SURFACE PROPERTIES AND MEMORY EFFECT – KEY FACTORS IN DETERMINING THE CATALYTIC EFFICIENCY OF SULFATED ZIRCONIA

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Three series of zirconia catalysts based on various precursors and grafted with sulfates were synthesized, then calcined at two different temperatures (500 and 600 °C) and tested in the *n*-hexane isomerization. The catalysts based on commercially sulfated zirconium(IV)-hydroxide, and alkoxide prepared at two altered pH values were characterized by means of BET, XRD, SEM, and FTIR methods and relevant procedures. The final catalytic efficiencies were correlated with their physico-chemical properties (surface, textural, structural and morphological ones). It was recognized that the sulfated zirconia catalyst based on commercially sulfated zirconium(IV)-hydroxide and calcined at the lower temperature demonstrated the highest initial activity among all the tested catalysts due to the favorable total acidity, the density of sulfates, the type of acidic active sites, the mesoporous system and nanostructure. Slightly lower but comparable activity of the sulfated zirconia catalyst based on alkoxide and prepared at lower pH is the result of the different memory effect of the starting material and its original properties, and also something different physico-chemical features.

Keywords: catalytic efficiency, memory effect, precursors, sulfated zirconia, surface properties

Introduction

A traditional industrial process of *n*-alkane(s) isomerization to obtain high research octane number (RON) and motor octane number (MON) gasoline (ON $\geq$ 98) practices liquid acids such as H₂SO₄ and HF/HCl as catalysts. Unfortunately, these acids cause serious problems related to corrosion of reactor units, then potential environmental impacts and risks to human health [1,2].

The mentioned is the reason to motivate researches for alternative solid acid catalysts to efficiently replace liquid acids and consequences of their applications. In addition, current environmental legislations have announced strong restrictions on the contents of aromatic compounds, unsaturated hydrocarbons and oxygenated compounds in gasoline, which are contributors to high RON and MON. These environmental standards set a request for the establishment of catalytically supported processes and relevant catalysts that would provide high RON and MON without negative effects on the environment.

The so called "first generation" of the solid acid catalysts covers ex. platinum/chlorinated alumina that works as an efficient catalyst at temperatures from 120 to 165 °C, but it suffers from low levels of catalytic poisons (i.e. from sulfur up to 0.5 ppm, water up to 0.1 ppm, oxygenated compounds up to 0.1 ppm, 5 ppb of metals, 1 ppm of chlorides, 0.1 ppm of nitrogen and 1 wt. % of alkenes).

Moreover, the use of this catalyst imposes the need to continuously provide chlorides to the catalyst support that may seriously damage the equipment and the environment [3,4].

The second generation of the catalysts consists of zeolites doped with noble metals (ex. platinum, palladium). These catalysts express the activity at higher temperatures, over 200 up to 270 °C while at the same time being resistant to impurities from the feed (to sulfur up to 100 ppm and to water up to 100 ppm) [5,6]. The catalytic activity of the Pt/Mordenite (Pt/MOR) catalyst in the reaction of *n*-hexane isomerization was investigated in dependence on the platinum content [7]. Besides, a series of platinum loaded zeolites such as Pt/H-ZSM-5, Pt/HM, Pt/H β and Pt/mazzite were tested in the *n*-hexane isomerization, and the Pt/H β catalyst showed the best catalytic performances, the highest activity and selectivity to branched isomers [8,9].

It seems that the third generation of the catalysts may overcome drawbacks of the previous ones. These materials based on the solid acids are potential candidates as efficient and environmental friendly catalysts for isomerization of straight C₅ - C₇ alkanes [10,11]. Zirconium(IV) - oxide modified with acid groups may exhibit the so called "super-acidity", and a superior catalytic activity [12,13]. Zirconium(IV)-oxide is a non-toxic and non-corrosive one,

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catalytically active and stable under different conditions. The catalyst based on modified zirconium(IV)-oxide may be prepared in a number of various procedures. It is known that the properties of sulfated zirconia (SZ) may highly depend on the preparation method, the activation procedure and the precursor type [14-16]. In addition, it is believed that sulfate groups increase the surface acidity and the stability of zirconia [17-21]. Namely, sulfate acid functions have been related to the stabilization of the SZ tetragonal crystal phase, but the explanations are still not totally defined [17,19,20,22].

Although there are a number of papers which have reported the results on different preparation methods and precursors used for the synthesis of sulfated zirconia catalysts [20,22-24], there is still no consensus on the primary importance of some surface features of the catalysts on the final catalytic efficiency (i.e. density of acid groups, type of acid groups, etc.). Moreover, there are scientific debates on the correlation between catalytic efficiency and the content and type of acid groups.

