

## Content of sulfates and their stability – key factors determining the catalytic activity of sulfated zirconia catalysts

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(Received 27 October 2006)

**Abstract:** Two series of sulfated zirconia catalysts were synthesized from various precursors using mono- or multi-step sequence preparations under laboratory conditions. Their activities/selectivities in the isomerization reaction of *n*-hexane were correlated to their textural, structural and morphological properties. The slightly higher activity of a commercially sulfated Zr(OH)<sub>4</sub>-based catalyst is in agreement with the differences in the content of SO<sub>4</sub><sup>2-</sup> ions and their thermal stability, textural and structural properties, *i.e.*, crystallite size and possible imperfection of the incorporation of sulfate groups in the multi-step synthesis of the catalyst having a nitrate origin. The employment of H<sub>2</sub> as the carrier gas resulted in no catalytic activity, regardless of the catalyst precursor, preparation method and calcination temperature. When the isomerization reaction was performed under He, the relatively short life-times of all catalyst samples were caused by fast deactivation due to coking in the absence of H<sub>2</sub>.

**Keywords:** sulfated zirconia, sulfate contents, isomerization of *n*-hexane, activity, textural, structural and morphological properties

### INTRODUCTION

The selective transformation of straight-chain hydrocarbons to high octane number isomers is of great industrial importance, particularly for gasoline blending. Solid acids have become very popular as catalysts for the isomerization of alkanes. Among them, sulfated zirconia (SZ), alone as well as together with promoters, represents a promising solution in view of both activity and stability. Namely, its activity is better than those of zeolite-based catalysts and its poison and water resistance makes the position of SZ somewhere between the previous and traditional chlorinated Pt–alumina catalysts.<sup>1</sup>

Zirconia modified with sulfate ions may behave as a solid acid depending on its preparation method, differing in the synthesis and activation parameters.

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doi: 10.2298/JSC0707679Z

These are temperature, pH, duration of precursors aging, nature of sulfating agents, *etc.*<sup>1,2</sup> In addition, the order and number of steps in the preparation sequence can affect the final textural and structural features of the catalyst.<sup>3</sup>

The catalytic activities of SZ are found to be different depending on both the pre-calcination and calcination temperature, indicating the importance of an optimal activation temperature for the increase in acidity.<sup>4,5</sup> The correlation of the calcination temperature with activity indicated the importance of the tetragonal phase of SZ and its acidic behavior.<sup>6</sup>

In the present study, two series of SZ catalysts were prepared from different precursors by related preparation methods following calcination. The aim of the work was to link the different amount of sulfates with stability in terms of phase transformation, as well as to compare the catalytic performances of a catalyst fully synthesized under laboratory conditions, including sulfation with another one obtained from a sulfated commercial precursor. Both precursors were calcined at three different temperatures and their characterization was performed in respect to textural and structural properties. These were correlated to catalytic activity tested in the isomerization of *n*-hexane reaction.

#### EXPERIMENTAL

Two SZ catalysts were prepared from different precursors: 1) from a commercially sulfated zirconium(IV)-hydroxide (Aldrich Co.) by its calcination (catalyst 1), and 2) from zirconium(IV)-oxynitrate (Aldrich Co.) by the precipitation/impregnation method following calcination (catalyst 2). For the preparation of the latter, a watery solution of Zr(IV)-oxynitrate (15 mass %) was permanently stirred at room temperature for 2 h, keeping the pH 9.5 by the addition of 25 % NH<sub>4</sub>OH as the precipitating agent. The obtained Zr(IV)-hydroxide was aged for 2 h, filtrated, rinsed with distilled water several times and finely dried at 110 °C for 24 h. The subsequent sulfation of the hydroxide was realized by impregnation of the dried solid with the desired volume of sulfuric acid (0.5 M H<sub>2</sub>SO<sub>4</sub>) for the intended sulfur content of 3 mass % S. Finally, both precursors samples were dried at 110 °C for 3 h and then calcined at either 500, 600 or 700 °C for 3 h in an air flow of 20 ml min<sup>-1</sup>. In total, six SZ catalyst samples were obtained, denoted as 1 and 2 depending on the precursor type, followed by A, B or C indicating the applied calcination temperature, 500, 600 or 700 °C, respectively. The accomplishment of the sulfation of the samples, *i.e.*, the amount of SO<sub>4</sub><sup>2-</sup>, was checked by the TG method employing a Baehr STA 503 instrument in the temperature range 30 – 1000 °C using a temperature ramp of 10 °C min<sup>-1</sup>.

