Dedicated to Prof. Sorin Rosca on
the occasion of his 70th birthday

The Influence of the Preparation of $Zr(OH)_4$ Precursor on the Catalytic Performances of ZrO_2/SO_4^{2-} in the Isomerization of *n*-butane

MIHAIELA ROPOT[1]*, EMILIAN ANGELESCU[1], RODICA ZĂVOIANU[1], RODICA BÎRJEGA[2]
[1] University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis, Bd. Regina Elisabeta, Nr. 4-12, 030018, Bucharest, Romania
[2] National Institute for Physics of Plasma, Lasers and Radiations, Măgurele, Romania

In the preparation of sulfated zirconia catalysts, the properties of products, including catalytic activity, are influenced by the precursor from which $Zr(OH)_4$ *is obtained, by agents of precipitation and solvents. The most active catalysts for the isomerization of n-butane to izobutane was obtained from* $ZrCl_4$ *precipitated with* $N_2H_4 \cdot H_2O$ *and maturated, but a better selectivity was obtained when* $ZrOCl_2 \bullet 8H_2O$ *was using.*

Keywords: sulfated zirconia catalysts, catalytic activity, agents of precipitation, isomerization of n-butane

The isomerization of alkanes into corresponding branched isomers is one of the important processes in petroleum refining. The isomerization of C_4–C_6 hydrocarbons is already performed at industrial scale. Through the so-called bifunctional catalysts are used in industrial processes, the improvement of their catalytic performances is still a challenge. Isobutane obtained by the isomerization of butane is also used for alkylation process and for MTBE synthesis after dehydrogenation to isobutene. Skeletal rearrangement of hydrocarbons is also important in hydrocracking of higher hydrocarbons to obtain the products with higher octane numbers. This paper deals with a class of solid catalysts, based on sulfated zirconium dioxide, that are able to catalyze the isomerisation of alkanes at relatively low temperature [1, 2].

The influence of the preparation parameters, i.e., zirconium precursor, sulfation agent and sulfation procedure, and calcination temperature has been extensively studied [3-5]. However, no general consensus on the more suitable preparation method has been reached.

We have used for preparation $ZrOCl_2{\cdot}8H_2O$ or $ZrCl_4$ as precursors and NH_4OH (28% g/g) solution or hydrazyne hydrate as precipitation agents.

The activity and selectivity of sulfated zirconia in the skeletal isomerization of *n*-alkanes depend in high extent on the sulfate content, the crystallization degree and the concentration of tetragonal, monoclinic or cubic phase of ZrO_2. Extensive researches have showed that good catalytic performances are associated to a high content of well-crystallized tetragonal phase of ZrO_2 [2, 3, 7-13].

The balance between crystalline and amorphous phase as well as the prevailing crystalline phase depend on ZrO_2 genesis conditions namely: the nature of zirconium salts, the precipitation agent and the operating parameters during the precipitation of $Zr(OH)_4$ precursor, the modality used for the dehydration of zirconium hydroxide, and the temperature regime during the calcinations.

When treating the aqueous solutions of $ZrOCl_2{\cdot}8H_2O$ with alkali hydroxides solutions or with NH_4OH the following phases may be formed [14]:

- α-zirconic (*orto*-zirconic) acid H_4ZrO_4 or tetravalent zirconium hydroxide $Zr(OH)_4$, white precipitate with amphoter character, which forms easily colloidal solutions;
- β-zirconic (*meta*-zirconic) acid $ZrO(OH)_2$ obtained by the precipitation of warm $ZrOCl_2{\cdot}8H_2O$ solutions with warm alkali hydroxides solutions or by long-lasting boiling of *orto*-zirconic acid. This white jelly precipitate of $ZrO(OH)_2$ may be obtained if $Zr(OH)_4$ is maturated by heating in the mother solution during several tens of hours.