In the present paper, two series of sulfated zirconia catalysts based on alkoxide were prepared by using the adequate synthesis method, different process parameters and similar thermal treatments. The catalytic efficiency (i.e. activity, selectivity, stability) was tested in the isomerization of *n*-hexane as a model reaction. These primary catalytic features were correlated with the physico-chemical features of SZ-solid acid catalysts. Additionally, the role of the material memory effect was examined and related to the final catalytic performance. Finally, the catalytic performances of these laboratory synthesized SZ-catalysts based on alkoxide were linked with the same ones of the SZ-catalysts based on the commercially sulfated zirconium(IV)-hydroxide.

Experimental part

Preparation of SZ-based catalysts

The series of the SZ-based catalysts obtained from commercially sulfated zirconium(IV)-hydroxide $\text{SO}_4\text{-Zr(OH)}_4$ (Aldrich Co.) was prepared by calcination the precursor at selected temperatures 500 and 600 °C. Another two series of the SZ-based catalysts from an alkoxide precursor (zirconium (IV)-propoxide, 70% solution in 2-propanol (Aldrich Co.)) were synthesized by using the modified sol-gel method formerly reported [16]. During the applied sol-gel method of zirconium(IV)-hydroxide synthesis from alkoxide, the pH value was varied in order to study the influence of some process parameters. The sulfating procedure of the synthesized zirconium(IV)-hydroxide was completed by the incipient-wet impregnation method using 0.5 M sulfuric acid to obtain a nominal content of sulfates 4 wt. %. Such prepared catalysts were then dried for 3 h at 105 °C, and calcined at 500 and 600 °C for additional 3 h in the synthetic air flow 25 cm³/min. The calcination procedures were applied at two temperatures to examine the impact of the thermal treatments. The catalysts samples were denoted as SZ-

rO₂-P-pH-T, where T is the calcination temperature used and P – stands for the initial letter of the precursor type.

Physico-chemical characterization of SZ-based catalysts

The selected textural properties of the catalysts were studied by using the low temperature nitrogen adsorption/desorption method. The adsorption/desorption isotherms of liquid nitrogen performed into catalytic samples were recorded using the Micro-meritics ASAP 2010 instrument. Brunauer-Emmett-Teller (BET) equation was used to calculate BET specific surface areas of the catalysts [25]. The average pore diameter was determined as the Barrett-Joyner-Halenda (BJH) desorption mean pore diameter [26].

In order to investigate structural characteristics of the catalysts, the X-Ray Diffraction (XRD) analysis was applied by using the instrument X-ray diffractometer Phillips APD-1700 with a Cu-anticathode and mono-chromator at 40 kV and 55 mA. Structural properties such as the volume fraction of the selected crystal phases and crystallite sizes were obtained on the basis of XRD diffractograms. The crystallite sizes were calculated by using Scherrer's equation [16,22].

Thermal properties of the catalysts were examined by means of Thermo Gravimetric (TG) and Differential Thermal Analyses (DTA). This was performed on the instrument Baehr STA 503 in the programmed regime in the temperature range from 25 to 1000 °C using the ramp of 10 °C/min.

The related total acidity of the catalyst surface was evaluated by Fourier Transformed Infrared spectrophotometry (FTIR) practiced onto the surfaces of the samples pre-adsorbed by pyridine as a probe molecule for the estimation of the acidic active sites. The FTIR spectrophotometer Nicolet Nexus 670 was used in order to define the surface properties of the SZ-based catalysts.

With the purpose of obtaining images concerning morphological features of the catalyst surface, the Scanning Electron Microscopy (SEM) was applied. The SEM microscope JEOL JSM-6460LV was used at accelerating voltage 25 kV and magnification 100,000x.

Isomerization of *n*-hexane – the testing of the catalysts

The isomerization of *n*-hexane was realized as the test reaction to probe the primary catalytic properties (activity, selectivity, stability). The test reaction was conducted in a quartz fixed-bed micro-reactor under the atmospheric pressure. The reaction conditions were: temperature 200 °C, partial pressure of *n*-hexane 60.5 mbar, space velocity $6 \cdot 10^{-2}$ mmol *n*-C₆/g_{cat} · min, the molar ratio of He as the carrier gas to *n*-hexane was 15.5. The fresh catalyst loading of 0.5 g was activated *in situ* at the constant temperature of 500 °C for 1 h in the synthetic air flow 25 cm³/min. The reaction was carried out as long as the catalytic activity was registered (from 0 to 120 min).

The reaction products were firstly separated on the 30 m long PONA GC-capillary column and then analyzed by means of Gas Chromatography (GC) on the instrument GC-HP 5890 Series II equipped with a Flame Ionization

Detector (FID). The injected volume of the gas sample was 0.5 ml.