Surface area and porosity measurements were carried out on a Micromeritics ASAP 2010 apparatus following low temperature N<sub>2</sub> adsorption/desorption and using the BET procedure. Before each measurement, the sample was outgassed at 200 °C for 1 h in order to desorb impurities on its surface. The crystal structure was determined by X-ray diffraction analysis (XRD) using a Philips APD-1700 diffractometer, at 40 kV and 55 mA. Powders of samples were packed in a 20×20 mm polymer frame and exposed to radiation in the 2θ angle range from 20 – 70°. The average crystallite sizes were estimated from the full width at half-maximum employing the Scherrer equation. The surface morphology of catalysts samples previously coated with gold was investigated by scanning electron microscopy (SEM) using a Jeol JSM-6460LV instrument with an acceleration voltage of 25 kV.

The activity testing was carried out on the *n*-hexane isomerization reaction at atmospheric pressure and 300 °C, using a space velocity 6·10<sup>-2</sup> mmol *n*-C<sub>6</sub> g<sup>-1</sup> min<sup>-1</sup>. The molar ratio of carrier

gas (He or H<sub>2</sub>) and *n*-C<sub>6</sub> was 15.5 at a constant partial pressure of *n*-C<sub>6</sub> of 60.5 mbar. The activation of 0.5 g of fresh sample was performed *in situ*, in a synthetic air flow of 20 ml min<sup>-1</sup> at 500 °C for 1 h. The reactor effluent was analyzed by gas chromatography, a HP 5890 equipped with a Pona column and a FID detector. The catalyst activity was calculated as the conversion of *n*-hexane and the selectivity as the sum of the isomerized hydrocarbons. Finally, the yields of the isomers were calculated as the product of conversion and selectivity to C<sub>6</sub>-isomers.

#### RESULTS AND DISCUSSION

The part of X-ray diffractograms of catalysts 1 and 2 including the most characteristic peaks of SZ phases are shown in Fig. 1. The corresponding phase composition and crystallite size, calculated from the XRD-line broadening, are presented in Table I, together with the textural properties of the samples. The prevailing zirconia phase in the samples was estimated from the intensities of the XRD lines of the tetragonal and two monoclinic phases by a procedure given previously.<sup>7</sup> The related catalytic activity performances are given in Table II.

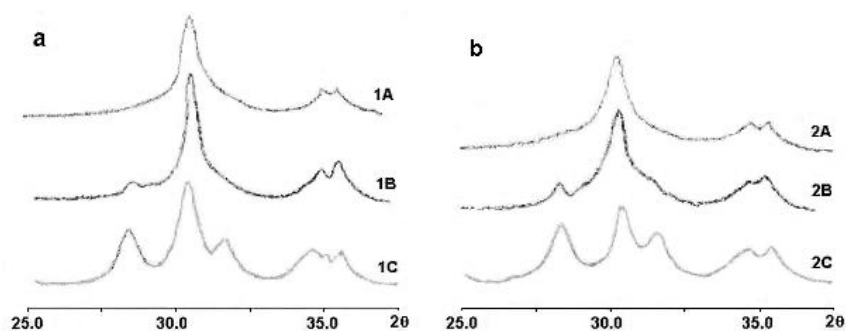


Fig. 1. XRD Pattern of catalysts 1 (a) and 2 (b) after calcination at 500 °C (A), 600 °C (B) and 700 °C (C).

TABLE I. Textural properties, phase composition and crystallite size

Sample	Surface area m <sup>2</sup> g <sup>-1</sup>	Mean pore diameter nm	SO <sub>4</sub> <sup>2-</sup> mass loss %	Crystallite size* / nm	
				Tetragonal phase	Monoclinic phase
1A	130	2.3	5.0	10.3 (+)	–
1B	103	3.3	3.8	11.8 (+)	11.7
1C	69	5.7	2.1	12.7 (+)**	13.7 (+)**
2A	144	3.2	2.6	8.2 (+)	–
2B	117	4.4	2.6	12.7 (+)	9.1
2C	89	6.0	2.6	13.7	10.2 (+)

\*Prevailing phase is denoted with “+” in parentheses, \*\*Equal fractions of both phases

The XRD patterns of samples of series A (samples 1A and 2A in Figs. 1a and 1b) show the presence of only tetragonal SZ phases at  $2\theta = 30.30^\circ$ , despite the precursor type and the preparation method of the catalysts. On increasing the

calcination temperature to 600 °C (series B), a new peak appearing at  $2\theta = 28.25^\circ$  may be assigned to the monoclinic SZ phase, however its contribution is still minor. A further increase of the calcination temperature to 700 °C (series C) resulted in an abundance of monoclinic phases (peaks at  $2\theta = 28.25^\circ$  and  $2\theta = 31.25^\circ$ ), which finally prevailed, but only in the case of catalyst 2 tailored in the laboratory (sample 2C in Fig. 1b, and Table I).

