The balance between acidity and tetragonal phase fraction in the favorable catalytic act of modified zirconia towards isomerized *n*-hexane(s)

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Zirconia-based catalysts were promoted by acid functions (sulfate and phosphate anions) and tested in order to establish catalyst efficiency in test reaction of *n*-hexane isomerization. The impact of surface and structural properties on the final catalytic performance is also investigated. It is proven that well-established balance between total catalyst acidity, acidic surface density and crystal phase nano-structure determines the catalytic activity in the reaction towards isomerized products. Type of acidic promoter strongly affects the resulted catalytic act. This stands for pyrosylfate groups in sulfated zirconia catalysts and orthophosphate groups in phosphated zirconia catalysts both essential in the favorable reaction run.

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1. Introduction

The (hydro)isomerization of normal chain alkanes without by-reactions (cracking) has become a key reaction for providing high research and/or motor octane number (RON and MON) in the modern petroleum production of various fuels [1,2]. *Iso*-alkanes are considered as appropriate alternatives for the application of ON boosters based on aromatics and oxy-genates whose contents are seriously restricted by current specifications on the gasoline quality in order to protect the environment. Namely, recent and proposed new regulations on gasoline standards (parameters) have stressed the necessity for so called "reformulated" fuels containing high-octane number molecules in the gasoline pool.

Isomerization of the C_5-C_7 cut has the right combination of RON/MON parameters that are in compliance with the environmental necessities. Linear alkanes such as *n*-hexane and *n*-heptane are normally constituted in light naphtha/crude oil both characterized with low RON, 25 and 0, respectively. On the other side, their isomerized counterparts (multi-branched/di-branched alkanes, ex. *i*-hexane/*i*-heptane) are characterized with much higher RON, 74 and 45, specifically [3,4].

Traditionally, functional metal/acid catalysts are used in industrial (hydro)isomerization of C_5-C_7 alkanes. Highly chlorinated platinum/alumina catalysts are applied at lower process temperatures (up to 180ºC). However, unfortunately, these catalysts are very sensitive to catalytic poisons (ex. water vapor, sulphur) in the feedstock and easily undergo to a deactivation. Moreover, chlorine based compounds have to be continuously added to maintain catalyst acidity and thus the catalyst efficiency [5,6]. It is widely known that chlorine compounds can cause serious corrosion problems in the plants, and health hazards. Normal alkanes transformation comprises hydrogenation and dehydrogenation steps on the metallic sites, and isomerization or undesirable cracking steps on the acid sites, the last ones taking place on highly acidic sites. Acidic centers also play important role in final products desorption and mass transfer processes between former and the latest.

Zeolites based bi-functional catalysts exhibited resistance to feed impurities and have been conventionally used in the petroleum processes, but operated at higher temperatures around 250 °C [7,8].

It is highly important to highlight when the catalyst is quite balanced, the acid function is the limiting one, while the mass transfer of intermediates, and the product distribution depends essentially on the catalyst acidity and pore structure of the solid acid [9,10]. Consequently, the activity and selectivity of the catalyst depend on the characteristics of the acid and metal sites.

The investigations for new environmental friendly and highly active catalytic material with both appropriate nano-structure and strong acidic properties, and without the cited drawbacks have attracted considerable scientific interest. That is a challenging task for the near future in the heterogeneous catalysis field.

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In compliance with these necessities, various types of acidic solid materials have been subjected to a range of researches. Particularly, metal oxides (oxides of titanium, zirconium, iron, niobium), complex metal oxides, heteropoly acids, inter-layer compounds, solid super-acids are represented as most interesting catalytic materials [11,12]. Among the solid acids reported, zirconia based materials (sulfated, tungstated, and rarely phosphated ones) have been accorded to the greatest share of scientific interests [13-15].

Pure ZrO_2 is found useful for a wide range of industrial applications [16] and well-known in the field of heterogeneous catalysis. It is proven as active catalyst in a number of industrial processes such as: *n*-alkanes isomerization, alkylation, hydrogenation, oxidation and esterification [17]. The successful usage of zirconia is strongly influenced by the preparation conditions, *i.e.* consequently, the resulted texture (well-developed pore structure), nano-crystallinity and thermal stability. Zirconia-based catalyst may be synthesized in a number of different procedures, while organic precursors are nowadays frequently used. The synthesis from these starting materials provides numerous advantages regarding nano-structure and highly-ordered, homogeneous materials [18]. Special interest was given to achievement of the surface acidity required for desirable catalytic efficiency in isomerization reaction [13,19].