The conversion of *n*-hexane (X) was determined for each one of the gas products and normalized by total C-atoms in both the reactant and products. The selectivity to the individual gas product (S) was calculated by a division between the normalized conversion of *n*-hexane to the particular product and the total *n*-hexane conversion. The yield (Y) was considered as a product of the conversion and the selectivity.

Results and discussion

The selected textural properties (BET surface area, BJH desorption pore volume and average pore diameter) of the sulfated zirconia catalysts of different origin are presented in Table 1. The chosen textural properties are in line with the precursor type, the process parameters used in the preparation of catalysts and the applied thermal treatment.

Table 1. Specific surface areas, pore volumes and average pore diameters for the sulfated zirconia catalysts of different origin

Catalysts	BET surface area, m ² /g	BJH pore volume, cm ³ /g	Average pore diameter, nm
SZrO ₂ -A-9.5	200	0.19	3.2
SZrO ₂ -A-9.5-500	125	0.16	4.5
SZrO ₂ -A-9.5-600	93	0.18	5.4
SZrO ₂ -A-13.0	170	0.18	3.9
SZrO ₂ -A-13.0-500	103	0.17	5.8
SZrO ₂ -A-13.0-600	73	0.15	7.2
SZrO ₂ -C	215	0.07	1.7
SZrO ₂ -C-500	130	0.06	2.3
SZrO ₂ -C-600	103	0.10	3.3

The BET surface areas of the sulfated zirconia catalysts calcined at 500 °C and based on the alkoxide precursor are 125 and 103 m²/g for two catalysts (SZrO₂-A-9.5-500 and SZrO₂-A-13.0-500) prepared at different pH values during the modified sol-gel synthesis: 9.5 and 13.0, respectively. It seems that the use of lower pH value during the synthesis procedure of the sulfated zirconia catalysts from alkoxide affected more favorable textural properties, i.e. higher BET surface areas, larger pore volumes and somewhat smaller pore diameters (Table 1).

The obtained very high BET surface areas (> 100 m²/g) of the mentioned sulfated zirconia catalysts calcined at lower temperature may be related to the presence of micropores besides mesopores. This fact especially stands for the sulfated zirconia catalyst based on the commercially sulfated zirconium(IV)-hydroxide precursor and calcined at 500 °C, which is characterized with the highest BET surface area, 130 m²/g (Table 1). The reported data for sulfated zirconia catalysts based on alkoxide prepared with higher nominal wt. % of sulfates have presented comparable BET surface areas [23] to the analogous ones obtained in the present paper. On the other side, having in mind that the nominal wt. % of acidic groups in the catalysts samples of other authors is higher than in

the present investigations, it should be emphasized that here obtained textural properties, precisely BET surface areas, are greater than usually reported in the scientific results concerning sulfated zirconia(s) with the same thermal history [12,14,18,27,28-31]. It is also possible that greater contents of acidic groups efficiently affected textural properties of the sulfated zirconia catalysts. To the best of the author's knowledge, the equal synthesis sequence of the sulfated zirconia catalysts using the same process parameters as well as the equivalent final catalysts has not been reported previously. Specific differences in the textural properties between two series of the sulfated zirconia catalysts based on the alkoxide precursor and commercially sulfated zirconium(IV)-hydroxide are in line with the memory effect connecting with the original features of different starting materials used in the preparation of the catalysts. This is the reason why the author in the present paper suggests that the BET surface area of the sulfated zirconia-based catalysts can be correlated with the sequence in synthesis, the process parameters applied and the memory effect, which origins from the starting materials. Initially, the precursor SZrO₂-C of the catalyst series SZrO₂-C-T was characterized with a high BET surface area (Table 1) that caused a high BET surface area of the final catalyst, SZrO₂-C-500, after performing the step of the calcination in the preparation procedure. The mentioned catalyst SZrO₂-C-500 possesses the highest BET surface area among all the investigated catalyst samples that is related to the memory effect transferred from the precursor. The precursors denoted with SZrO₂-A-9.5 and SZrO₂-A-13.0 were characterized with the BET surface areas greater than the corresponding final catalysts SZrO₂-A-9.5-500 and SZrO₂-A-13.0-500 (Table 1). The BET surface areas of precursors SZrO₂-A-9.5 and SZrO₂-A-13.0 are smaller than the BET surface area of the SZrO₂-C precursor, and consequently the BET surface areas of the final catalysts SZrO₂-A-9.5-T and SZrO₂-A-13.0-T are smaller than the same one of the SZrO₂-C-T catalyst. These textural features of the SZrO₂-A-9.5-T and SZrO₂-A-13.0-T catalytic series are in line with the textural properties of the precursors, and after the application of the thermal treatment in the preparation procedure, the catalytic series SZrO₂-A-9.5-T and SZrO₂-A-13.0-T still had a relatively high BET surface areas but lower than the catalytic series SZrO₂-C-T.

