Temperature imposed textural and surface synergism affecting the isomerization activity of sulfated zirconia catalysts

ALEKSANDRA ZARUBICA1*, BRANISLAV JOVIĆ2, ALEKSANDAR NIKOLIĆ2, PAULA PUTANOV3# and GORAN BOŠKOVIĆ1*#

1Faculty of Technology, University of Novi Sad, 21000 Novi Sad, 2Faculty of Sciences, Department of Chemistry, University of Novi Sad, 21000 Novi Sad and 3Serbian Academy of Sciences and Arts, Knez Mihailova 10, 11000 Belgrade, Serbia

(Received 15 October, revised 29 October 2009)

Abstract: Using sulfuric acid as the sulfating agent, two catalyst series were obtained from hydroxide and nitrate precursor with a sulfate loading identical to commercial sulfated hydroxide, i.e., 4.2 mass %. After calcination at 500, 600 and 700 °C, all nine samples had various contents of residual sulfates depending on the origin of the catalyst. Accordingly, their surface properties were different, which, together with various textural properties, govern the formation of the active phase and their catalytic activity in the \( n \)-hexane isomerization reaction. The dominant activity and yield of mainly mono-branched isomers were attained in reaction at 200 °C with a commercially sulfated zirconia catalyst calcined at 500 °C. Among the SZ catalyst series synthesized from hydroxide and nitrate, the second according to its activity profile was similar to that of the commercially sulfated one, while samples originating from hydroxide showed some activity only after calcination at 600 °C. This is due to the poorer textural properties of the hydroxide series, necessitating a higher calcination temperature in order to promote the simultaneous decomposition of S-containing species and their re-adsorption into the zirconia matrix following interaction and active phase formation. It seems that the tetragonal zirconia phase was not responsible for the catalytic activity but a synergistic effect of the textural properties of the samples and the sulfate loadings, which determine different acid strengths on the catalyst surface.

Keywords: active phase formation; calcination temperature; isomerization activity; sulfated zirconia catalyst; synergism of textural and surface properties.

*Corresponding author. E-mail: boskovic@uns.ac.rs
# Permanent address: Faculty of Sciences, Department of Chemistry, University of Niš, 18000 Niš, Serbia.
# Serbian Chemical Society member.

doi: 10.2298/JSC0912429Z
INTRODUCTION

Strong legislative restrictions eliminated harmful but at the same time high octane number (ON) substances, making the production of motor gasoline of required quality a challenging task for refineries. Hydro-isomerization of straight C₅–C₇ paraffins, thereby producing high-ON isomers for gasoline blending, is one possibility of solving the ON-issue.¹ The reaction requires a bifunctional catalyst: a noble metal on an acidic support, i.e., chlorinated alumina or zeolites. The former, however, faces environmental and expense drawbacks, while the latter, although resistant to impurities, are not satisfactory due to their relatively low activity.² Therefore, for the near future, an important challenge is to develop a new environmental friendly and active catalyst.

Solid acids, such as sulfated zirconia (SZ), are potential candidates for the isomerization of light alkanes.³ Zirconia modified with sulfates exhibits superior catalytic activity. The presence of sulfates increases the stability of zirconia as well as the content of the tetragonal crystal phase, which is the one believed to be catalytically active.⁴ Several detailed investigations indicated, however, that the type of zirconia phase is only of secondary importance and emphasized the significance of labile sulfate groups for catalytic activity.⁵–⁸ Generally speaking, the properties of SZ depend on the preparation method, the type of precursor and the activation procedure.⁸–¹² Although a number of methods and various zirconium compounds have been suggested for the preparation of SZ, there is still no consensus on the correlation of activity with the fraction of tetragonal phase, the quality and content of sulfates or textural and surface properties.

In the present study, three series of SZ catalysts were synthesized from different precursors by suitable preparation methods, followed by calcination at different temperatures. The catalytic activities of the prepared catalysts were measured in the isomerization of n-hexane, as a model reaction, and the results were correlated with their physico-chemical properties, which emphasized the importance of the textural environment for the utilization of their surface properties in the formation of the active phase.

