.

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