The increase of the calcination temperature to 600 °C of the sulfated zirconia catalysts based on alkoxide caused the BET surface areas decrease to 93 and 73 m²/g for the samples prepared at pH values 9.5 and 13.0, respectively. The same is valid for the BET specific surface area of the catalyst based on commercially sulfated zirconium(IV)-hydroxide, which decreased from 130 to 103 m²/g with increasing the temperature of the thermal treatment from 500 to 600 °C (Table 1). The decrease of the BET surface area is followed simultaneously with broadening of the average pores diameters. This usually indicates that the sintering process of the catalytic mate-

rial occurs. Consequently, the decrease of the specific surface area is coupled with the increase of the average pore diameter with maximizing the calcination temperature. Accordingly, the sintering process probably leads to a consolidation of the catalytic material [16,20,32].

Liquid nitrogen isotherms for the $\text{SZrO}_2\text{-C-500}$, $\text{SZrO}_2\text{-A-9.5-500}$ and $\text{SZrO}_2\text{-A-13-500}$ catalysts are shown in Fig. 1. The adsorption/desorption nitrogen isotherms exhibit a typical s-shape behavior of type-IV with type-H1 desorption hysteresis. In the series of the sulfated zirconia catalysts based on alkoxide, H1-type hysteresis is at somewhat higher p/p_0 values of relative pressures in the case of the catalyst sample prepared at lower pH, 9.5.

Figure 1. Nitrogen adsorption/desorption isotherms for the selected sulfated zirconia catalysts:

a) $\text{SZrO}_2\text{-C-500}$, b) $\text{SZrO}_2\text{-A-9.5-500}$, c) $\text{SZrO}_2\text{-A-13-500}$

The sulfated zirconia catalysts originated from commercially fabricated sulfated zirconium(IV)-hydroxide are characterized with a monomodal pore size distribu-

tion (PSD), and with a substantial fraction of micropores and/or the pores near the edge micro-pores/small mesopores (not shown). On the contrary, both catalysts series based on the alkoxide showed a bimodal pore size distribution, preferably in the mesopores range between 30 and 80 nm (not shown). In the series of the sulfated zirconia catalysts based on the organic precursor, the pore size distribution is slightly distinguished and shifted towards the bigger average pore diameter with diminishing pH value during the synthesis of the catalysts. Generally speaking, for the sulfated zirconia catalysts originated from alkoxide there is a maximum of the average pore diameter around 50 nm, and the additional narrow maximum in the region at the edge of mesopores/micropores around 2.5 nm. These two maxima in the PSD may be quite important during the catalytic reaction. Namely, the author has previously reported that the existence of mesopores in contrast to micropores affected the mechanism of slower deactivation of the catalyst and accordingly its longer catalytic-life [33].

In general, transformations of micro- and mesopores as functions of the used calcination temperatures are predictable; the average pore diameters are increased when calcination temperatures are increased from 500 to 600 °C in the particular catalysts series. This is the indication on the pore broadening for all the investigated catalysts regardless the precursor applied. Hence, the sintering process occurred at higher temperatures.

The amorphous phase of the zirconium(IV)-hydroxide transformed a mixture of tetragonal and monoclinic zirconium(IV)-oxide to fine crystalline after heating from 400 to 600 °C (Fig. 2). This is in accordance with the results of the same author [16,22]. The crystallization to monoclinic ZrO_2 was intensified with the increase of the calcination temperature analogously to the results of other authors [19,34].

Table 2. Crystal phase composition, the crystallite size of zirconia, density of sulfates for the sulfated zirconia catalysts

Catalysts	Crystallite size (t- ZrO_2), nm	Volume fractions t/m crystal phases, %	Surface sulfates density per nm^2	Residual sulfates after calcinations, %
$\text{ZrO}_2\text{-A-9.5-500}$	14.5	92.2/7.8	(not shown)	(not shown)
$\text{SZrO}_2\text{-A-9.5-500}$	11.8	100	1.96	4.1
$\text{SZrO}_2\text{-A-9.5-600}$	12.5	93.3/6.7	2.14	3.7
$\text{ZrO}_2\text{-A-13.0-500}$	16.7	86.1/13.9	(not shown)	(not shown)
$\text{SZrO}_2\text{-A-13.0-500}$	12.1	100	1.99	3.6
$\text{SZrO}_2\text{-A-13.0-600}$	13.7	88.03/11.97	2.23	3.3
(S) $\text{ZrO}_2\text{-C-500}$	12.0	95.90/4.10	(not shown)	(not shown)
$\text{SZrO}_2\text{-C-500}$	10.3	100	2.03	4.3
$\text{SZrO}_2\text{-C-600}$	11.8	96.64/3.36	2.38	3.8

The volume fractions of the crystal phases of all the catalysts calcined at 500 °C despite different origin demonstrate the exclusive existence of the tetragonal crystal phase of zirconia (Table 2, Fig. 2). The tetragonal crystal phase of zirconia was earlier referred to as a very active crystal phase in heterogeneous catalytic reactions [12,27,28,35,36].