EXPERIMENTAL

Catalysts preparation and characterization

Three types of SZ catalysts were prepared, two as self-made from materials of different origin and the third from a commercial sulfated zirconia. The same procedures required to obtain SZ samples with the same temperature history were applied using the following precursors: sulfated zirconium hydroxide, SO₄−Zr(OH)₄ (Aldrich); zirconium hydroxide, Zr(OH)₄ (97 %, Aldrich) and zirconium oxyxnitrate, Zr(NO₃)₂·xH₂O (Aldrich). Different steps were performed for each particular precursor: a) lone calcination of the commercially sulfated Zr hydroxide; b) sulfation and calcination when starting from the Zr hydroxide precursor and c) precipitation of the nitrate precursor (with 25 % NH₄OH) to Zr hydroxide, followed by its sulfation and calcination in order to obtain the third catalyst. The sulfating procedure was realized by wet-impregnation using 0.50 M H₂SO₄ for the intended content of sulfates (4.2 mass
The subsequent calcination was performed at different temperatures for 3 h in a synthetic air flow of 25 cm\(^3\)/min. Consequently, a total of nine SZ-catalyst samples were obtained, denoted as: SZ-C-X, SZ-H-X or SZ-N-X, where C, H and N reveal the catalyst origin, i.e., commercially sulfated hydroxide, hydroxide and nitrate, respectively, and X (X = 5, 6 or 7) stands for the applied calcination temperature: 500, 600 or 700 °C, respectively.

The specific surface area of the catalysts was investigated by the BET procedure following low temperature N\(_2\) adsorption on a Micromeritics ASAP 2010 apparatus. X-Ray diffraction analysis (XRD, Philips APD-1700 diffractometer with a Cu-anticathode and monochromator) was used for the zirconia determination of the crystal structure. The fraction of sulfates removed during the calcination was measured by thermogravimetric analysis (TG) in a manner explained previously. The density of sulfates was calculated from the amount of remaining SO\(_4^{2-}\) obtained by TG and BET data, assuming a surface area of 0.25 nm\(^2\) for a sulfate group. The related acid strength properties of the catalysts were evaluated by following the change of color of Hammett indicators in contact with the surface of the catalyst samples. The following indicators were used: \(p\)-dimethylaminoazobenzene, 2-amino-5-azotoluene, benzeneazodiphenylamine and crystal violet, covering the range of \(pK_a\) values from 3.3 to 0.8. The nature of acidic sites present was studied by Fourier transformed infrared spectrophotometry of the catalyst samples with previously adsorbed pyridine by means of a Thermo Nicolet Nexus 670 FTIR spectrophotometer. Preceding the IR analysis, the samples were evacuated in order to remove physically adsorbed pyridine.

**Catalysts activity measurements**

The isomerization of \(n\)-hexane was used as the test reaction to probe the activity and selectivity of the catalysts. The reaction conditions were as follows: 200–300 °C, atmospheric pressure, the molar ratio of He, as the carrier gas, and \(n\)-C\(_6\) was 15.5 at a constant partial pressure of \(n\)-C\(_6\) of 60.5 mbar and a space velocity of 6x10\(^{-2}\) mmol \(n\)-C\(_6\)/g\(_{\text{cat}}\)·min. As a rule, 0.50 g of a fresh catalyst sample was loaded into a quartz microreactor and \textit{in situ} activated at 500 °C for 1 h in a synthetic air flow of 20 cm\(^3\)/min. By switching the carrier gas stream to the saturator with \(n\)-hexane, the reaction commenced and the products were analyzed in the GC jet after 5 min (initial activity). The procedure provided catalyst activity testing free of deactivation, which usually occurs under similar conditions due to intensive coking. The reaction products were separated on the 30 m long PONA GC-capillary column and analyzed by gas chromatograph (GC-HP 5890, Series II) equipped with an FID detector. Conversion of \(n\)-hexane was measured to each of the individual gas-phase products and normalized by the number of C-atoms in both the reactant and product. The corresponding selectivity for the formation of an individual product was calculated by dividing the normalized conversion of \(n\)-hexane to the particular product with the total \(n\)-hexane conversion. Finally, the catalysts were classified by their yields, calculated by means of the product of the conversion and the selectivity.

