

Development of an ESR technique for testing sulfated zirconia catalysts

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Abstract

Sulfated zirconia catalysts active in the isomerization of *n*-butane have been synthesized by sulfating crystalline monoclinic and cubic zirconia supports precalcined at 700°C. Strong acceptor sites capable of ionizing chlorobenzene have been observed on all active catalysts irrespective of the crystalline structure. A simple instrumental technique based on the chlorobenzene adsorption has been suggested for probing sulfated zirconia catalysts. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Sulfated zirconia; *n*-Butane isomerization; ESR; Acceptor sites

1. Introduction

Sulfated zirconia materials have recently attracted considerable attention of researchers as potential catalysts for isomerization of lower alkanes [1–4]. Despite intensive studies, there is no universally accepted theory as sites of what type account for the unique catalytic activity of sulfated zirconia. Recent studies of the strength of Brønsted and Lewis acid sites do not support the early hypothesis on the superacidity of such systems [3]. Meanwhile, it has been reliably proven that active sulfated zirconia catalysts have uniquely strong one-electron acceptor sites [5]. Surface acceptor sites of different strength are usually revealed by the ability of catalysts to

initiate one-electron oxidation of adsorbed aromatic compounds with the formation of primary radical cations and products of their transformations.

It used to be considered [1–3] that sulfated zirconia prepared by impregnation of crystalline zirconia is not active in the isomerization of alkanes. This fact was naturally associated with the difference of the crystalline structure as traditional sulfated zirconia catalysts had tetragonal structure whereas calcined pure ZrO₂ was monoclinic. Low-temperature tetragonal and cubic ZrO₂ structures can be stabilized by doping with different cations, such as Mg²⁺, Y³⁺, Sc³⁺, Ca²⁺, etc. [6]. Only recently first publications appeared, which describe the preparation of monoclinic sulfated zirconia catalysts active in the isomerization of alkanes [7,8].

In the present communication, the first results on development of a simple ESR technique for testing sulfated zirconia catalysts and the syn-

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thesis of active sulfated zirconia catalysts by the impregnation of monoclinic ZrO_2 and binary zirconium–calcium oxide compositions with the crystalline structure of cubic ZrO_2 are reported.

2. Experimental

Zirconium dioxide and zirconium–calcium oxide compositions were prepared by precipitation from solutions of corresponding salts with bases at definite pH and temperature followed by washing, drying and calcination according to Ref. [9]. The final thermal treatment was calcination at 700°C in dry air flow for 4 h. The phase composition and surface area of the samples prepared are presented in Table 1. Then, the samples were subjected to incipient wetness impregnation with ammonium sulfate (Fisher, Certified A.C.S.) to yield nominal SO_3 loading of 8 wt.%, dried at 120°C overnight and calcined in a furnace at 600°C for 2 h. The sulfating procedure had practically no effect on the specific surface area of the samples. Sulfated samples will be hereafter designated as SZC-*N*, where *N* is the molar CaO concentration in the initial compositions.

A sample of sulfated zirconia prepared according to a traditional method (denoted as SZ) was used for comparison. Hydrous zirconia was precipitated from an aqueous solution of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Alfa Aesar, 99.9% metals basis) with aqueous ammonium hydroxide (Fisher, 28–30 wt.%) added dropwise under continuous

stirring up to pH ~ 10 . The precipitate was filtered, thoroughly washed with hot distilled water, dried at 120°C overnight, and subjected to incipient wetness impregnation with ammonium sulfate (Fisher, Certified A.C.S.) to yield nominal sulfur loading of 17 mol%. The resulting material was dried at 120°C overnight and calcined at 600°C in a furnace for 2 h. This catalyst had the surface area of 100 m^2/g and was shown to have high activity in the isomerization of *n*-butane [10].

The catalytic activity in *n*-butane isomerization was tested in an integral flow reactor in the kinetic region at 200°C and *n*-butane space velocity 600 h^{-1} . One cubic centimeter of a catalyst with the grain size in the range of 0.25–0.5 mm was used. Prior to the catalytic tests, the samples were subjected to a standard pretreatment. They were calcined in situ in a dry air flow at 500°C for 1 h, and cooled down to the reaction temperature. Then, the reactor was purged with nitrogen for 15 min prior to the introduction of *n*-butane. The reaction products were analyzed in a gas chromatograph with the thermal conductivity detector. Besides isobutane, which was the major product, methane, propane and pentane were detected.

XRD spectra were recorded on a URD-6 diffractometer with Cu K_α irradiation. Elemental cell parameters were determined with the precision of $\pm 0.002 \text{ \AA}$.

X-band ESR spectra were recorded at room temperature on an ERS-221 spectrometer. Prior to adsorption of chlorobenzene (Reakhim, For chromatography), the catalysts (0.1 g) were activated in quartz ampoules in air at 500°C for 2 h.

Table 1
Phase composition and surface area of zirconium–calcium oxide compositions calcined at 700°C

Sample	CaO concentration (mol%)	Surface area (m^2/g)	ZrO_2 structure (<i>a</i> , \AA)
ZC-0	0.0	65	Monoclinic
ZC-10	10.0	110	Cubic: <i>a</i> = 5.113
ZC-25	25.0	90	Cubic: <i>a</i> = 5.128
ZC-49	48.6	70	CaZrO_3^a , cubic: <i>a</i> = 5.150

^aPredominant crystalline phase.