TABLE II. Catalytic performances of the SZ samples calcined at various temperatures in the isomerization of *n*-hexane at 300 °C

Sample	<i>X</i> %	Selectivity to <i>i</i> -C <sub>6</sub> / %	Yield to <i>i</i> -C <sub>6</sub> / %	Hydrocarbons composition of the products / %			
				$\Sigma$ <i>i</i> -C <sub>4</sub> , <i>i</i> -C <sub>5</sub>	$\Sigma$ Cracked C-H	Mono-branched isomers	Di-branched isomers
1A	50.4	12.0	6.0	46.8	41.2	9.5	2.5
1B	22.1	13.5	3.0	39.5	46.7	11.2	2.3
1C	0	–	–	–	–	–	–
2A	40.0	10.3	4.1	41.9	47.7	8.4	1.9
2B	10.5	21.5	2.3	35.2	42.6	18.5	3.0
2C	8.5	39.2	3.3	30.2	29.7	22.7	16.5

An increase of the height/width ratio of the peaks corresponding to both SZ phases in the XRD patterns accompanied the phase transformation, confirming the increase the crystallite size as an indication of the sintering process (Table I). Although the prevailing phase and crystallites sizes of both series of catalysts samples were similar, catalyst 1 was more stable regarding the transformation of the favorable tetragonal phase and retained its smaller crystallites sizes when exposed to higher calcinations temperatures. The activity of the catalysts samples (Table II) are in accordance with a conclusion of the importance of the tetragonal SZ phase in the isomerization reaction of *n*-hexane.<sup>8</sup> The importance of the presence of sulfate groups attached to tetragonal zirconia for the formation of an active SZ catalyst was reported previously.<sup>9</sup> As can be seen from Table I, higher amount of sulfates in the samples of catalyst 1 seems to have been beneficial for retarding the transformation from the tetragonal to the monoclinic phase.

The obtained values of the BET surface areas (Table I) are higher than those obtained by other authors.<sup>5,10</sup> As expected, the BET surface areas declined and the mean pore diameters increased for both catalyst series with increasing calcination temperature. The high BET surface area of sample 2A is in accordance with it having the smallest crystallite size, which obviously influenced its activity/selectivity performances (Table II).

The XRD (Fig. 1) and SEM (Fig. 2) results indicate to the nano-structure of both investigated catalysts. The SEM studies, however, support the assumption based on the dependence of the particle size on the precursor type, preparation procedure and sulfates content. Namely, the SEM microphotographs reveal the

presence of nano-sized particles in both samples originating from the commercial precursor (catalyst 1) after calcination at the higher temperatures, since the majority of the particles were smaller than 100 nm (Figs. 2a and 2b). In contrast, the particles of the catalyst 2 samples, having the same temperature history as catalyst 1, are of different morphology and definitely of larger size (Figs. 2c and 2d). The difference in the particle size and their morphology may be attributed to the different procedures of preparation, *i.e.*, only the calcination step for the preparation of catalyst 1 *versus* a number of steps in the sequence of the synthesis of catalyst 2. The specific change of the morphology observed for both catalysts samples exposed to the highest temperature treatment, reflected in the agglomeration of individual particles to aggregates of larger sizes, confirms the sintering process (series C) (Figs. 2b and 2d).