Sulfation of zirconia creates mainly Lewis acid sites on the surface of the solid [14-20]. Initially it has been assumed that after sulfation, zirconia becomes a solid with superacid properties [1,2, 21-24]. Ulterior researches have showed that ZrO_2/SO_4^{2-} posses strong Lewis acid sites as well as Brönsted acid sites which have a strength comparable to the acid sites in MFI zeolite [16]. Anyway, ZrO_2/SO_4^{2-} is a solid-acid catalyst that may promote reactions that are taking place through carbenium ions intermediates such as the isomerization of *n*-butane or of the higher alkanes.

Experimental part

Preparation of the catalysts

$ZrCl_4$ and $ZrOCl_2{\cdot}8H_2O$ (Merck, GR for analysis), respectively, have been solved under stirring on ice-bath in different solvents such as: i) methanol-ethanol mixture (1/1 volumes), ii) *i*-propanol or ethanol solutions.

In the obtained solution, an aqueous solution of the precipitation agent was added drop-wisely during 120 min under stirring at 50°C. The *p*H reached by the end of the thermo-hydrolysis was 8.

The precursors obtained by precipitation with hydrazine hydrate have been aged at 60°C, during 72 h, while maintaining the *p*H value at 8.

Zirconium hydroxide has been separated by vacuum filtration, washed with distilled water until the washing water became free of chlorine ions (as determined by reaction with $AgNO_3$), and dried at 120°C during 24 h. The dried zirconia precursor has been submitted to sulfation with $(NH_4)_2SO_4$. The amount of $(NH_4)_2SO_4$ was calculated in order to achieve a final sulfur content of 2 wt. %. After sulfation the catalyst has been dried at 120°C during 24 h and calcined in air flow at 600°C during 2 h .

Characterization of $Zr(OH)_4$ *precursors and* ZrO_2/SO_4^{2-} *catalysts*

Both hydroxilic and sulfated precursors as well as the derived catalysts have been submitted to the following

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* email: mihaiela_ropot@yahoo.com

textural, structural and physical-chemical characterization techniques:

- determination of the porous structure using a Carlo-Erba equipment for recording nitrogen adsorption-desorption isotherms at –196 °C using BET equation.
- the acidity of the catalysts has been determined by ammonia termoprogrammed desorption TPD-NH_3 using the technique described in a previous paper.
- X-Ray diffraction using a DRON-3 diffractometer with $CuK_{\mathring{a}}$ (1,5406 Å) radiation of 40 kW, 20 mA and a Ni filter.
- transmission electronic microscopy using TEM – TESLA BS – 540 apparatus with acceleration tension of 120 kV. The metal carbon replicas of the samples have been investigated under an angle of 30 °.
- thermal analysis TG/DTA in the temperature range 25-800°C with a heating rate of 10°C/min using MOM – Q 1500 D apparatus.

Catalytic tests

The calcined catalysts have been tested for the isomerisation of *n*-butane in the temperature range 50-250 °C under atmospheric pressure using:0.5 g catalyst (d_p = 0.4-0.5 mm) using a U-shaped microreactor coupled to a gas-chromatograph Perkin-Elmer 3920 B with FID detector equipped with a column (8 m length, 5mm i.d.) filled with 25% bismetoxi ethyladipate on chromosorb P (60-80 mesh). Prior to the catalytic test the catalysts have been activated at 250°C either in H_2 or in air flow during 30 min. The reactant flow consisted of a mixture of nitrogen and *n*-butane with a molar ratio N_2 / n-C_4H_{10} =2/1.

The catalytic activity was expressed as:

$$Conversion(\%) = \frac{moles \text{ of } n - C_4H_{10} transformed}{moles \text{ of } n - C_4H_{10}\ introduced} \bullet 100$$

$$r_i = \frac{mmoles \text{ of } iso - C_4H_{10} formed}{g_{catalyst} \bullet \text{sec}ond}$$

r_i = rate of isomerisation

$$Selectivity(\%) = \frac{moles \text{ of iso} - C_4H_{10} formed}{moles \text{ of } n - C_4H_{10} transformed} \bullet 100$$

Results and discussion

Characterization of catalysts

a) The physico-textural characterization and the determination of the acidity of ZrO_2/SO_4^{2-}

Table 1 presents the physico-textural characteristics as well as the acidity determined by TPD-NH3 for the sulfated zirconia catalysts depending on the nature of Zr source, the precipitation agent and the solvent utilized for the dissolution of the Zr-containing compound.