The catalytic activity of zirconia is previously attributed to acidic, basic, oxidizing and/or reducing surface properties [20]. It is also established that zirconia, can exist in three polymorphic crystalline structures: monoclinic, tetragonal and cubic one [21] in dependence on the preparation conditions, thermal treatments, precursor material and acidic promoters used.

Although there are many papers dealing with structural and surface properties of zirconia, it is still a controversy on the acidic features of sulfated zirconia [13,22] and related activity. Similarly, the real explanation on stabilizing status/role of acid functions on the desired tetragonal crystal phase in zirconia is not yet fully understood [13,19,22-24].

In the case of phosphate anions incorporated it is found an increase in surface acidity and bulk crystallinity of the zirconia oxide [25]. The group of authors has researched structural properties of a number of sulfated and phosphated zirconia materials samples prepared in various procedures and under different conditions [15,16,24,26].

To the best of our knowledge, there are no results on the experimental data of phosphated zirconia activity in isomerization reactions. In addition, still, there is no finally published data and explanation on the relation of particular crystal phase stabilization and total acidity or nature of the surface catalyst acidity, and resulted catalytic efficiency.

The aim of this paper is to determine physico-chemical and structural properties of zirconia promoted by sulfates and/or phosphates anions, and to test their efficiency in the isomerization of *n*-hexane. It is expected that some details on structural and surface properties would light the potential relation between particular features and final positive consequences on the catalytically directed conversion toward desirable products.

2. Experimental procedure

Synthesis of catalysts

Zirconia-based catalysts were synthesized by hydrolysis of zirconium propoxide (70% solution in 2-propanol; Aldrich Co.) using the modified sol-gel method reported earlier [18,27]. The acid promotion with sulfate anions was realized by incipient wet technique using 0.5 M sulfuric acid for the nominal sulfate content of 4 wt. %. In the series of zirconia based catalysts promoted with phosphate groups, the introduction of intended 4 or 10 wt. % was performed by using conc. phosphoric acid over the same technique.

The subsequent thermal treatment of catalytic samples was done for 3h in dynamic atmosphere of synthetic air flow of 25 cm^3/min with a heating rate of 15ºC. Sulfated and phosphated catalytic series were treated at two chosen temperatures: 600 and 700ºC.

Catalysts of both series were denoted as it follows: X-SZ-Y and/or X-PhZ-Y, where X represented weight percentage of anionic promoter, and Y stands for the calcination temperature applied.

Characterization

X-ray diffraction analysis (XRD, APD-1700 diffractometer with a Cu-anticathode and monochromator) was used for the determination of the crystal structure of the modified zirconia-based catalysts.

Basic textural properties (surface area, cumulative desorption pore volume, average pore diameter, and pore size distribution) were investigated by low temperature nitrogen adsorption/desorption method using Micromeritics ASAP 2010. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation [28]. The pore size distribution (PSD) was determined by the Barrett-Joyner-Halenda (BJH) method [29]. The average pore diameter was determined based on the BJH desorption mean pore diameter [29]. The PSD curves were plotted and used in calculation based on the implementation of the Kelvin equation [30].

The surface characteristics of catalysts, *i.e.* nature of acidic sites, were studied by Fourier transformed infrared spectrophotometry with previously adsorbed base (pyridine) by means of Thermo Nicolet Nexus FTIR spectrophotometer. The related total acidity of the catalyst surface was evaluated by following the color change of Hammett indicators. The following selected indicators: *p*-dymethylaminoazobenzene and crystal violet were used covering the range of H_o values from 3.3 to 0.8 [31].

TEM characterization was carried out using a TEM/EDX microscope CM20, Philips, Lab 6 operated at 200 KeV. Electron micrographs were recorded at magnification of 600.000x. Catalysts samples were supported on holey carbon-coated copper grids by simply grinding the specimen between two glass plates and bringing the powder into contact with the grid.

Catalysts efficiency – test reaction

The isomerization of *n*-hexane as test reaction was used to probe the efficiency of the modified zirconia-based catalysts. The catalytic reaction was completed in a quartz fix-bed micro-reactor. The reaction conditions were: operating temperature 300 ºC, 1 bar pressure, partial pressure of *n*-hexane 60.5 mbar, and the molar ratio of helium to *n*-hexane was 15.5. An activation of catalysts (0.5 g of each sample) was done *in situ* in synthetic air flow of 25 cm^3/min at 500ºC during 1h.