**RESULTS**

The basic textural properties of the sulfated zirconia catalyst samples are given in Table I. Obviously, these properties are functions of the precursor of the catalysts and the thermal history of the samples. Catalysts of SZ-C and SZ-N series were characterized with high BET surface areas, while the series of catalyst samples from hydroxide (SZ-H) showed significantly lower surface areas. Very high specific surface areas (far above 100 m\(^2\)/g) are due to the presence of mic-
ropores in the case of the samples from SZ-C and SZ-N series calcined at 500 °C. Moreover, the latter is characterized with a bimodal pore distribution, having, simultaneously, a substantial fraction of mesopores, which are responsible for the considerable pore volume of the sample. Samples of SZ-H series had the lowest total pore volume compared to their counterparts from different origins. The general feature of the textural characteristics of all samples is that the surface areas were not proportional to the total pore volumes, since the porosities and the pore size distributions were different among the series. The mean pores size decreased with increasing calcination temperature, transforming the pores with diameters close to those of micro- to the meso-pore size. This was followed by an increase in the pore volume and a decrease in the specific surface area; this trend was, however, the slowest in the SZ-H series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area, m²/g</th>
<th>Pore volume, cm³/g</th>
<th>Mean pore diameter, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-C-5</td>
<td>130</td>
<td>0.059</td>
<td>&lt; 2.0</td>
</tr>
<tr>
<td>SZ-C-6</td>
<td>103</td>
<td>0.096</td>
<td>3.3</td>
</tr>
<tr>
<td>SZ-C-7</td>
<td>69</td>
<td>0.105</td>
<td>5.7</td>
</tr>
<tr>
<td>SZ-H-5</td>
<td>82</td>
<td>0.053</td>
<td>2.6</td>
</tr>
<tr>
<td>SZ-H-6</td>
<td>68</td>
<td>0.064</td>
<td>3.9</td>
</tr>
<tr>
<td>SZ-H-7</td>
<td>67</td>
<td>0.089</td>
<td>5.0</td>
</tr>
<tr>
<td>SZ-N-5</td>
<td>144</td>
<td>0.139</td>
<td>&lt; 2.0; 3.2</td>
</tr>
<tr>
<td>SZ-N-6</td>
<td>117</td>
<td>0.139</td>
<td>4.4</td>
</tr>
<tr>
<td>SZ-N-7</td>
<td>89</td>
<td>0.141</td>
<td>6.0</td>
</tr>
</tbody>
</table>

*Pores smaller than 2 nm were beyond the limit of the equipment

The similar properties were found by Matsuhashi et al.,12 who reported values of the specific surface area and mean pore diameter in the range of 60–90 m²/g and 2–20 nm, respectively, for SZ samples differing in origin, as well as in sulfating agent and sulfation procedure.

From Table II, it can be concluded that all the samples calcined at 500 °C were characterized by only the tetragonal zirconia phase, while increasing the calcination temperature resulted in an increasing fraction of the monoclinic crystal phase. The latter phase prevailed in the catalysts pretreated at the highest temperature; the highest value of 72.7 % was in the catalyst sample prepared from the hydroxide precursor.

The range of acid strength, \( H_0 \), of the catalyst samples relative to color changes of applied Hammett indicators are given in Table II. Although quite a modest range of \( pK_a \) values was covered with the available indicators, all the samples, except SZ-C-5, were within the acidity range \( 3.3 \geq H_0 \geq 0.8 \). The sample SZ-C-5 possessed a higher acid strength, characterized with \( H_0 < 0.8 \). For a more accu-
rate acidity categorization, probes with indicators of basicity higher than that of the most basic available crystal violet would be required.\textsuperscript{15}

