



Influence of alumina addition on structural and catalytic properties of sulphated zirconia in isomerization of *n*-hexane

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Abstract

New binary catalytic systems based on sulphated zirconia-alumina were synthesized by controlled hydrolysis of alkoxides using relative molar ratios of constituents 1:1, 1:2 and 1:3 in favour of zirconia. The obtained differences in the final catalytic material's properties may be related to organic precursor memory effect, the applied calcinations temperatures and used alumina contents. The addition of alumina to zirconia affected the structural and surface properties stabilizing bare zirconia by means of slower phase transformation of tetragonal zirconia crystal phase into monoclinic one, further resulting in smaller crystallites sizes and higher surface density of acidic function (sulphates). The best alumina impact on physico-chemical properties was achieved when the highest amount of alumina (e.g. 50%) and lower calcination temperature (500 °C) were used, causing relatively high steady-state activity in isomerization of *n*-hexane at reaction temperature 250 °C. On the other hand, higher calcination temperature (600 °C) played a role in the genesis of greater sulphate density. Catalytic activity and selectivity are expressed as a complex synergistic function of relative density of acid sites together with positive status of other optimized physico-chemical properties of the catalytic material (by activation and calcination temperatures).

Keywords: zirconia, alumina, sol-gel processes, catalytic properties, nanostructures

I. Introduction

Alkylation directed toward production of high octane number motor fuels (i.e. research octane number (RON) > 94) and skeletal isomerization of *n*-alkanes [1] are reactions of growing importance in modern petroleum refining industry due to environmental legislations recently established. These predicted restrictions on the use of lead-based additives, sulphur and benzene derived compounds generally known as superior octane number boosters in gasoline have pressed the petroleum industry to produce reformulated fuels with suitable constituents and high research octane number (RON) [2]. Conventional industrial processes of the isomerization of *n*-butane have been per-

formed over Pt/chlorinated- and Pt/fluorinated-alumina catalyst in the temperature range from 150 to 300 °C and Pt/zeolite-based catalysts at reaction temperatures over 250 °C [3]. The first class of catalysts requires continuous addition of chlorine or fluorine, which are highly toxic and can cause serious corrosion problems in industrial plants. On the other hand, the second class of zeolite-based catalysts is less reactive, but more resistant to catalytic poisons in the feed, e.g. up to 10 ppm of S and 100 ppm of water [4].

These disadvantages of traditionally used catalysts for isomerization process have motivated investigations on a design of new alternative generation that would exhibit benefits on catalytic act in reaction run and satisfy environmental tasks. Solid acid catalysts as alternatives for liquid acids used to promote acid-catalysed reactions have attracted intensive scientific attention. Sulphated zirconia (SZ) has become the catalyst of remark-

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able interest due to its strong acidity and activity in short chain alkanes isomerization at relatively mild conditions [5–8].

The catalytic activity of SZ at intermediate working temperatures, and especially its short working cycle during reaction run caused by fast deactivation is not entirely suitable for industrial applications. Different transition metals (e.g. Fe, Mn, Ni, Cr, V and Pt) as promoters have been incorporated into SZ matrix, resulting in catalysts with higher activity and/or stability than unmodified SZ [9–16]. Such promotional effects are usually consequences of synergism between favourable structural and surface features of metal-modified SZ catalysts (metal = Fe, Mn, Ni, Cr, V) [16,17]. Unfortunately, substantial promoting effect of these transition metals was rather low at higher reaction temperatures (over 250 °C) in hydrogen atmosphere [18,19].

Lately, it was reported that the addition of small amounts of alumina to SZ catalytic system has enhanced the catalytic activity and stability of *n*-butane isomerization at 250 °C in the presence of H₂ [18,20]. This improvement is attributed to the retardation of tetragonal crystal phase transformation to monoclinic one in the presence of Al [21,22], and simultaneous existence of Brønsted and Lewis acid sites determining surface properties of the catalyst [22]. Some distinctive results on this topic were interpreted based on the preparation conditions of zirconia-alumina mixed oxides, with different relative compositions, which were tested in the dehydration of 2-propanol and isomerization of *n*-hexane [23].