Conversion of reactant, *n*-hexane, was evaluated regarding each particular gas product and normalized it by the number of C-atoms in both the reactants and products. The reaction gas-phase products were firstly separated on the PONA (30 m) GC-capillary column and then analyzed using the GC chromatograph (GC-HP 5890, Series II) equipped with FID detector. Selectivity to the particular gas-product was calculated by division of normalized conversion to the selected particular compound with the total conversion of the reactant. The final catalyst efficiency parameter, yield, was evaluated as multiplication of the expressed activity and selectivity data.

3. Results and discussion

XRD patterns (Fig. 1) and some of our previously reported results on crystallization of zirconia-based materials upon heating [26,27,32,33] showed that an amorphous material based on zirconium-hydroxide transformed to well crystalline a mixture of tetragonal (t-ZrO_2) and/or cubic zirconia (c-ZrO_2), and monoclinic one (m-ZrO_2) after thermal treatment beginning with 450 ºC.

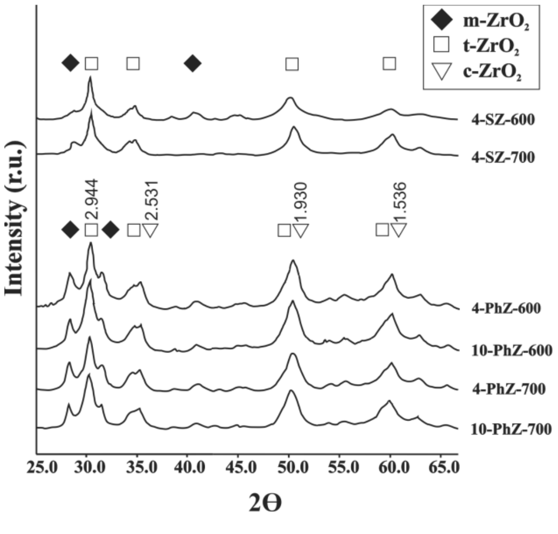

Fig. 1. XRD patterns of the sulfated and phosphated zirconia-based catalysts.

Heating in synthetic air, *i.e.* calcination of zirconia-based materials up to 450 ºC, caused non-crystalline zirconium-hydroxide existence, claimed in our recent results [19,32]. This “limited” temperature marks zirconia crystallization into metastable t-ZrO_2 and minority of m-ZrO_2. It is similarly observed that unstable t-ZrO_2 up to 600 ºC underwent partly to atomic rearrangement in non-crystalline form, and also marginal intergrowth of m-ZrO_2 [34]. Direct investigation of the cited data on zirconia structural polymorphs presented that each of these phases may exist in stable, metastable and/or thermally or mechanically stabilized state. It is proved that m-ZrO_2 may be stable to 700 ºC, and transforms into t-ZrO_2 at higher temperatures from 650 to 1100 ºC. Finally, upon further heating up to 2000 ºC, tetragonal polymorph arranges in cubic one [34-36].

Specifically, it is interesting an influence of foreign-ion additives (anions and/or cations) on the polymorph transformations of zirconia. The influence of some oxidic forms of cations, ex. Y^{3+}, Ce^{4+}, Ca^{2+}, and Mg^{2+} in stabilization of some zirconia crystal phase at lower temperatures is proved earlier [36-38]. In the case of anions used as additives, there are only few reports on sulfate stabilization role on structural properties of zirconia [13,19,22,32,39]. However, analogous investigations bearing in mind the impact of other anions on structural properties of zirconia are rarely faced in the scientific literature.

In general, the results derived from Fig. 1 and summarized in Fig. 2 showed favorable effect of anionic species (sulfate and/or phosphate) incorporated in bare zirconia taking into account the increased amount of tetragonal crystal phase and diminished zirconia crystallite size comparing to unmodified zirconia. In the case of phosphate anion used, this stands exclusively for higher content applied (10 wt. %).

Grafting with sulfate ions in the sulfated zirconia-based catalysts calcined at both temperatures indicated tetragonal ZrO_2 structure prevailed (more than 70%) with a few small intensity peaks (at 28.25º, 2θ) that are assignable to a minor fraction of monoclinic zirconia.