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fraction of sulfates removed during the calcination step\textsuperscript{a}</th>
<th>Sulfates remaining after calcination, %</th>
<th>Sulfate density (per nm\textsuperscript{2} of surface)</th>
<th>( H_0 )</th>
<th>Volume fraction of tetragonal/monoclinic phases, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-C-5</td>
<td>0</td>
<td>4.2</td>
<td>2.03</td>
<td>( H_0 &lt; 0.8 )</td>
<td>100</td>
</tr>
<tr>
<td>SZ-C-6</td>
<td>7.2 (7.2)</td>
<td>3.9</td>
<td>2.38</td>
<td>( 3.3 &gt; H_0 \geq 0.8 )</td>
<td>93.3/6.7</td>
</tr>
<tr>
<td>SZ-C-7</td>
<td>55.9 (48.7)</td>
<td>2.0</td>
<td>1.81</td>
<td>( H_0 &gt; 3.3 )</td>
<td>48.3/51.7</td>
</tr>
<tr>
<td>SZ-H-5</td>
<td>45.2</td>
<td>2.3</td>
<td>1.76</td>
<td>( 3.3 &gt; H_0 \geq 0.8 )</td>
<td>100</td>
</tr>
<tr>
<td>SZ-H-6</td>
<td>45.2 (0)</td>
<td>2.3</td>
<td>2.12</td>
<td>( 3.3 &gt; H_0 \geq 0.8 )</td>
<td>71.9/28.1</td>
</tr>
<tr>
<td>SZ-H-7</td>
<td>66.9 (21.7)</td>
<td>1.8</td>
<td>1.69</td>
<td>( 3.3 &gt; H_0 \geq 0.8 )</td>
<td>27.3/72.7</td>
</tr>
<tr>
<td>SZ-N-5</td>
<td>28.6</td>
<td>3.0</td>
<td>1.31</td>
<td>( 3.3 &gt; H_0 \geq 0.8 )</td>
<td>100</td>
</tr>
<tr>
<td>SZ-N-6</td>
<td>31.9 (3.3)</td>
<td>2.9</td>
<td>1.55</td>
<td>( 3.3 &gt; H_0 \geq 0.8 )</td>
<td>80.3/19.7</td>
</tr>
<tr>
<td>SZ-N-7</td>
<td>42.2 (10.3)</td>
<td>2.6</td>
<td>1.83</td>
<td>( 3.3 &gt; H_0 \geq 0.8 )</td>
<td>37.5/62.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated based on the identical initial sulfates loading of 4.2 mass % for all samples determined by TGA; the fraction of sulfates released for the applied calcination temperature gradient of 100 °C are given in parentheses.

The initial activity and selectivity to total isomers of the catalysts are given in Table III as a function of the origin of the SZ samples and of both calcination and reaction temperatures. Catalyst SZ-C-5 showed the maximal initial activity of all the prepared catalysts at both applied reaction temperatures. The selectivity to \( i-C_6 \) of the same catalyst was also considerable; altogether resulting in the highest isomer yield, Fig. 1. The samples from the SZ-N and SZ-C series exhibited similar catalytic properties when exposed to the most favorable calcination and reaction temperatures, \textit{i.e.}, 500 and 200 °C, respectively, resulting in a more or less comparable isomer yield, given in Fig. 1. Increasing the calcination temperature generally led to a decline in the catalyst activity, except for the sample SZ-H-6, for which a considerable increase in the yield relative to the same sample calcined at 500 °C was registered, Fig. 1. However, the substantially lower activity of the samples of the SZ-H series relative to other two catalyst series of different origin should be emphasized. The product distribution was similar for all tested catalysts regardless of their origin, showing a lack of the highly desirable di-branched isomers, \textit{i.e.}, 2,2- and 2,3-dimethylbutane, with methylpentanes as the major isomers. In the absence of a metallic dehydrogenation function, which produces olefins as intermediates of isoparaffins, direct isomerization of paraffins is possible on acidic sites throughout a carbonium ion, which additionally requires higher reaction temperatures.\textsuperscript{17}
TABLE III. Initial activity and selectivity of the catalysts as a function of the precursor and both the calcination and reaction temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>200 °C Conversion of n-hexane (%)/selectivity to i-C₆ (%)</th>
<th>300 °C conversion of n-hexane (%)/selectivity to i-C₆ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-C-5</td>
<td>14.0/45.8</td>
<td>50.4/11.9</td>
</tr>
<tr>
<td>SZ-C-6</td>
<td>13.8/36.8</td>
<td>22.1/13.6</td>
</tr>
<tr>
<td>SZ-C-7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SZ-H-5</td>
<td>0</td>
<td>2.2/90.9</td>
</tr>
<tr>
<td>SZ-H-6</td>
<td>4.4/66.4</td>
<td>11.5/26.0</td>
</tr>
<tr>
<td>SZ-H-7</td>
<td>0</td>
<td>3.7/87.5</td>
</tr>
<tr>
<td>SZ-N-5</td>
<td>20.0/15.4</td>
<td>40.0/22.5</td>
</tr>
<tr>
<td>SZ-N-6</td>
<td>3.1/89.8</td>
<td>10.5/21.5</td>
</tr>
<tr>
<td>SZ-N-7</td>
<td>6.2/39.4</td>
<td>8.5/38.6</td>
</tr>
</tbody>
</table>