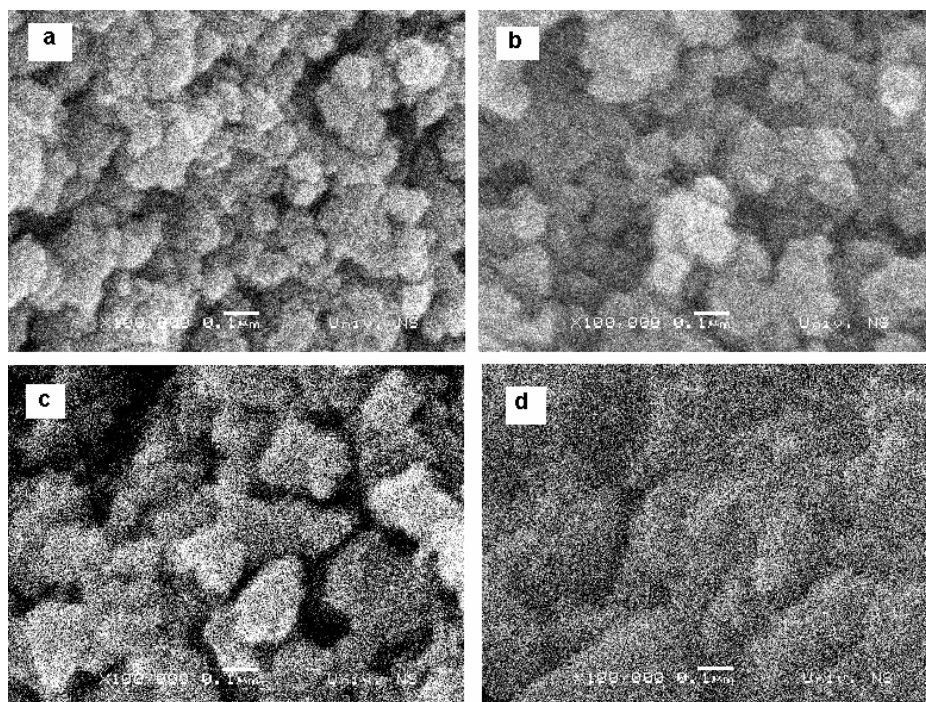


Fig. 2. SEM Images of catalyst 1 calcined at 600 °C (a) and 700 °C (b), and catalyst 2 calcined at 600 °C (c) and 700 °C (d) ( $\times 100,000$ ).

The discussed structural and textural properties of the catalysts have an impact on the corresponding activity and selectivity results of the samples. In experiments performed in He as carrier gas, the catalysts were quite active at the very beginning of the time-on-stream (TOS), but a fast deactivation followed. The reaction tests were performed for as long as activities were recorded (Fig. 3.), *i.e.*, the TOS changed from 30 – 115 min depending on the applied cata-

lyst. The catalyst samples from series A calcined at the lowest temperature exhibited the highest conversions and the longest TOS. The relatively short life-time of all the catalyst samples caused by the fast deactivation can be attributed to the process of coking in the absence of  $H_2$ . This was even visually evident by the black color of the samples at the end of the TOS and was proved by the successful regeneration of the deactivated catalysts in an air flow at  $500\text{ }^\circ\text{C}$  for 2 h. Using  $H_2$  as the carrier gas in the same test-reaction-set-up resulted in no catalytic activity, regardless of the catalyst precursor, amount of sulfates, preparation method and calcination temperature. In contrast, some initial activity of SZ under  $H_2$  was claimed previously but with poor isomerization selectivity.<sup>11</sup>

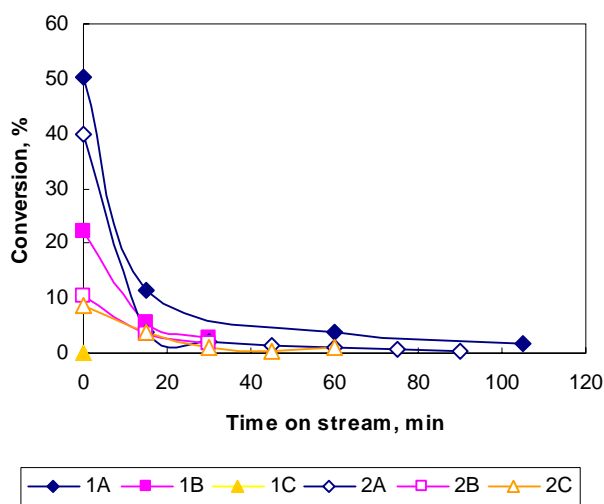


Fig. 3. *n*-Hexane conversion as a function of time-on-stream using He as the carrier gas.

The obtained results of *n*-hexane conversion (Table II) indicate catalysts of similar activities, with significantly higher yield attributed to series A compared to samples exposed to the higher calcination temperatures (series B and C). This is in particular the case with catalyst 1, which showed no activity after calcination at  $700\text{ }^\circ\text{C}$ . This may be connected to sample 1C having the lowest surface area of all the catalyst samples.