The results showed that :

-the catalyst prepared by precipitation without aging, using a solution of $ZrOCl_2 \cdot 8H_2O$ in methanol-ethanol (1/1 vol.) solvent and an aqueous solution of NH_4OH, has the lowest specific surface area;

-the samples prepared by precipitation with $N_2H_4 \cdot H_2O$ and aged at 60°C during 72 h have the largest specific surface areas;

-even if the highest total acidity is presented by the catalyst ZrO_2/SO_4^{2-} prepared from aqueous solution of $ZrOCl_2 \cdot 8H_2O$ precipitated with $N_2H_4 \cdot H_2O$, the highest concentration of strong acid sites corresponds to the catalyst ZrO_2/SO_4^{2-} prepared by precipitation without aging, using a solution of $ZrOCl_2 \cdot 8H_2O$ in methanol-ethanol (1/1 vol.) solvent and an aqueous solution of NH_4OH;

-the catalysts ZrO_2/SO_4^{2-} obtained from $ZrCl_4$ dissolved in ethanol solvent precipitated with $N_2H_4 \cdot H_2O$ or NH_4OH have similar concentration of strong acid sites even if their total acidity is different.

b) XRD Analysis

The powders of the calcined catalysts have been examined by X-Ray diffraction. Figure 1 displays the XRD patterns of ZrO_2 and ZrO_2/SO_4^{2-} calcined at 600 °C during 2 h.

The sample ZrO_2 contains mainly tetragonal crystallized phase with the dimensions of the elementary cell a_0=5.12Å, b_0=5.20 Å, as well as monoclinic phase with baddeleyte structure with the dimensions of the elementary cell a_0=5.1477 Å, b_0=5.2030 Å, c_0=5.3156 Å.

The sulfated zirconium oxide consists almost completely of tetragonal crystallized ZrO_2 impurified only by traces of monoclinic phase (fig. 1).

c) TEM Analysis

The above mentioned samples have been also examined by transmission electronic microscopy. This analysis revealed:

-non-uniform distribution of the particle size,

ZrO_2/SO_4^{2-} precursor	Precipitation agent	Solvent	Aging	Specific surface area (m^2/g)	Diammeter of majoritary Pores (Å)	Acidity (mmoles $NH_3/g_{cat.}$)		
						Total (100-500°C)	Strong acid sites (350-500°C)	% strong sites
$ZrOCl_2 \cdot 8H_2O$	NH_4OH	methanol-ethanol	No	72	54	0.82	0.56	68.12
$ZrOCl_2 \cdot 8H_2O$	NH_4OH	*iso*-propanol	No	112	30	0.76	0.47	62.68
$ZrOCl_2 \cdot 8H_2O$	$N_2H_4 \cdot H_2O$	Water	Yes	126	42	1.08	0.60	56
$ZrCl_4$	NH_4OH	ethanol	No	110	63	0.57	0.32	56.14
$ZrCl_4$	$N_2H_4 \cdot H_2O$	ethanol	Yes	114	50	0.78	0.40	51.28