Fig. 1. Initial yield of SZ-C, SZ-H and SZ-N catalyst samples as a function of both the calcination and reaction temperatures.
DISCUSSION

All the catalyst samples of series SZ-C and SZ-N calcined at the two lower temperatures had high BET surface areas, greater than usually reported in the literature for SZ with the same temperature history.\(^4\)\(^-\)\(^7\)\(^,\)\(^9\)\(^,\)\(^10\)\(^,\)\(^12\)\(^,\)\(^14\)\(^,\)\(^17\)\(^,\)\(^18\)\) Samples of the series SZ-H had a low surface area range which was not affected significantly by the pretreatment temperature, Table I. Transformation of the pore structure as a function of calcination temperature is predictable; the mean pore diameter was doubled when the temperature was increased from 500 to 700 °C, indicating a broadening of the pores openings for all the investigated samples regardless of their origin. This, coupled with the decrease in the specific surface area, usually indicates the sintering process occurring at higher temperatures.

The volume fraction of the crystal phases of all samples calcined at 500 °C showed the presence of only the tetragonal zirconia phase, the one which is widely referred to as the active catalytic phase in the scientific literature.\(^4\)\(^,\)\(^5\)\(^,\)\(^18\)\(^-\)\(^20\)\) Table II. When higher calcination temperatures were applied, both tetragonal and monoclinic phases existed, the last finally prevailing at 700 °C regardless of the catalyst precursor type. This phase transformation was the fastest with the SZ-H catalyst series, showing its lowest stability among all the catalyst samples. For example, the SZ sample originating from hydroxide when calcined at 700 °C was left with the lowest tetragonal phase fraction, which coincided with its lowest content of sulfates, Table II. This is in agreement with claims that the tetragonal zirconia phase aids the formation of labile sulfates giving the active sites responsible for a high \(n\)-butane isomerization activity.\(^7\)\) The phase structure of the SZ-H-7 sample, i.e., with the monoclinic phase dominant, might be responsible for the abundant release of sulfate, which gives no chance for the sulfates to react with the zirconia matrix and consequently provide active sites, Tables II and III. Correspondingly, the prevailing tetragonal phase structure of the SZ synthesized from the other two precursors (SZ-C and SZ-N) demonstrated values which seem to be fully utilized in terms of catalytic activity. Quite opposed to this, there was no registered activity for the SZ-C-7 sample that still had a considerable fraction of the tetragonal phase, implying that some other characteristics other than the SZ phase structure governs the catalytic activity, Tables I–III.

Comparing surface, textural and structural properties of the catalysts, Tables I and II, with their catalytic efficiency, Table III and Fig. 1, some correlations might be imposed. Firstly, it is obvious that there is a direct proportion between the fraction of the tetragonal zirconia phase and catalyst activity, however, this property may not be sufficient to deliver activity, as can be seen from the case of sample SZ-C-7. Namely, this sample, having the highest fraction of the tetragonal phase relative to the other samples calcined at the same temperature nevertheless exhibited no catalytic activity, Table II. Thus, some other factors, such as the amount and quality of sulfates remaining on the samples after calcination,
might be equally or even more responsible for the efficiency of the catalysts. After calcination, the remaining sulfate groups stay embedded in the zirconia matrix and form certain densities of sulfates on the surface, which might require a minimal value to act as catalytically active sites. Finally, the surface acid strength may also play a vital role in determining the catalytic efficiency of the samples.

It was recently found that the acidic strength of residual Lewis acidic sites ( coordinative unsaturated site Zr\(^{4+}\) in the vicinity of sulfate groups) was significantly enhanced by sulfation, provided that the sample had been calcined at a proper temperature. In fact, active sites are claimed to have been created through the selective elimination of sulfates located on the side terminations of the crystallites following tetragonal phase formation only as a coincidence. Other authors also indicated the importance of labile sulfate groups for activity. However, they assumed the formation of active sites on both monoclinic and tetragonal phases of SZ, the latter case resulting in preferentially higher concentrations of such sites. In addition, the procedure of the calcination step seems to be important. Thus sulfate decomposition providing an adequate contact time between the released SO\(_3\) and zirconia is a necessity for the formation of active sites.