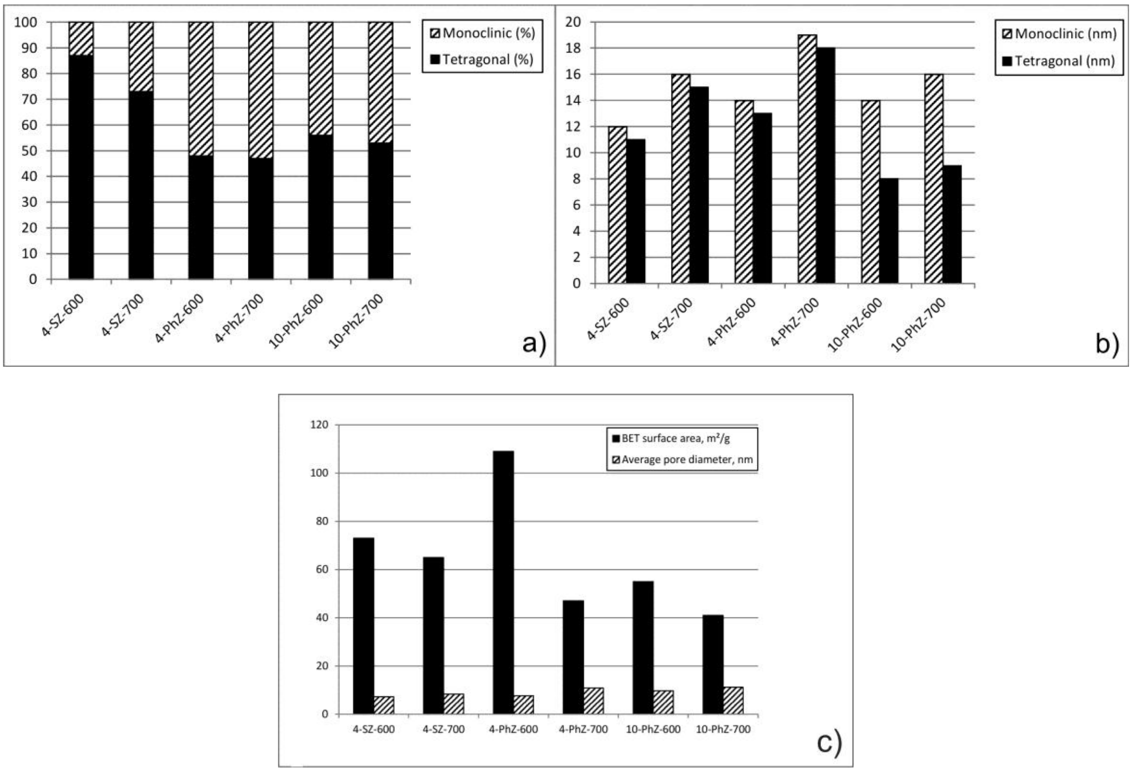

Fig. 2. Structural and textural properties of zirconia based catalysts: a) zirconia crystal phase structure; b) zirconia crystallite size; c) BET surface area and average pore diameters.

On the other side, XR - diffractograms of the phosphated zirconia-based catalysts with incorporated 10 wt. % ions (Fig. 1) demonstrated surpression of monoclinic zirconia phase with the peaks originated from tetragonal and/or cubic zirconia phases. Zirconia modified with phosphate ions also resulted with stabilization of cubic crystal phase at lower temperatures, even at 700ºC what is difference to the literature fact that it is only stable at ≥ 2000 ºC [34-36].

Calcination at 600ºC of both sulfated and phosphated zirconia-based catalysts gave rise to XRD patterns characterized with dominant presence of t-ZrO_2 in sulfated samples and t- and/or c-ZrO_2 in phosphated ones with higher weight contents of phosphate additives used.

Accordingly, sulfate additives may be seen to retard the crystallization of zirconia into unfavorable monoclinic ZrO_2 phase to occur near 600 ºC whereas phosphate additives in higher weight amount retard such the crystallization up to 700 ºC.

It is worth to underline that tetragonal zirconia phase is widely referred to as the active catalytic phase for the reaction of *n*-hexane isomerization [40,41].

Moreover, the authors claim the influence of acidic groups – promoters on the tetragonal zirconia crystallite size that may highly affect final catalytic performances in the test reaction. Explicitly, sulfate groups maintained particle size of t-ZrO_2 from 12 to 15 nm, but it is much more maintained in phosphated zirconia-based catalyst with 10 wt. % of phosphate, explicitly, below critical 10 nm (Fig. 2). It is believed that this parameter (particle size to 10 nm) is essential for the zirconia-based catalysts favorable efficiency in the isomerization reaction [19,32].