Furtheron, it may be expected that the addition of alumina to the zirconia modified by sulphates may generate a new binary catalytic system characterized by moderate surface area and acidity. Despite the extensive research efforts on sulphated zirconia-alumina binary oxides, the understanding of their preparation, characterization and catalytic behaviour is still incomplete. The present paper has focused on the evaluation of structural and catalytic behaviours of sulphated zirconia promoted by alumina and tested in the reaction of *n*-hexane isomerization.

II. Experimental

2.1. Catalysts preparation and characterization

Zirconia-alumina binary oxides were synthesized by controlled hydrolysis of related alkoxides, widely known as sol-gel preparation method, here used in modified version. Zirconia oxide as precursor of designed binary oxide was synthesized from Zr(IV)-propoxide (70 wt.% solution in 1-propanol, Aldrich Co.) by mixing two solutions: the first one based on zirconium(IV)-propoxide dissolved in isopropyl alcohol under an inert atmosphere, and the second one consisted of solvent mixed with de-ionized water. Molar ratios alkoxide/alcohol = 1 and water to corresponding propoxide being 2 were kept as constants during the synthesis procedure in order to obtain zirconia-sol of 0.5 M concen-

tration. Such molar ratios were previously proved as important factors in the synthesis of highly homogeneous nanomaterials based on the organic precursors [8,24–26]. Analogously, alumina oxide was prepared by calcination of the product obtained by hydrolysis of aluminium propoxide (Aldrich Co.) precursor using *n*-butanol as a solvent.

Afterwards, such prepared zirconia and alumina sols/reactants were mixed (250–300 rpm) in a Pyrex glass reactor under nitrogen, where pH = 2 was initially adjusted by using a small volume of hydrochloric acid. The mixture was stirred at an ambient temperature for 1 h, leading to the generation of corresponding gel, which condensed at 80 °C after 3 h during further course of preparation procedure. In due course, ammonium hydroxide (25%) was added into medium to arrange the desired pH = 11. Gels were aged at room temperature next 3 h under mild mixing conditions. Accordingly, solids were centrifuged, rinsed by using large volumes of de-ionized water in small portions and finally by alcohol, then filtered and dried at 110 °C for 12 h.

The sulphating step of the materials was performed by incipient wetness technique of impregnation with 0.5 M sulphuric acid to achieve nominal 3 wt.% SO₄²⁻ per 1 g of the dried zirconia-alumina binary hydroxide. The obtained sulphated zirconia-alumina based materials were calcined alternatively at 500 or 600 °C for 3 h under synthetic air flow of 25 cm³/min. Surface sulphates density was determined by a method reported earlier [15,27]. A series of three sulphated catalytic systems having relative alumina/zirconia molar ratios 1:1, 1:2 and 1:3 were synthesized, and denoted as: SAZ-x:y-T, where - x:y stands for molar ratio of constituents and T as calcination temperature.

Nitrogen adsorption-desorption isotherms were collected on a Sorptomatic 1990 Thermo Finningen at 77 K. Specific surface area (S_{BET}) was calculated by applying the Brunauer-Emmet-Teller equation using the linear part of the adsorption isotherm for $p/p_0 \leq 0.35$, while the total pore volumes (V_{tot}) were obtained from the N₂ adsorption expressed in liquid form, applying Gurevitch's rule at $p/p_0 = 0.98$. X-ray diffraction analysis (XRD) was used for the determination of crystal phases by means of Philips APD-1700 diffractometer with Cu-anticathode and a monochromator at 40 kV and 55 mA. Calculation of crystallites sizes was done using the Scherer equation. Thermal properties were investigated via thermogravimetric (TG) and differential thermal analysis (DTA) on Baehr STA 503 in the controlled flow of synthetic air. Measurements were performed in temperature range from 30 to 1000 °C at constant rate of 10 °C/min under conditions earlier reported in the literature [28]. Surface morphology of the catalysts was observed using scanning electron microscopy (SEM) by using the JEOL JSM-6460LV instrument with an acceleration voltage 25 kV. SEM samples were coated by ion-sputtered thin film of gold. Transmission electron microscopy (TEM) was performed using the JEOL JEM-