Furthermore, the sulfated zirconia catalysts calcined at both temperatures indicated the tetragonal crystal phase of zirconia prevailed (Table 2, Fig. 2) irrespective

on the calcination temperatures applied, 500 or 600 °C. These may highly positively affect the efficiency of all the sulfated zirconia catalysts in the catalytic run(s).

It can be noticed that the use of lower pH values during the modified sol-gel synthesis of the sulfated zirconia catalysts based on alkoxide caused better structural properties regarding a higher amount of tetragonal crystal phase of zirconia and smaller crystallites sizes. The author presumes that these more favorable structural, together with desirable textural features which have been formerly produced by lower pH value during the synthesis procedure, can in further course highly attribute to favorable catalytic efficiency of the sulfated zirconia catalyst (*i.e.* SZrO₂-A-9.5-500) in the isomerization of *n*-hexane. Moreover, it appears that the presence of sulfates stabilizes the tetragonal crystal structure of zirconia at 500 and 600 °C. Also, sulfates have retarded the crystallization of zirconia to monoclinic and/or cubic phases up to 600 and 700 °C. The similar effect was demanded earlier by other authors [19], and happened after the use of additives such as Y³⁺, Ce⁴⁺, Ca²⁺ and Mg²⁺-based compounds [37,38].

Figure 2. XRD patterns of the sulfated zirconia catalysts based on different origin

Among all the investigated sulfated zirconia catalysts, the series based on commercially sulfated zirconium(IV)-precursor possess the most promising structural properties considering a higher amount of tetragonal crystal phase and a smaller crystallite size after the identical thermal treatments. Such results are in agreement with the memory effect that is reflected from unique features of the starting materials used in the preparation of catalysts (Table 2). The precursor (S)ZrO₂-C-500 is characterized with a small t-ZrO₂ crystallite size and high volume fraction of the tetragonal crystal phase, and therefore the final catalysts SZrO₂-C-500 and SZrO₂-C-600 are also characterized with small crystallites sizes

and very high fractions of tetragonal crystal phases (Table 2). These favorable structural features of the catalytic series SZrO₂-C-T are transferred from the original properties of the starting material in the preparation procedure. The precursors denoted with ZrO₂-A-9.5-500 and ZrO₂-A-13.0-500 have relatively small t-ZrO₂ crystallites sizes and relatively high volume fractions of tetragonal crystal phases and thus the corresponding final catalysts SZrO₂-A-9.5-500 and SZrO₂-A-13.0-500 have even more smaller t-ZrO₂ crystallites sizes and greater volume fractions of the tetragonal crystal phases after the application of the sulfating procedure performed in the sequence of the catalyst preparation. The sulfating procedure caused the additional stabilization effect.

The additional verifying of the sintering process occurred is the fact that both crystallite sizes of tetragonal and monoclinic phases grow in parallel with the transformation of tetragonal to monoclinic crystal phase of zirconia at higher temperatures (Fig. 2). Nonetheless, according to the present results, these tetragonal crystallite sizes obtained after the thermal treatments applied are still very close to critical values (10-12 nm) reported earlier as significant ones for the catalytic efficiency [27,39]. Such values are maintained by a grafting of bare zirconia with sulfates additives.

Positive effects of the presence of sulfates additives and acidic properties of zirconia surface are in compliance with the calculated crystallite size and a potential existence and/or distribution of crystal defects. These possible imperfections, as the results of the presence of oxygen or metal vacancies can influence local or total charge imbalances on the zirconium(IV)-oxide surface. The oxygen vacancies and charge imbalances may become responsible for the catalytic efficiency as real catalytic active sites.

The surface density of sulfates is calculated by using the contents of residual sulfates after calcinations estimated by TG, then the values of the BET surface areas assuming that the surface area of the sulfate group is 0.25 nm², similarly to the calculation procedure given by other authors [18]. Therefore, having in mind that all the sulfated zirconia catalysts possess acceptable textural properties, it is predictable that all the catalysts would have a relatively high surface density of the sulfates (Table 2). Furthermore, bearing in mind that the value of the BET surface area is indirectly proportional to the density of sulfates, among all the catalytic series, the catalysts samples calcined at higher temperature (600 °C) would be characterized with greater density of the sulfates. Because of some limitations of the calculation procedure of the density of sulfates, it is clear that the density of sulfates is an important contributor, but not the unique one and is not a crucial factor for determining the efficiency of the sulfated zirconia catalyst.