FTIR spectra recorded for the acid-modified zirconia-based catalysts are shown in Fig. 3. In the case of sulfated zirconia-based catalyst (4-SZ-600), stretching vibrations of –OH groups located in the region (3800-3300 cm^{-1}) present broad band of lower intensity at 3400 cm^{-1}. This band with maximum at about 3450 cm^{-1} is characteristic for the acidic features of –OH groups, and a “tail-band” at higher frequency, 3630 cm^{-1}, which is typical for the –OH groups of the highest acidity [42,43]. This may indicate the catalyst (4-SZ-600) containing catalytic active centers of highest acidity. Besides, such double-bands pattern is already claimed as exclusive characteristic for the tetragonal ZrO_2 phase [42]. Tetragonal crystal phase is earlier proved as essential one for the catalytic activity in the isomerization of *n*-hexane [40,41]. These data are in line with reported XRD results on dominant presence of t-ZrO_2 in the catalyst 4-SZ-600 (Figs. 1-3).

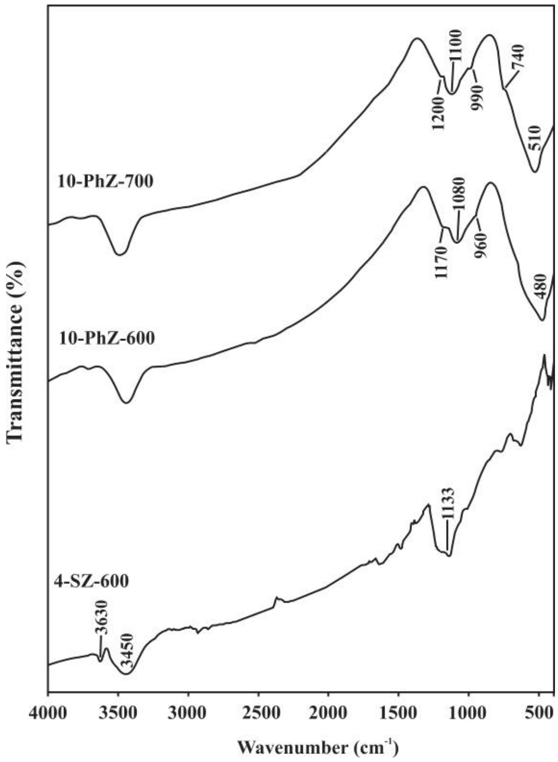

Fig. 3. FTIR spectra of the 4-SZ-600, 10-PhZ-600 and 10-PhZ-700 catalysts.

Characteristic bands in the S=O stretching region (1440-1300 cm^{-1}) with more or less typical maxima are verified in the catalyst 4-SZ-600 at about 1333 cm^{-1}. Such bands presented at higher frequencies are assigned to pyrosulfate groups [42]. Somewhat broaden band at 1133 cm^{-1} in the catalyst 4-SZ-600 demonstrates a possibility of labile pyrosulfate groups existence. Previously reported catalytic tests for isomerization reaction showed that conversion of *n*-butane highly depended on the amount of pyrosulfate groups [44]. Here, the authors suppose presence of two types of pyrosulfate groups (more or less stable) in the 4-SZ-600 catalyst. In such a way total amount of highly acidic pyrosulfate groups significantly contributes to a favorable catalytic activity of the catalyst 4-SZ-600 (Fig. 4.).

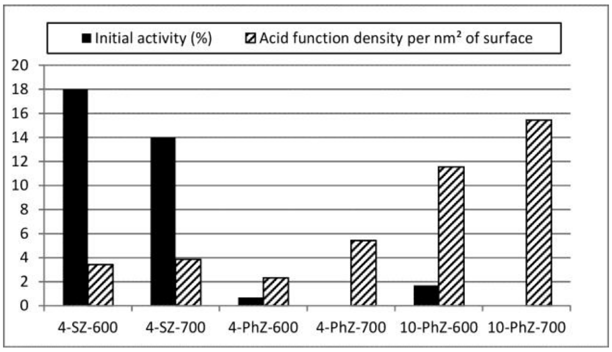

Fig. 4. Initial catalyst activity and acid function density of zirconia-based catalysts.