2100 LaB₆ instrument operated at 200 kV. TEM images were acquired with a Gatan Orius CCD camera at 2× binning.

2.2. Catalysts activity measurements

The isomerization of *n*-hexane was used as test reaction to evaluate the activity and selectivity of the catalysts. Catalytic runs were carried out under subsequent conditions: 200 or 250 °C at atmospheric pressure, molar ratio He to *n*-C₆ of 15.5; *n*-C₆ constant partial pressure of 60.5 mbar, and space velocity $6 \cdot 10^{-2}$ mmol *n*-C₆/g_{cat} min. Before each catalytic run, 0.50 g of a fresh catalyst was loaded into a quartz micro-reactor and *in situ* activated at 500 °C for 1 h in synthetic air flow of 25 cm³/min. The reaction products were separated on 30 m long PONA GC-capillary column and analysed by gas chromatography (GC-HP 5890 Series II) equipped with a FID detector. Products composition included hydrocarbons from CH₄ to benzene. Conversion of *n*-hexane was estimated over sum of each gas-phase product and normalized by number of C-atoms in both reactant and product(s). Corresponding selectivity was calculated as a fraction of summarized desirable compound or product (e.g. dibranched C₆-isomers – 2.2- and 2.3-dimethylbutanes) and total conversion of *n*-hexane (a sum of both reactant and products). The catalysts were classified by exhibited yields calculated as a multiplication of total conversion and selectivity.

III. Results and discussion

3.1. Structural characterization

Surface areas (Table 1) corresponding to both catalysts series decrease with increasing calcination temperature from 500 to 600 °C due to the effect of sintering. In addition, the increase of the zirconia content slightly reduces surface area of catalyst (only up to 2%). Pore volume is also reduced in line with the increase of the zirconia amount. Bimodal pore size distribution (dominant pore sizes 5 and 60 nm; not shown) is registered in all catalysts samples as a result of prolonged precursor memory effect [24]. The estimated surface areas of the sulphated zirconia modified with alumina are much higher than analogous ones of the bare zirconia [29]. The domain sizes of zirconia crystallites were also calculated by the Scherer equation and summarized in Table 1.

Structural properties, type of crystal phase and crystallite size of sulphated zirconia-alumina binary oxides are resolved by means of X-ray diffraction analysis. XRD patterns of the complete SAZ-x:y-500 series (Fig. 1) confirmed the presence of amorphous phase despite the zirconia content, previously postulated as a factor that may improve poor crystallinity of alumina [23]. Similar results are claimed earlier [29–31] obtained with comparable but different amounts of zirconia used in mixed oxide system in comparison with the conditions reported here. Diffractograms corresponding to these mixed oxides, the series SAZ-x:y-500, showed only a broad peak in the high angle region originating from highly amorphous nature of the material (Fig. 1). The presence of relatively weak peaks in the high angle region at ~30.30° and two feature peaks less defined at 52 and 61° (the series SAZ-x:y-600) is attributed to the tetragonal ZrO₂ phase. This suggests that higher calcination temperature (series SAZ-x:y-600, Table 1) is required for the formation of tetragonal crystal phase, which plays a crucial role in the catalytic activity [24,25]. Besides, low intensity peaks at Bragg angles 46 and 67° identified as γ-alumina (or even δ-alumina) [32] are also seen. This observation may also correspond to an amount of low crystallized γ-AlO(OH) at the applied calcination temperature [33].

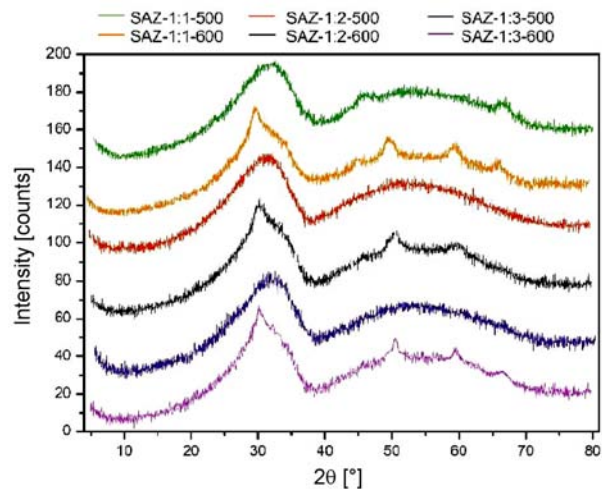


Figure 1. XRD patterns of sulphated zirconia-alumina binary oxides calcined at different temperatures: SAZ-1:1-500, SAZ-1:1-600, SAZ-1:2-500, SAZ-1:2-600, SAZ-1:3-500 and SAZ-1:3-600