The selectivity profiles for all the samples were, as expected, inversely proportional to their conversions. Cracked hydrocarbons dominated in the composition of the product hydrocarbons, coupled with rather low values of the highly desirable di- and mono-branched  $C_6$ -isomers (Table II). Catalyst 2C, however, had a better selectivity in terms of both cracking and  $C_6$ -isomers. At the first glance, this could be related to the formation of stronger acidic sites at the higher calcination temperatures, as a general acidity feature reported for some other catalysts,<sup>12,13</sup> avoiding a simultaneous dramatic decrease of the surface area (Table I). In the inert atmosphere employed here, however, a mechanism including

acid sites may be quite questionable. It is more likely that during *n*-hexane isomerization, an oxidative dehydrogenation reaction occurs leading to the reduction of  $S^{6+}$  to  $S^{4+}$ , water and oxidized hydrocarbon species.<sup>14</sup> The differences in the content and thermal stability of  $SO_4^{2-}$  reflected in the difference in the dynamic of their removal (Table I) are in accordance with the higher activity of catalyst 1 samples. The trend of decreasing activity of the samples of catalyst 2, however, having a constant amount of sulfates regardless of the calcination temperature, is due to a weakening of the textural and structural properties with increasing temperature. The inverse activities of samples 1C and 2C indicate the importance of the necessity of a minimum amount of sulfates and advantageous textural properties, which are both absent in the case of the sample 1C.

A general feature of all the investigated samples, revealed as a minor fraction of highly desirable dimethyl butanes in the products, could be understood in terms of the insufficient acidity of the catalysts and the absence of  $H_2$  and metal functions, both necessary for the bifunctional mechanism.<sup>15</sup> The direct isomerization of *n*-hexane is possible through a carbenium ion, which requires a very strong acid site, or a carbonium ion, which demands a high reaction temperature.<sup>16</sup> It is likely that sites of required acidity and/or mandatory reaction conditions were missing in the catalytic runs of the present investigations.

#### CONCLUSIONS

Two sulfated zirconia catalysts with different amounts of sulfates, prepared by appropriate methods and from different precursors, showed similar activities when calcined at the lower temperature. Both the amount and quality of the sulfate groups incorporated into the zirconia matrix influenced the stability of the catalysts in terms of tetragonal to monoclinic phase transformation. In addition, the manner of catalyst preparation, reflected as the order and number of steps in the preparation sequence, affected the final textural and structural features of the catalyst. As a result, a somewhat lower conversion was obtained in the case of the catalyst completely tailored under laboratory conditions *vs.* a commercially sulfated precursor based catalyst. Both the existence of a minimum amount of sulfates and advantageous textural properties are prerequisites for satisfactory catalyst activity.

In an inert atmosphere and at a relatively low reaction temperature, the isomerization reaction *n*-hexane occurred although by the mechanism of oxidative dehydrogenation rather than by the mechanism including acid sites.

*Acknowledgement:* The financial support of the Serbian Ministry of Science and Environmental Protection (Project No. 142024: "To Green Chemistry *via* Catalysis") and the Serbian Academy of Sciences and Arts is highly appreciated.

## ИЗВОД

## САДРЖАЈ СУЛФАТА И ЊИХОВА СТАБИЛНОСТ – ОДРЕЂУЈУЋИ ФАКТОРИ АКТИВНОСТИ КАТАЛИЗАТОРА НА БАЗИ СУЛФОНОВАНЕ ЦИРКОНИЈЕ

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Две серије катализатора на бази сулфоноване цирконије су синтетисане из различитих прекурсора одговарајућим једно- или више-степенним секвенцама припреме у лабораторијским условима. Њихове активности/селективности у реакцији изомеризације *n*-хексана су корелисане са текстуралним, структуралним и морфолошким особинама. Виша активност катализатора на бази комерцијално сулфонованог Zr(OH)<sub>4</sub> је у сагласности са вишим садржајем SO<sub>4</sub><sup>2-</sup>, њиховом различитом термичком стабилношћу, текстуралним и структуралним својствима. Начин уградње сулфатних група у вишестепеној синтези катализатора нитратног порекла додатно одређује величину кристалита, са негативним утицајем на активност. Коришћење водоника као носећег гаса не даје активан катализатор без обзира на прекурсор, методу синтезе и температуру калцинације. Изомеризација изведена у присуству хелијума резултира релативно кратким животом свих узорака катализатора услед акумулације кокса у реакционим условима који онемогућавају ауторегенерацију.

(Примљено 27. октобра 2006)

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