The FTIR spectra of the selected SZ catalysts, after the adsorption of pyridine as the probe molecule for the estimation of the acidic active sites, are presented in Fig. 3. It is known from the scientific literature [40] that the

band at around 1540 cm^{-1} is characteristic for the pyridinium ion bonded to Brönsted Acid Sites (BAS), while the bands between 1445 and 1460 cm^{-1} are attributed to molecular pyridine adsorbed on Lewis Acid Sites (LAS). The bands typical for the BAS are presented in the FTIR spectra of the SZ catalysts series based on the commercially sulfated zirconium (IV)-hydroxide and alkoxide. However, these bands are highlighted in the catalysts samples calcined at the lower temperature ($500\text{ }^{\circ}\text{C}$).

The intensity of the band characteristic for the pyridinium ion in the FTIR spectrum of the catalyst sample $\text{SZrO}_2\text{-C-500}$ is higher than for the catalysts samples from the SZ catalysts series based on alkoxide. Moreover, within the series of the SZ catalysts based on alkoxide, such confirmation of the existence of BAS is more prominent in/on the SZ catalyst prepared at lower pH, 9.5. The order of total acidity projected on the basis of the BAS: $\text{SZrO}_2\text{-C-500} > \text{SZrO}_2\text{-A-9.5-500} > \text{SZrO}_2\text{-A-13.0-500}$ may be recognized. The specified BAS may significantly contribute to the catalytic efficiency.

Figure 3. The FTIR spectra of the selected sulfated zirconia catalysts after the adsorption of pyridine:

a) $\text{SZrO}_2\text{-C-500}$, b) $\text{SZrO}_2\text{-A-9.5-500}$

The genesis of both BAS and LAS is associated with the surface bonded sulfate that causes changes in the electron densities [41,42]. Some authors have claimed that LAS are located on sulfates additives in the proximity of the Zr^{4+} -ion, the fact which includes the existence of both ionic species in S-O-Zr and coordination species in S=O [43]. The other authors think that the acid strength of BAS is lower than the one of LAS [44], which may together influence the SZ catalysts reported in this paper to be very active.

There is a direct correlation between the presence of the acidic sites of different nature (BAS and LAS) and the SZ catalytic efficiency. The band typical for BAS at 1540 cm^{-1} is valid as the characteristic one for the active catalytic site of the highest acidity [45]. The authors report on the importance of the presence of strong BAS in the SZ catalyst in order to achieve a high catalytic activity in the reaction of *n*-heptane conversion [45]. In addition, the band representative for the LAS is registered in the FTIR spectrum of the SZ catalyst sample, $\text{SZrO}_2\text{-A-9.5-500}$.

After the adsorption of pyridine in the FTIR spectra of the SZ catalysts the bands attributed to adsorbed molecules of water are of higher intensity than before the adsorption of the probe molecule. This is especially emphasized in the SZ catalyst series based on alkoxide. Specifically, a high intensity of this band is registered in the sample $\text{SZrO}_2\text{-A-9.5-500}$ at 1635.07 cm^{-1} .

Under the conditions of a higher level of surface hydration, the acidic catalytic active sites are more available in the test reaction. A certain level of hydration of the SZ catalyst surface is necessary for the SZ to be a catalytically active material. After the activation of the surface hydrated SZ catalyst in the synthetic air flow, it should be effective in the reaction of *n*-hexane isomerization. These surface features of the SZ catalysts provide the existence of sulfur in the +6 oxidation state in/onto the catalyst bulk, which is a key factor affecting the catalytic activity.

The FTIR bands associated with S=O vibrations are shifted towards lower wavenumbers, 1249.97 cm^{-1} in the $\text{SZrO}_2\text{-C-500}$ and 1139.00 cm^{-1} in the $\text{SZrO}_2\text{-A-9.5-500}$ (Fig. 3). The mentioned shift can be correlated with the inductive effect of the adsorbed pyridine onto LAS. On the other side, this may be related to the weakening S=O ability to withdraw electrons from Zr^{4+} -ions [46,47]. Also, pyridine may remove water from LAS, and in further course it can interact with S=O groups thus changing their covalent nature [18].

Before the adsorption of pyridine, in the FTIR spectra (not shown) the characteristic bands for S=O were located in the region $1440\text{--}1300\text{ cm}^{-1}$ and may be shifted towards lower wavenumbers depending on the surface hydration level. The SZ catalyst samples $\text{SZrO}_2\text{-C-500}$ and $\text{SZrO}_2\text{-A-9.5-500}$ possess distinctive bands for S=O. These bands, positioned at higher wavenumbers indicate pyrosulfate groups while those at lower wavenumbers specify monosulfate groups [47,48]. A relatively

wide band at 1139.00 cm^{-1} in the SZ catalyst sample $\text{SZrO}_2\text{-A-9.5-500}$ may designate the presence of labile pyrosulfate groups. These pyrosulfate groups can be a key factor determining the SZ catalytic activity towards branched isomers.