Contrary to some zirconia samples, sulfated by a procedure similar to that applied in this work, in which the amount of incorporated sulfates were directly proportional to the surface area of the SZ, all the samples investigated in this study had the same amount of sulfates, i.e., 4.2 mass %, Table II. This and the dynamics of sulfate removal during calcination at a particular temperature were calculated from TG data reported earlier. In contrast to the same amount of initial sulfates, their stability was quite different, which, together with textural and structural properties, as well as the magnitude of the applied calcination temperature determined the formation of the active phase resulting in catalyst activity, Tables I–III. The loss of a significant fraction of the sulfates in a single calcination step at the lower temperature may not result in the same activity, as can be seen from the cases of the SZ-N-5 and SZ-H-5 samples. Obviously, sulfates of similar stability behave differently depending on their environment defined by its textural rather than its structural characteristics. Namely, the presence of the full amount of tetragonal zirconia phase in both samples calcined at 500 °C did not guarantee the same activity output, as seen from Tables II and III. Thus, the superior activity performance of the SZ-N-5 sample might be the consequence of its good textural properties (high specific surface area), providing conditions for the re-adsorption of S-containing species on the zirconia matrix, their interaction and active sites formation. The textural properties of the samples from the SZ-H series required, however, higher temperatures for the same mechanism of active sites formation. Since there was no extra sulfate removal when the calcination temperature differed by 100 °C (comparison of the sample SZ-H-6 and SZ-H-5), as shown in Table II, a question arises as to the origin of the catalytic
activity of the SZ-H sample exposed to the higher temperature. Obviously, the magnitude of the calcination temperature has to be a compromise between the dynamics of sulfate decomposition and the rate of interaction of the released S-containing species and the zirconia host. While for the SZ-N series 500 °C was the preferential temperature, for their counterparts from the hydroxide series, a minimum of 600 °C was required for both processes to occur simultaneously. Thus, the same fraction of sulfates was liberated at 600 and 500 °C, however, at the higher temperature, the sulfates underwent interaction with the zirconia host, formed active sites and the SZ-H-6 sample performed with satisfactory activity for this particular series, Table III. The behavior of SZ-C-5, showing at the same time no sulfate release and the maximal activity, casts doubts on the association of the release of labile sulfate groups with the formation of the active phase. However, the sulfating procedure and, possibly, some additional stabilization process during sulfation remain unrevealed by the manufacturer of the SZ-C series. This fact makes comparison with samples of this series partly impossible, at least when the sulfating agent and sulfating procedure are concerned. However, the same original sulfate loading as in the cases of the catalysts of other origin makes all of them interesting for comparing the impact of temperature on the dynamics of sulfate release. It has to be understood, however, that the release of a small fraction of the sulfates, as in the favorable cases of the SZ-N series, does not necessarily mean the presence of inactive sulfates. Again, it is a consequence of the synergistic effect of the calcination temperature and preferable textural properties allowing the released sulfates to interact with the zirconia host thereby forming active centers for isomerization. The magnitude of the calcination temperature is nevertheless one of the main factors determining the formation of the active phase; thus 700 °C is too high temperature regardless of the sample origin, leaving in all cases, except in the case of SZ-N-7, amounts of sulfates lower than the critical value necessary to contribute to the activity.

The sulfates density has been considered in the past as a clue for the explanation of the activity of SZ.23 Considering this characteristic in the case of the SZ-N series, it seems, however, that the sulfate density is not a crucial factor for SZ-catalyst activity, at least not in a way the density of sulfates was defined14 and calculated in the present work, Tables II and III, Fig. 1. Namely, from the textural characteristics of the whole series of SZ-N samples, it seems that some fraction of sulfates located within the zirconia matrix can participate in the catalytic reaction once there are pores of certain openings and volume providing the environment for the operation of the active sites. Indeed, the mean pore diameters and total pore volumes of the series of SZ-N samples leave room for such a speculation, giving recognition to the textural characteristics of a catalyst as the prevailing factor in determining its catalytic properties.11 Accordingly, the considerable sulfate density obtained for the only active catalyst in hydroxide series, i.e.,