In the literature, to the best of our knowledge, there is no similar data on the two type of pyrosulfate groups on the zirconia-based catalyst derived from an alkoxide, and no relation with the expressed affirmative catalytic efficiency. On the other side, at the surface of the corresponding catalyst, but calcined at 700ºC (4-SZ-700), no scanned bands indicated highly acidic groups that may contribute to the catalytic activity in the isomerization reaction.

FTIR spectra of 10-PhZ-600 showed three bands at around 1170, 1080 and 960 cm^{-1} due to P-O band vibrations of phosphate groups/species (PO_4^{3-}) [35]. The single band is observed at 480 cm^{-1} originated from metastable c-ZrO_2. In the higher temperature calcined catalyst, 10-PhZ-700, evident is a large frequency shift of the 480 cm^{-1} band to around 510 cm^{-1}, and additional occurrence of a shoulder at about 740 cm^{-1}. These differences in the FTIR spectra of 10-PhZ-700 in comparison with the same of the catalyst 10-PhZ-600 may be attributed to an appearance of a fraction of m-ZrO_2. The all these results are in correlation with the results of the XRD analysis (Figs. 1,2), and consequently related catalytic activity. In the FTIR spectra of the catalyst series with lower phosphate content (not shown) there are no observed bands that indicate vibrations of ortho-phosphate species and/or particular crystal phases of zirconia.

Surface of nano-structured and microcrystalline modified zirconia may possess a large number of imperfections originating from oxygen and/or metal vacancies that can cause local or regional charge or crystal disproportions. These surface and crystal imperfections together with acidic groups onto zirconia-based catalyst may result in quite beneficial catalytic activity and selectivity to high ON products.

The surface density of the acidic groups in the case of sulfated zirconia-based catalyst has been previously reported as a clue for the catalytic activity [45]. Here, the authors suggest that also surface density of phosphate groups may be taken as essential in the determination of the final catalytic efficiency. The higher acid function density is calculated in both catalytic series sulfated and phosphated ones higher catalytic activity is achieved, too (Fig. 4). In addition, not only acid function density but exclusively together with total acidity is beneficial in contribution to the final catalytic efficiency. The way of the acid group density definition applied in the present investigation [13] may be somewhat limited by the textural characteristics of the particular catalytic sample (*i.e.* specific surface area). Total acidity was expressed relative to color change of the applied Hammett indicators as the range of H_0 values covered by the available indicators. The catalyst 4-SZ-600 exhibited the highest total acid strength ($H_0 < 0.8$) among all the tested catalysts. All other catalysts samples are characterized with surface acidity within the range $3.3 \geq H_0 \geq 0.8$ (not shown). The catalyst 4-PhZ-700 impregnated with lower phosphate wt. % and calcined at higher temperature presented the lowest total surface acidity. Generally speaking, zirconia-based catalysts modified by sulphate groups possess higher total acidity than those promoted with phosphate groups. The final catalytic efficiency over sulfated zirconia-based catalysts is previously ascribed to both the total acidity and surface dispersion of active acid sites [43]. In the present investigation, the authors impose wider discussion taking into account also catalytic performances of phosphated zirconia-based catalysts associated with both total acidity and acid sites density.

The BET surface areas of the sulfated zirconia-based catalysts are 73 and 65 m^2/g for catalysts calcined at 600 and 700ºC, respectively. Exactly, the authors predict that BET surface area of zirconia-based catalysts should be correlated with the preparation method and parameters used. In the phosphated zirconia-based catalysts series the BET surface areas are in the range from 40 to 55 m^2/g, while the catalyst with 4 wt. % of phosphate and calcined at 600ºC possesses specific surface area greater than 100 m^2/g (Fig. 2). This unexpectable high specific surface area is in line with the significant fraction of mesopores/micropores also reflected over considerable pore volume of the catalyst (0.24 cm^3/g).

Based on the textural characteristics of both catalytic series it is evident that grafting of bare zirconia with sulfate groups did not affect surface area much more than introduction of phosphate groups in the catalytic series synthesized under the same preparation procedure.

The increase of the calcination temperature from 600 to 700ºC has caused BET surface areas decrease, and the average pore diameter broadening, *i.e.* transformation of (meso)pores structure as a function of calcination temperature. Consequently, the sintering process is imposed, that, authors believe, leads to a modified zirconia-based material consolidation [24,27].