SEM micrographs of the selected SZ catalysts samples are presented in Fig. 4. It is visible that the catalysts denoted as $\text{SZrO}_2\text{-C-500}$ and $\text{SZrO}_2\text{-A-9.5-500}$ have small particles of comparable sizes. This observation is in accordance with the XRD results concerning the crystallite sizes (Table 2, Fig. 2).

Most of the particles of all the investigated SZ catalysts samples are nano-scale in size. Particles of both SZ catalysts series based on alkoxide are characterized with a high level of surface and bulk homogeneity and only slightly greater particles than the same ones of the SZ catalysts based on the commercially sulfated zirconium(IV)-hydroxide. These differences are in line with the memory effect of different starting precursors, corresponding synthesis methods and process parameters applied. Correspondingly, it is noticeable that in the SZ catalysts series based on alkoxide and prepared at lower pH, the particles of the SZ catalysts are smaller. The catalytic materials obtained from the alkoxide precursors are traditionally characterized with a very high level of surface and bulk homogeneity. Therefore, the high level of homogeneity was transferred from the precursors denoted with $\text{ZrO}_2\text{-A-9.5-500}$ and $\text{ZrO}_2\text{-A-13.0-500}$ to the corresponding final catalysts labelled with $\text{SZrO}_2\text{-A-9.5-500}$ and $\text{SZrO}_2\text{-A-13.0-500}$ (Fig. 4.). This phenomenon was realized over memory effect from the starting materials in the catalysts preparation procedures.

Figure 4. SEM micrographs of the selected sulfated zirconia catalysts: a) $\text{SZrO}_2\text{-C-500}$, b) $\text{SZrO}_2\text{-A-9.5-500}$, c) $\text{SZrO}_2\text{-A-13.0-500}$

The surface morphology of the catalyst $\text{SZrO}_2\text{-C-500}$ seems as grainier and consists of the particles of smaller size comparing to its counterpart calcined at $600\text{ }^{\circ}\text{C}$, the surface of which appears to be more bulky. When the higher calcination temperature is applied, the greater particles sizes are obtained inside the concrete series of the SZ catalysts regardless the precursors used. This is the additional evidence on the sintering process and the agglomeration of primary particles, the broadening of mean pore diameters and the decrease of the BET surface areas.

The SEM characterization of morphology also demonstrates the dependence of the particle size on the acidic groups and their contents/densities [15,22]. It is expected that morphological properties of the SZ catalysts would additionally influence final catalytic performances in the test reaction of *n*-hexane isomerization.

Specific important correlations might be forced after the comparisons between the surface, textural, structural, and morphological properties of the sulfated zirconia catalysts with their catalytic performances in the test reaction. Firstly, there is a direct relation between the total acidity and catalytic efficiency. Secondly, the total acidity, the type of acidic groups/acidic active sites and also the density of acidic groups may play the essential role in defining the catalytic activity of the SZ catalysts. Thirdly, the memory effect concerning the original properties of the starting precursor materials may significantly influence the final catalytic performances.

Namely, all the discussed catalytic properties together determined the corresponding total catalytic efficiency. The active SZ catalysts presented the initial activities in helium used as a carrier gas after first 5 min of the time-on-stream. The total time-on-stream differed from 15 up to 150 min depending on the particular catalyst applied. No catalytic activity was registered under hydrogen as a carrier gas, and in such reaction conditions a fast deactivation of most catalysts samples occurred because of the coke accumulation and/or pores blocking in the absence of auto-regeneration conditions [33].

Table 3. Catalytic performances and the yield of the selected products

Catalysts	X, %	S to <i>i</i> -C ₆ , %	Y, %	
			Di-branched isomers	Mono- branched isomers
SZrO ₂ -A-9.5 – 500	28.1	16.6	3.99	45.60
SZrO ₂ -A-9.5 – 600	14.0	40.9	2.65	35.85
SZrO ₂ -A-13.0-500	5.9	57.6	0.26	57.32
SZrO ₂ -A-13.0-600	5.2	67.4	0.17	45.79
SZrO ₂ -C -500	53.9	11.9	2.46	19.48
SZrO ₂ -C -600	25.6	13.6	2.33	11.23

The sulfated zirconia catalysts series based on the commercially sulfated zirconium(IV)-hydroxide and alkoxide showed a favorable initial activity, the acceptable selectivity to *i*-C₆ and yield to mono-branched isomers (Table 3). This especially stands for the SZ catalysts from the catalytic series based on the commercially sulfated zirconium(IV)-hydroxide and alkoxide synthesized at lower pH, and both catalysts calcined at lower temperature (500 °C). Among all the investigated SZ catalysts, the catalysts SZrO₂-C-500 demonstrated the most favorable catalytic activity that can be attributed to the highest total acidity, high density of sulfates, the exclusive presence of tetragonal crystal phase, a great BET surface area and the appropriate porous system. Relatively desirable primary catalytic properties of the catalyst SZrO₂-A-9.5-500 can be explained by the existence of the adequate mesoporous texture, the presence of only tetragonal crystal phase, high total acidity and sulfates density and a specific memory effect originated from the starting material and its original features.