Available online at www.shd.org.rs/JSCS/
the SZ-H-6 sample, is just a coincidence due to the low surface area of all the SZ-H series. The previously mentioned mechanism of sulfate release at a certain temperature preceding the interaction is equally valid, requiring a critical minimal amount of sulfate to react with the zirconia host and form active sites. From Fig. 2, a direct correlation between sulfate loading and the amount of tetragonal SZ phase can be assumed, while the sulfate density function is ambiguous. Given the fact that the specific surface area directly contributes to the sulfates density calculation, the latter indicates that the textural properties of SZ, although following the same temperature dependence, are not directly correlated to its phase structure.

![Fig. 2. Sulfate loading (filled patterns) and sulfate density (empty patterns) as a function of the fraction of tetragonal phase in the SZ.](image)

From the applied Hammett indicators, although covering a quite modest range of acidity, some interesting points can be extracted. First of all, there is the peculiar behavior of the SZ-C series of samples exhibiting two extremes: sample SZ-C-5 showing the highest and sample SZ-C-7 the lowest acid strength among all the samples.\(^\text{15}\) Simultaneously, the dynamics of sulfates removal during calcination showed the full amount of remaining sulfates in the sample calcined at 500 °C and one of the lowest sulfate loading for its counterpart exposed to 700 °C. While the dynamics of sulfate removal relative to the acid–base properties is difficult to discuss due to the unknown (post)sulfating procedure in this particular series, the acid strength of the SZ-C samples directly reflects the amount of remaining sulfate. The acid strength correlation for the other series is rather diffi-
cult. Thus, the nitrate and hydroxide samples calcined at 600 °C exhibited similar activities and had more or less equal acid strength, the first, however, having a significantly higher amount of remaining sulfates and simultaneously the lowest sulfate density.

The quite irregular catalytic behavior of the applied samples in terms of their structural, textural and surface properties imposes the consideration of the presence of acid sites of different nature as being partly responsible for differences in catalytic activity. The results of some investigations advocate the presence both Brønsted (BAS) and Lewis acid site (LAS) on SZ. These sites being of different acid strength would, consequently, have different abilities for the isomerization of linear or branched alkanes. The FTIR spectra of several samples are given in Fig. 3, which show different bands of previously adsorbed pyridine.

![Fig. 3. FTIR Spectra of pyridine pre-adsorbed on the SZ samples as a function of origin and calcination temperature: a) ZS-C-5; b) SZ-C-5; c) SZ-C-5; d) SZ-H-7 and e) SZ-N-7.](image-url)
From the literature, in most instances, the band around 1540 cm\(^{-1}\) is assumed to be characteristic for a pyridinium ion sitting on BAS, while bands between 1445 and 1460 cm\(^{-1}\) are attributed to pyridine coordinative adsorbed on a LAS.\(^{25}\) According to literature data,\(^{26,27}\) the formation of both BAS and LAS is connected to surface bonded sulfate groups imposing electron shifts and changes in the electron densities in the proximity of Z\(^{4+}\), as shown in Fig. 4. In contrast, other authors see LAS not sitting on the zirconia matrix but on S-additive, comprising both ionic, S–O–Zr, and coordination, S=O, bonds.\(^{28}\) According to the FTIR spectra shown in Fig. 3, there is a direct correlation between the activities of the catalyst samples and presence of acidic centers of different nature, as well as the acid strength of the samples given in Table II. Namely, the band at 1450 cm\(^{-1}\) witnesses the presence of BAS in the sample with the highest acid strength, Table II, while the band at 1466 cm\(^{-1}\) indicates the presence of LAS, the concentration of which rapidly decreases with increasing calcination temperature. Other results from the literature claim, however, that the acid strength of BAS is lower than that of LAS,\(^{29}\) but the temperature history of the catalysts was quite different from that applied in the present investigation. Some other studies, nevertheless, do report on the importance of the presence of strong BAS in SZ in order to obtain high catalytic activity in reaction with \(n\)-heptane.\(^{30}\) In any case, the obtained distribution of the isomeric products, \(i.e.,\) mainly mono-branched hydrocarbons at the expense of the more desirable 2,2- and 2,3-dimethylbutane, indicates a monomolecular isomerization mechanism, including the carbenium ion.\(^{24}\)