Table 1. Structural characteristics of zirconia-alumina binary oxides as a function of molar ratios and calcinations temperatures (specific surface area S_{BET} , pore volume V_p , volume fraction of tetragonal/monoclinic zirconia phases $F_{t/m}$, zirconia crystallite size D and sulphates density)

Catalyst	S_{BET} [m ² /g]	V_{tot} [cm ³ /g]	Crystallinity	$F_{t/m}$ [%]	D [nm]	Sulphates density [per nm ²]
SAZ-1:1-500	189	0.285	A	-	-	1.720
SAZ-1:1-600	133	0.227	C	100	3.9	1.930
SAZ-1:2-500	178	0.192	A	-	-	1.163
SAZ-1:2-600	131	0.157	C	100	5.4	1.244
SAZ-1:3-500	172	0.117	A	-	-	0.913
SAZ-1:3-600	127	0.085	C	100	6.9	1.125

In the XRD diffractogram of the catalyst sample SAZ-1:3-600 very small intensity peak characteristic for γ -alumina at 67° is observed probably because of lower amount of alumina and possible overlapping of alumina crystal phase with predominant zirconia crystal phase (Fig. 1). Furthermore, increasing the amount of alumina phase in the binary oxides provoked an increase of the peak intensity at 67° (the catalyst SAZ-1:1-600; Fig. 1). Relatively lower structure ordered alumina at higher concentration of zirconia may be explained by an interaction of alumina and zirconia, and also alumina overlapping with zirconia crystallites at higher temperatures [33,34] or even formation of solid solutions [35] under an extreme thermal treatments (not used here).

Some authors have claimed previously that no crystallinity was observed in zirconia-alumina oxides after calcinations at temperatures below 650°C [33,34]. Here, the authors imposed tetragonal crystal phases of zirconia and γ -alumina after heating at 600°C that is connected with the stabilization effect of sulphates and alumina reported previously [28,36]. The stabilization of the metastable tetragonal zirconia phase and retardation of the sintering process preserving the average crystallites sizes smaller than 10 nm were also confirmed when different amount of alumina was added and precursors were mixed at very fine scale [37]. The stabilization of the metastable tetragonal ZrO_2 has also been reported to occur with the incorporation of different metal oxides [19,20]. Similarly, the authors suggest that the addition of alumina stabilized the metastable tetragonal zirconia phase and hinders the coarsening of crystallites. Additionally, a precursor type may affect the stabilization of the material structure and a level of homogeneity in a similar way [24].

The addition of alumina to zirconia (molar ratio 1:1) has a dramatic but positive influence, causing a decrease

of the sulphated zirconia crystallite size. Namely, zirconia crystallite size of the sample synthesized from alkoxide and calcined at 600°C under the same experimental conditions as applied here, was 13.7 nm [8,38]. That is more than three times greater compared with crystallite size of the zirconia promoted and stabilized with alumina (3.9 nm, Table 1). The lower the amount of alumina, the larger is zirconia crystallite size, i.e. it is 3.9, 5.4 and 6.9 nm for the catalysts SAZ-1:1-600, SAZ-1:2-600 and SAZ-1:3-600, respectively (Table 1). The absence of monoclinic phase in sulphated zirconia-alumina binary oxides (Fig. 1) implies that the addition of alumina retarded transformation from tetragonal zirconia crystal phase to monoclinic one, and moreover stabilizing catalytic material against undesirable sintering. In the case of sulphated zirconia prepared on the alkoxide base after calcinations at 600°C , volume fraction of monoclinic phase is 13.36% [8,38], while after alumina doping monoclinic phase is omitted (Table 1, Fig. 1).

It is important to underline that the calculated zirconia crystallites are smaller than 7 nm (Table 1), in the catalysts series SAZ-x:y-600, and significantly lower than the established critical value of 15 nm [28,30,39,40] claimed as a key factor for catalytic activity in the isomerization of *n*-hexane. However, catalytic activity is a complex synergistic function of catalyst physico-chemical features, such as: structural, thermal, textural and surface properties. Thus, favourable structural properties (stable active crystal phase and small grain size) are beneficial, but not enough for the expression of high catalytic efficiency.