3. Results and discussion

All the catalysts prepared by sulfating crystalline monoclinic zirconia and zirconium–calcium compositions with cubic ZrO_2 structure showed reasonable catalytic activity in *n*-butane isomerization (Fig. 1, solid line). The weight-

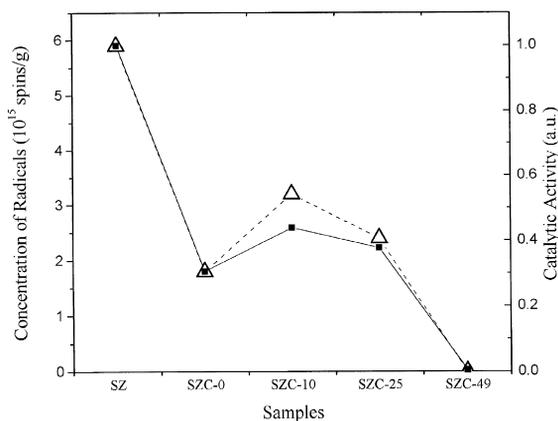


Fig. 1. Comparison of the specific catalytic activity of sulfated zirconia in *n*-butane isomerization with the concentration of radical particles formed in 1 h after the adsorption of chlorobenzene.

normalized activity of the sulfated zirconia sample prepared according to the standard procedure (SZ) was approximately twice higher than that of SZC-10, which exhibited the highest activity among the sulfated zirconium–calcium compositions. All the catalysts, except SZC-49, had practically the same selectivity to isobutane exceeding 90% and gradually increasing with time on stream.

All samples were calcined at 700°C and well crystallized prior to the sulfating procedure (Table 1). The latter resulted only in the surface modification of the oxide systems leading to the formation and stabilization of surface structures accounting for the acidity and catalytic activity without modification of the crystalline structure, except for the appearance of small amounts of CaSO_4 . This proves that, in addition to traditional tetragonal sulfated zirconia catalysts, $\text{SO}_4^{2-}/\text{ZrO}_2$ samples with monoclinic and cubic crystalline structure also may exhibit high catalytic activity in the isomerization of alkanes at low temperatures. Only SZC-49 was practically not active. Its main crystalline phase before the sulfur introduction was CaZrO_3 perovskite. It was destroyed after the sulfating procedure without formation of catalytically active sites.

Earlier, we have shown that active sulfated zirconia catalysts have the strongest one-elec-

tron acceptor sites among the known oxide systems and observed a qualitative correlation between the strength of the acceptor sites and the catalytic activity [5]. It was supposed that bimolecular light-induced disproportionation of pentane was initiated by the excitation of donor–acceptor complexes formed by alkanes adsorbed on such sites, with unstable radical cations formed as intermediates. However, *n*-pentane isomerization on sulfated zirconia is known to proceed predominantly via monomolecular mechanism [3], and we failed to find any evidences of the involvement of strong acceptor sites in it [5]. Meanwhile, as the bimolecular mechanism predominates in *n*-butane isomerization in the absence of hydrogen [3,11], it seems natural to check if there is any correlation between the concentration of strong acceptor sites and the isomerization activity.

The adsorption of various aromatic molecules with different ionization potentials is widely used for investigation of surface acceptor sites of different strength [12,13]. The stronger the acceptor sites, the weaker donors should be used for evaluation of their concentration.

Chlorobenzene appeared to be the most suitable probe molecule for testing the strongest acceptor sites of sulfated zirconia catalysts. It is not ionized to yield paramagnetic products after adsorption on weaker acid catalysts such as zeolites, fluorine- and chlorine-modified alumina, sulfated titania and alumina, catalytically inactive sulfated zirconia. Aromatic molecules with lower ionization potentials that have been successfully used for investigation of weaker acid catalysts [13] proved to be less informative in this case as the concentration of the radical particles formed after their adsorption on active sulfated zirconia catalysts was primarily a function of the surface area and showed no correlation with the catalytic activity.

A very good correlation (Fig. 1) between the concentration of radicals formed after the chlorobenzene adsorption (dashed line) and the activity of the catalysts in *n*-butane isomerization (solid line) has been observed. Among the

catalysts synthesized by sulfating crystalline oxides, the highest concentrations of acceptor sites capable of ionizing chlorobenzene was observed for zirconium–calcium compositions containing 10% CaO. Their concentration on the traditional sulfated zirconia catalyst SZ was approximately 1.5 times higher. No strong acceptor sites were observed on SZC-49. These results seem to support the idea [4,5] that the *n*-butane isomerization via the bimolecular mechanism is initiated by the charge transfer on strong surface acceptor sites.

This method suggested for testing the concentration of strong acceptor sites based on the formation of radical cations after adsorption of chlorobenzene seems to be an easy instrumental technique for probing sulfated zirconia catalysts and predicting their isomerization activity. It has been successfully used by us for investigation of a large number of sulfated zirconia catalysts.

The results obtained in this study prove that strong acceptor sites can be formed not only on tetragonal sulfated zirconia samples [5] but on monoclinic and cubic ones as well, and there is a correlation between their presence and concentration, and the catalytic activity in butane isomerization. Now, there is no doubt that only specific structure of surface sites accounts for the unique catalytic activity of sulfated zirconia catalysts, whereas tetragonal structure of zirconia crystallites is not required.

Binary zirconium–calcium oxide compositions reported in this paper are important not only from the fundamental point of view as the first example of catalysts with cubic ZrO₂ structure active in butane isomerization. They also

seem to be promising materials for synthesis of real catalysts as the introduction of calcium in ZrO₂ stabilizes high surface area of the support. Meanwhile, the possibility for preparation of active catalysts by sulfating crystalline zirconia supports may be employed for the catalyst regeneration after complete loss of activity due to the sulfur loss. One can also expect such catalysts to be more stable than traditional sulfated zirconia materials.

Acknowledgements

This work was supported in part by Russian Foundation for Basic Research under Grants 97-03-32566 and 96-15-97560.

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