Fig. 4. Model of the BAS and LAS formed upon sulfate incorporation into the zirconia matrix.\(^{26,27}\)

CONCLUSIONS

The presence of the tetragonal phase of zirconia probably only coincides with the real formation of the active phase as a consequence of zirconia phase transformation at the calcination temperature being responsible for the development of the active phase at the first place. The existence of thermally labile sulfates in the zirconia matrix is a necessity for active phase formation; however, it must be coupled with preferable textural properties. A large surface area and total pore volume, as well as larger pore openings, provide the environment for the formation and operation of effective active sites. The magnitude of the calci-
nation temperature has to be a compromise between the dynamics of sulfate decomposition and the rate of interaction of the released S-containing species and the zirconia host in order for an active phase to be formed. The active phase might partly include acidic centers of Brønsted and Lewis nature initiated by incorporation of S-containing species into the zirconia host. However, some critical sulfate loading above 2 mass % is required for catalytic activity in the n-hexane isomerization reaction under the conditions applied in this work. Nonetheless, it seems difficult to correlate sulfate density with catalytic activity, indicating that the catalytic activity is a complex function of textural and surface (acid strength) characteristics of the samples.

Acknowledgement. The financial support of the Ministry of Science and Technological Development of the Republic of Serbia (Project ON 142024: “To Green Chemistry via Catalysis”) is highly appreciated.

ИЗВОД

СИНЕРГИЗАМ ТЕКСТУРАЛНИХ И ПОВРШИНСКИХ СВОЈСТВА СУЛФОНОВАНОГ КАТАЛИЗАТОРА НА БАЗИ ЦИРКОНИЈУМ-ОКСИДА ПРОУЗРОКОВАН ТЕМПЕРАТУРОМ И ЊЕГОВ УТИЦАЈ НА АКТИВНОСТ КАТАЛИЗАТОРА У РЕАКЦИЈИ ИЗОМЕРИЗАЦИЈЕ

АЛЕКСАНДРА ЗАРУЧИЦА1, БРАНИСЛАВ ЈОВИЋ2, АЛЕКСАНДАР НИКОЛИЋ2, ПАУЛА ПУТАНОВО3 И ГОРАН БОСКОВИЋ1

1Технологијска факултети, Универзитет у Новом Саду, 21000 Нови Сад, 2Природно–математички факултети, Департман за хемију, Универзитет у Новом Саду, 21000 Нови Сад и 3Српска академија наука и уметности, 11000 Београд

Коришћењем суморне киселине као агента за сулфонање, синтетисане су две серије катализатора из хидроксидног и нитратног прекурсора са идентичним садржајем сулфата од 4,2 mas. %. Исти садржај сулфата установљен је и у сулфованом цирконијум-оксиду комерцијалног порекла, који је чинио основу за трећу серију узорака. Након калинцијације на 500, 600 и 700 °С, девет узорака катализатора садржали су различите количине сулфата у зависности од примећене температуре и порекла катализатора. Као резултат, њихова површинска својства се разликују, и заједно са текстуралним својствима воде формирању активне фазе у различитом степену, а самим тим и различитој активности у тест реакцији изомеризације нормалног хексана. Највећа активност и највећи принос, превасходно моно-раз-гранатих изомера, постиже се на температури од 200 °C у случају примене комерцијално синтетисаног сулфованог ZrO2 калинисаног на 500 °С. Узимајући у обзир следеће две серије катализатора, добијена из хидроксида и нитрата, ова друга је по свом профилу активност блика комерцијално сулфованом узорку, док узорци који за прекурсор имају хидроксид локализују веома ниску активност, али тек након калинцијације на 600 °C. Ова ниска активност одговара најнеповољнијим текстуралним својствима ове серије катализатора, а последица је веће температуре калинцијације потребне за симултану разградњу сулфатних врста, њихове редкосерције на матрици цирконијум-оксид и, на крају интеракције са њом и настања активне фазе. Намеће се закључак да тетрагонална фаза сама по себи није одговара за катализичку активност, већ да синергиза текстуралних и површинских својстава, одређених садржајем сулфата, одређује јачину активних центара катализатора, а тиме и интензитет његове активности.

(Примљено 15. октобра, ревидирано 29. октобра 2009)
REFERENCES