Moreover, already observed and here discussed catalyst crystallinity after thermal history at 600°C , beside the impact of alumina is possibly additionally improved with sulphates grafted in zirconia-alumina matrix as ad-

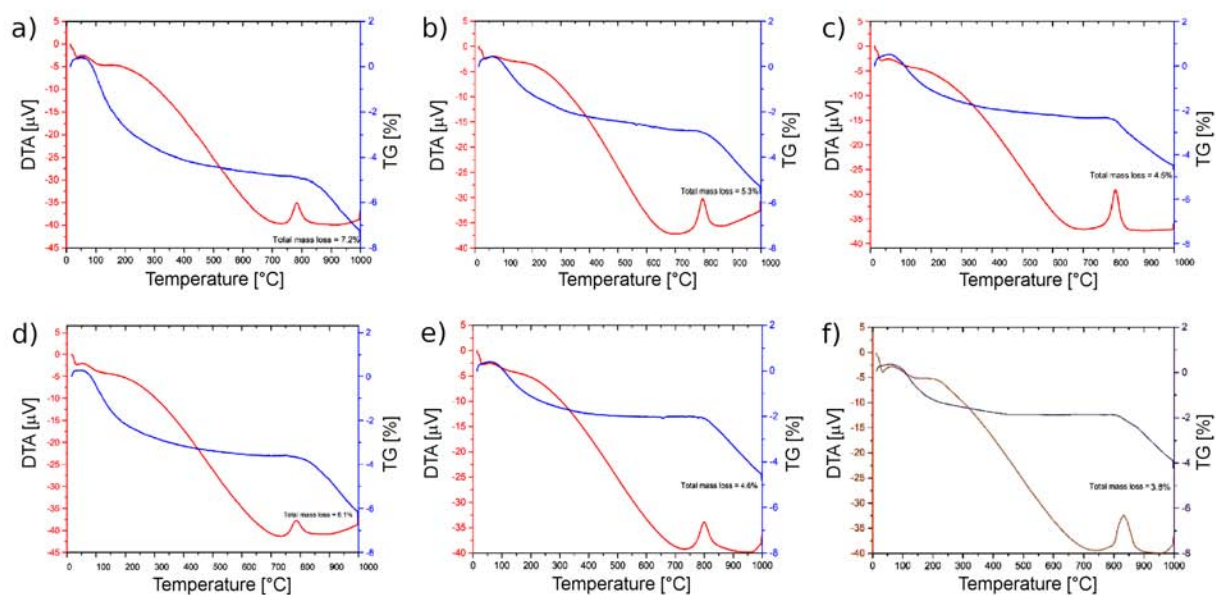


Figure 2. Thermal properties (TG/DTA) of catalysts: a) SAZ-1:1-500, b) SAZ-1:2-500, c) SAZ-1:3-500, d) SAZ-1:1-600, e) SAZ-1:2-600 and f) SAZ-1:3-600

ditives/acid dopants into host [24,28], what is further proved by thermal analysis.

TG curves (Fig. 2) show two/three mass decreases in the case of all investigated catalysts independent on the molar ratio of particular oxide in binary material, and also calcination temperatures. The first one taking place from an ambient temperature up to 200 °C is attributed to the dehydration of surface adsorbed H₂O, and amounts to about 2 wt.%. DTA profiles indicate endothermal effects of dehydration of surface H₂O, which occur in two stages (presented with so called “curve shoulders”) due to a small degree of heterogeneity of the catalyst surface. The second observed mass decrease at nearly 820 °C corresponds to the sulphates removal which probably originates from the decomposition of Zr(SO₄)₂. In the temperature range between 200 and 800 °C there is relatively smooth mass loss ascribed to the removal of labile forms of sulphates, previously reported in the case of sulphated zirconia [28,41]. This observation may impose the existence of at least two types of sulphates of different thermal stability which is already registered in sulphated zirconia [28,42]. In addition, this weight loss may be possibly recognized as a split out of coordinated H₂O and/or condensation of hydroxyl groups from hydroxides obtained as intermediates, which undergone chemical and phase transformations toward related oxide forms.