Despite the fact that the catalyst SZrO₂-A-13.0-500 has the exclusive tetragonal crystal phase, it does not show promising catalytic performances due to inadequate some physico-chemical properties that speaks in favor of a real complexity of the active phase genesis and activation. Previously, some authors have demanded that tetragonal crystal phase is the essential factor defining the catalytic activity [47,48]. The author proposes that structural benefits regarding crystal phase compositions are significant, but not crucial factors for the total catalytic efficiency.

Regardless the precursor type and thermal history of the concrete sulfated zirconia catalyst, the products composition and distribution are similar after the performed reaction over the particular catalyst. Di-branched isomers are presented with relatively small contents contrary to monobranched hydrocarbons that indicates the probable monomolecular mechanism of the isomerization reaction over carbenium ion [49]. This mechanism assumed the presence of very strong acid sites that operated [50]. It seems that acid sites of the required acidity are present only in the case of the SZrO₂-C -500 catalyst or that they are even missed in the present investigation.

It is imperative to underline that, in the laboratory, it is possible to design and synthesize the SZ catalyst series based on alkoxide characterized with quite comparable physico-chemical properties and final catalytic efficiency in the reaction with the ones of the SZ catalysts based

on the commercially sulfated zirconium(IV)-hydroxide.

Conclusion

Sulfated zirconia catalysts based on different precursors and synthesized by using various process parameters during the preparation procedure can demonstrate a favorable catalytic efficiency in the reaction of *n*-hexane isomerization under the process parameters used. Based on the obtained results, it can be concluded that there is a positive relation between total acidity and catalytic efficiency. Additionally, the type of acidic active sites and their densities may play a vital role in defining the catalytic activity and selectivity. Moreover, the memory effect of the precursors regarding the original properties of the starting materials should have a significant impact on the sulfated zirconia catalytic performances. Incorporated acidic additives into zirconia bulk/matrix influenced the catalyst stability regarding the undesirable crystal phase transformation to monoclinic one and the prolongation/extension of the catalytic life-time as well.

Combined roles of the sulfated zirconia catalyst surface, structural and textural properties in defining the final catalytic efficiency are proposed. Therefore, the sulfated zirconia catalysts presented the acceptable initial activity in the isomerization of *n*-hexane under helium used as a carrier gas because of the established balance between total acidity, sulfates density, mesoporous texture and nanostructure.

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Izvod

POVRŠINSKA SVOJSTVA I MEMORIJSKI EFEKAT – KLJUČNI FAKTORI U DETERMINISANJU KATALITIČKE EFIKASNOSTI SULFATIMA MODIFIKOVANOG CIRKONIJUM(IV)-OKSIDA

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Sintetisane su tri serije katalizatora na bazi cirkonijum(IV)-oksida modifikovanog sulfatima korišćenjem različitih prekursora, potom su kalcinirane na dve različite temperature (500 i 600 °C) i testirane u izomerizaciji *n*-heksana. Katalizatori na bazi komercijalno/fabrički modifikovanog cirkonijum(IV)-hidroksida sulfatima i na bazi alkoksida sintetisani na dve različite pH vrednosti sredine, karakterisani su sledećim metodama: BET, XRD, SEM i FTIR i odgovarajućim instrumentalnim procedurama. Finalne katalitičke efikasnosti su dovedene u korelaciju sa fizičko-hemijskim svojstvima katalizatora (površinskim, teksturalnim, strukturalnim i morfološkim). Uočava se da je katalizator na bazi komercijalno modifikovanog cirkonijum(IV)-hidroksida sulfatima, kalcinisan na nižoj temperaturi, pokazao najvišu inicijalnu aktivnost među svim testiranim katalizatorima zbog povoljne ukupne kiselosti, gustine sulfatnih grupa, te odgovarajućih vrsta kiselih aktivnih centara, mezoporoznog sistema i nanostrukture. Nešto niža aktivnost, ali uporediva, katalizatora na bazi alkoksida i sintetisanog pri nižoj pH vrednosti, rezultat je memorijskog efekta koji potiče od prekursora i njegovih svojstava, kao i nešto drugačijih finalnih fizičko-hemijskih svojstava primenjenog katalizatora.

Ključne reči: efikasnost katalizatora, memorijski efekat, prekursor, cirkonijum(IV)-oksid modifikovan sulfatima, površinska svojstva