HRTEM 2D micrograph of the selected locations on the 4-SZ-600 catalyst and crystallographic orientations is presented in Fig. 5. The registered dominant crystallographic orientation of zirconia, taking in mind three different orientations at an atomic level, is <010> characterized with presence of so called “short atomic steps” [46]. Besides, it is observed a plane orientation {001} that may include Schottky vacancies at the edges. The last two observed crystallographic orientations present potential very active catalytic and/or adsorption sites [47] located at/or near edge of crystallites with high Miller indices. The presence of these sites is closely connected with the expressed favorable initial catalytic activity of the catalyst 4-SZ-600.

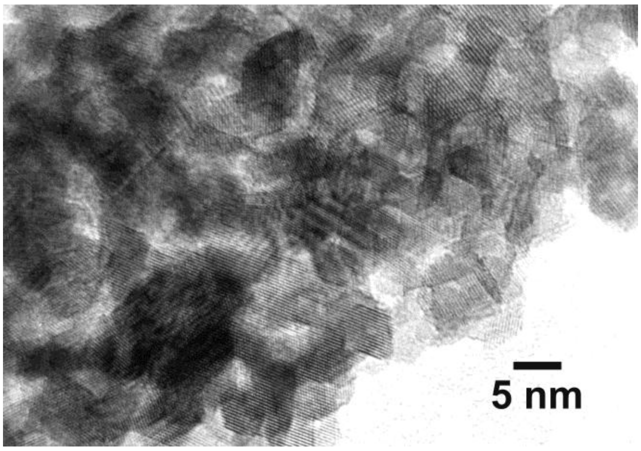

Fig. 5. HRTEM micrograph of the 4-SZ-600 catalyst.

Some important correlations may be imposed based on the withdrawn comparisons between physic-chemical properties of zirconia-based catalysts and the exhibited catalytic efficiencies. There is a direct affirmative relation between the fraction of the tetragonal crystal phase, and critical crystallite size, and finally the resulted catalytic activity. Fatherly, not only the total acidity but together with acid groups/sites density are of vital interest in determining the catalyst efficiency. Moreover, the authors suggest that a type of acidic promoter of bare zirconia matrix strongly affects the total acidity. In addition, besides sulfate groups essential are pyro-sulfate groups in determining catalyst acidity of the sulfated zirconia-based catalyst, and ortho-phosphates are of crucial importance contributing to the acidity of phosphated zirconia-based catalyst.

Catalyst 4-SZ-600 presented the most favorable initial catalytic activity that is the result of the synergistic balanced roles of catalyst structural, surface, morphological and textural features, that is, the highest total acidity and acceptable sulfate density together with the most appropriate crystal phase structure (Figs. 1,2,4). Relatively poor catalytic performance of the catalyst 10-PhZ-600 indicates on the needed balance between desirable total acidity, present acid sites density and favorable crystal phase composition with dominant content of tetragonal and/or cubic zirconia phase. Catalysts calcined at higher temperature in both catalytic series, and with smaller phosphate amounts in the phosphated zirconia-based series, are characterized with quite low initial activity because of not established harmony of the advantageous physico-chemical properties. This means that some/single catalyst feature may be developed to improve catalytic act in the test reaction, but it is not sufficient in determination of the total catalytic efficiency.

4. Conclusions

It is established that well-balance between total acidity, particular acid function surface density and an appropriate crystal phase nano-structure strongly determines the final catalytic performance of sulfated and phosphated zirconia-based catalysts in the test reaction of *n*-alkane isomerization. Limitedly present highly active pyrosulfate groups in sulfated zirconia catalysts are responsible for the most favorable catalyst activity performed.

Besides, it seems that sulfated zirconia-based catalysts showed advantageous efficiency due to well-adjusted high total acidity, proper nano-structure composition, particular crystallographic orientations with Schottky vacancies, and suitable meso-porous texture.

Oppositely, rather poor catalytic activity of the phosphated zirconia-based catalysts despite developed positive single physico-chemical property speaks on the complexity of active phases/sites genesis and balance establishing. Ortho-phosphate groups are of essential importance in improving the total surface acidity of the phosphated zirconia-based catalysts.

Type of acidic promoter onto zirconia matrix should highly affect catalytic acidity, and final performance in the reaction catalytic act. Variable surface density of acidic promoter originated from the heterogeneity of the surface together with total acidity, and balanced with favorable nano-structure phases strongly affect catalytic efficiency despite the status of other physico-chemical properties of the catalytic material.

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