It is important to emphasize a shift of the sulphates decomposition toward higher temperatures, exactly over 800 °C compared to the situation in the bare sulphated zirconia. Namely, in the case of the catalyst SAZ-1:1-500 sulphates decomposition starts at 840 °C, while in

sulphated zirconia based catalyst it begins much earlier, at 650 °C [28,42]. The registered shift to higher temperature, for 190 °C, may be explained by a stabilization effect of alumina on zirconia. Besides that, this also highly affects surface sulphate density (Table 1). This together should be beneficial for the formation of acidic/superacidic sites that are crucial in direct reaction of *n*-hexane isomerization over carbenium ion mechanism [43]. In addition, higher mass decreases of 7.2% (Fig. 2a) and 6.1% (Fig. 2d), are observed in the cases of the sulphated zirconia-alumina oxides with higher amount of alumina. This is contrary to the bare sulphated zirconia catalysts (which are 4.9% and 4.3% for the samples calcined at 500 and 600 °C, respectively), both catalysts series are previously tailored by the same thermal history [28,42]. Here claimed total mass losses may also include a release of H₂O, but the fact is that binary oxides contained higher amount of thermally more stable sulphates (almost two times) in the following way: 5.2% or 4.1% in the SAZ-1:1-500 and SAZ-1:1-600, respectively, as opposed to 2.6% and 2.5% in their counterparts without alumina [28,42].

Calcination temperatures are previously proved as critical in (super) acidic sites genesis in the synthesis of sulphated zirconia based catalyst [25,44]. Here the authors suggest that this applies to the sulphated zirconia-alumina based catalytic materials too. Namely, higher calcination temperatures also induced greater sulphate density (Table 1).

An exothermal peak on DTA curves may be described by a phase transformation of γ -Al₂O₃ in more stable δ -Al₂O₃, already suggested by XRD analysis. A small

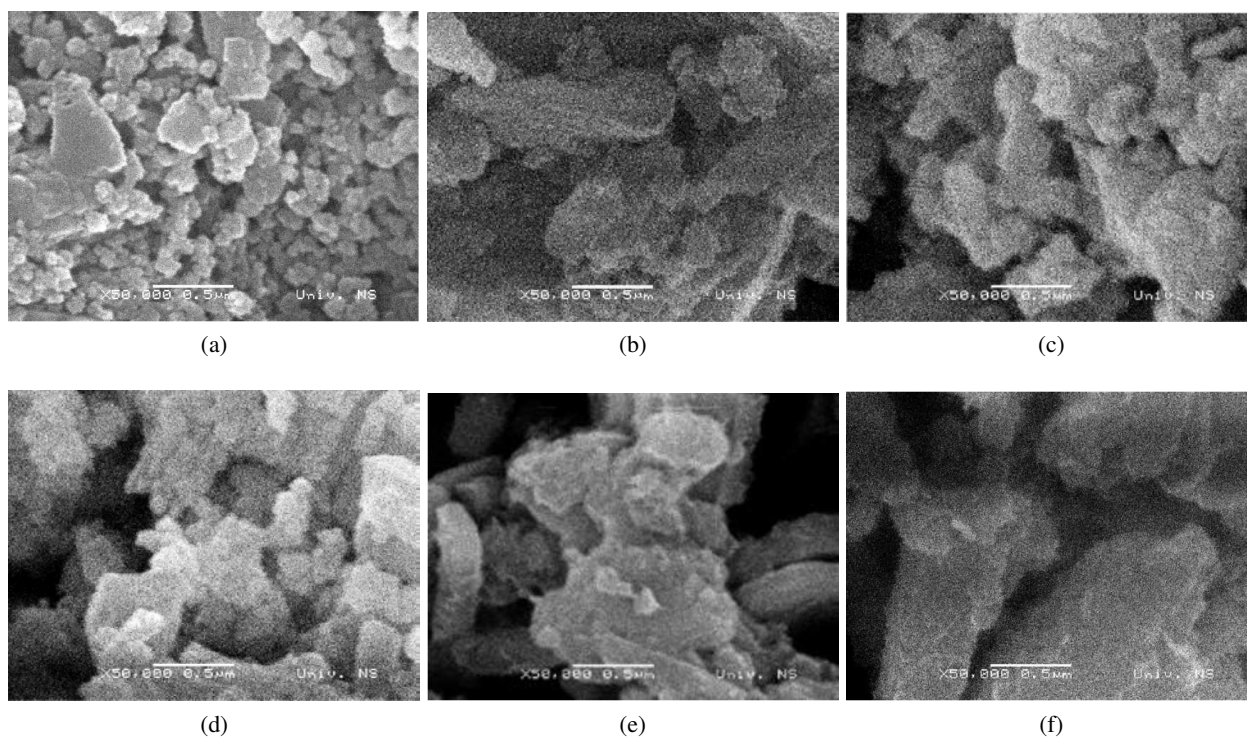


Figure 3. Morphological properties of catalysts: a) SAZ-1:1-500, b) SAZ-1:2-500, c) SAZ-1:3-500, d) SAZ-1:1-600, e) SAZ-1:2-600 and f) SAZ-1:3-600

shift of the peak toward lower temperature (at 790 °C, Figs. 2a and 2d), which indicates a crystallization process, is observed exclusively in the samples with higher amount of alumina. This crystallization process may be related to the binary catalytic system – sulphated zirconia-alumina.

Based on the morphological characterization of binary oxides (Fig. 3), it is observed that the most of particles are on nanoscale, which is expected taking into account the organic precursor used in this study [45].

The same stands for unmodified sulphated zirconia based catalyst [24,45]. The catalyst SAZ-1:1-500 is characterized by the finest grainy structure with the smallest primary particles. It is possible that the surface of this catalyst resulted in the inter-granulated dispersion of zirconia phases (smaller particles) similar to type known as Martens B1 type [33,42], more or less separated from the alumina secondary particles (Fig. 4).

The binary oxides samples with lower concentration of alumina, SAZ-1:2-500 (Fig. 3b) and SAZ-1:3-500 (Fig. 3c), calcined at the same temperature of 500 °C, possess larger particles. This may be in line with the lack of previously supposed stabilization effect of alumina whose content in these cases is lower than 50%. After calcination at 600 °C, the catalysts with the same

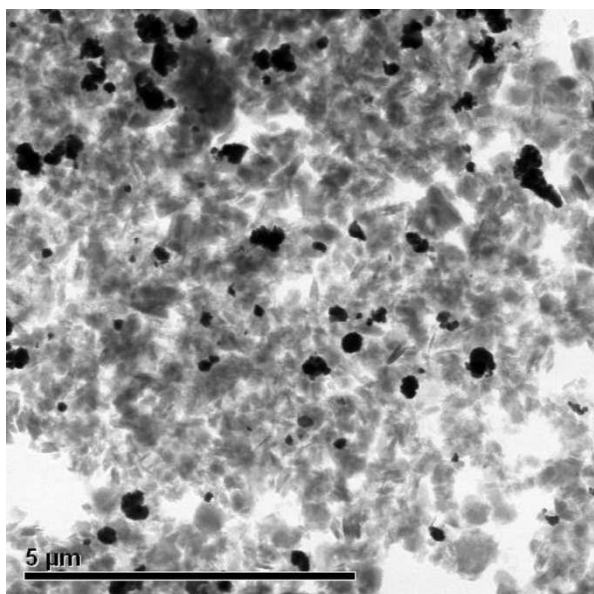


Figure 4. TEM image of sulphated zirconia-alumina based catalyst

and higher alumina ratios are characterized with larger particles in comparison with the sample SAZ-1:1-500. In the case of the catalyst SAZ-1:2-600, where zirconia is more abundant, an agglomeration of alumina particles is evident over which non-agglomerated tetragonal zirconia particles are distributed, already reported by XRD analysis. The calcinations at 600 °C have not caused a significant sintering of sulphated zirconia-alumina catalytic material in contrast to the thermal-treated bare sulphated zirconia [24]. Similar observation stands for the catalyst SAZ-1:3-600 (Fig. 3f). Moreover, this higher calcination temperature is of great importance because it provokes better material crystallinity (Table 1, Fig. 1) and homogeneity of the material surface. Furthermore, the alumina addition together with the impact of calcination temperature has caused a retardation of surface area reduction (a decline almost two times smaller than in the case of SZ counterparts) [29].

3.2. Catalysts activity

It is already reported that the catalytic properties together with structural and morphological features of SZ catalyst are affected strongly by its preparative conditions [24,28,36]. The authors extend this observation on the SAZ catalyst based on the SZ additionally modified by alumina in order to obtain catalyst characterized with moderate level of favourable physico-chemical properties originating from both zirconia and alumina. It has been previously shown that thermal history plays a vital role in occurred catalytic activity [24,36]. Raising the calcination temperature to 650 °C resulted in maximal conversion of *n*-alkanes (hexane and/or butane), as it is claimed for SZ and SAZ catalysts [46]. In the performed catalytic test experiments we have selected 500 and 600 °C as the highest temperatures of the SAZ catalysts thermal treatments. The intention was to avoid undesirable sintering of particles and to make catalyst with the corresponding acidic surface. Besides, hydrogen and/or helium are used as carrier gases because of the supposed various reaction mechanisms. In the experiments carried out in He, the catalyst with the highest amount of zirconia (SAZ-1:3-500), showed an initial activity at the beginning of the time-on-stream (Table 2). The initial activity at reaction temperature 250 °C was relatively poor probably due to the low calcination temperature used. In further reaction course, it is followed by a fast deactivation. Such short catalyst life-time of

Table 2. Catalytic performances and hydrocarbon distribution over zirconia-alumina binary oxides as a function of different reaction temperatures and molar ratios of primary oxides

Catalyst	Initial conversion [%]	Selectivity [%]	Products distribution [%]		
			Mono-branched isomers	Di-branched isomers	Cracked
250 ^a -SAZ-1:1-500-H ₂	55.9	2.7	2.6	0.1	0.1
200-SAZ-1:3-500-H ₂	51.1	3.6	3.4	0.2	0.0
250-SAZ-1:3-500-H ₂	49.9	3.9	3.7	0.2	0.2
250-SAZ-1:3-500-He ^b	0.9	91.1	86.5	4.6	0.0

^areaction temperature

^bcarrier gas used

20 min is probably caused by the reduction of surface sulphates and cooking process in the absence of hydrogen as well as the auto-regenerative conditions.

On the other hand, reaction run carried out in the same set-up under hydrogen as the carrier gas at 250 °C resulted in much higher activity reaching 56% over catalyst with the highest alumina content (50% of alumina; sample SAZ-1:1-500). Lower activity after the initial step (first 20–30 min of the reaction run) was also observed in the case of the catalyst used under hydrogen. Comparing the initial and steady-state activities (not shown) presented that the same SAZ catalyst exhibited up to 60% decreased conversion of the reactant. This reduction in activity in steady-state conditions may be related to the inhibiting effect of carrier gas already claimed in the literature [47,48]. Further investigations (results not shown here) indicate that the presence of Pt improves the catalytic stability of the SAZ based catalyst in the presence of hydrogen because of the hydrogenation of accumulated coke precursors keeping the catalytic activity during time-on-stream. Similar results on the role of Pt as promoter of the SZ catalyst activity and life-time have been already reported by the authors [16,49].

The selectivity profiles as inversely proportional to corresponding conversion percent, showed the dominant amount of mono-branched isomers in the composition of the hydrocarbon products distribution. In addition, this is joined with rather low values of highly desirable di-branched C₆-isomers. It seems that this reaction run comprised a kind of surface chain reaction consisted of few sequential steps, such as an initiation, propagation, termination and/or desorption of products comprising carbenium ions as intermediate state requiring strong acidic sites. It is likely that here used preparation conditions included inferior calcination temperatures than needed for the generation of the strong acid sites. Additionally, the absence of metallic sites caused the instability of catalyst during reaction run undergoing bimolecular reaction mechanism in contrast to monomolecular one over Pt/SAZ catalyst.

IV. Conclusions

The synthesis of sulphated binary oxide catalyst based on zirconia-alumina resulted in a material characterized by rather different structures in comparison with the primary sulphated zirconia catalyst. Namely, the addition of alumina to zirconia has showed a stabilizing effect on the zirconia structure, decreasing tetragonal crystal phase particles and reducing surface area at elevated temperatures. Moreover, it caused slower phase transformation of thermally metastable tetragonal crystal phase of zirconia into more stable monoclinic one. The importance of this thermal stabilization caused by alumina grafting is the best interpreted by the fact that tetragonal crystal phase is claimed as crucial one in the isomerization of *n*-hexane.

The alumina addition also contributed to better homogenization of catalytic material and exhibited a positive impact on the stabilization of acidic sulphate groups and consequently their density. Modification of sulphated zirconia by alumina grafting has caused a shift and delay of thermal degradation of catalyst acid functions.

Zirconia also stabilized alumina oxide in binary system by rising the temperature of its phase transformation, but only when used in higher alumina molar ratios.

The catalytic activity of the material based on the sulphated binary oxide consisted of zirconia-alumina is a complex synergistic function of favourable physical and chemical properties, and in order to be realized, the reaction should be conducted under the optimized conditions of catalyst activation.

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