Table 1
THE PHYSICAL-TEXTURAL CHARACTERISTICS AND THE ACIDITY OF THE CATALYSTS

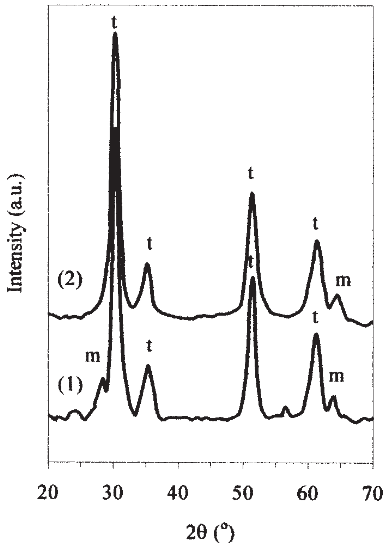

Fig. 1. XRD patterns of ZrO_2 (1) and ZrO_2/SO_4^{2-}(2) (obtained by thermo-hydrolysis of $ZrOCl_2 \cdot 8H_2O$ dissolved in methanol-ethanol 1/1 mixture)

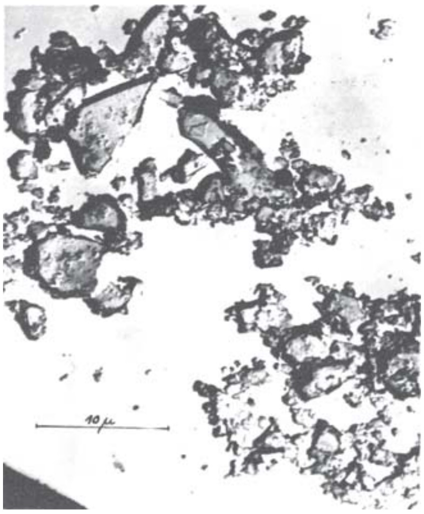

Fig. 2. TEM Image of ZrO_2/SO_4^{2-}; showing crystallites of 1-2μ

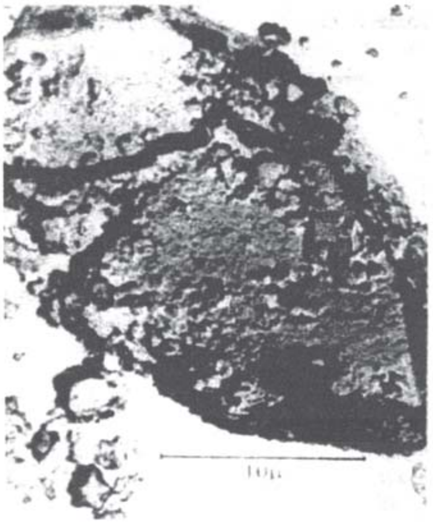

Fig. 3. TEM Image of ZrO_2/SO_4^{2-}; showing crystallites of 10-20μ

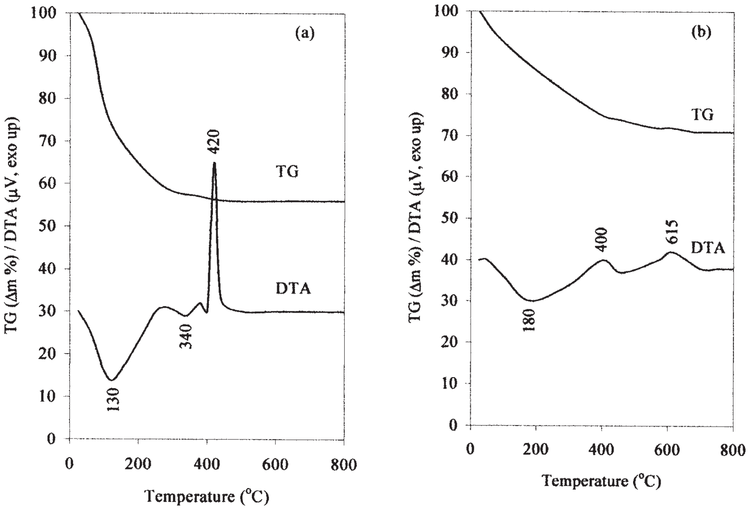

Fig. 4. DTA/TG curves for $Zr(OH)_4$ (a) and $Zr(OH)_4/SO_4^{2-}$ (b), precursors obtained by thermo-hydrolysis of $ZrOCl_2 \cdot 8H_2O$ dissolved in methanol-ethanol 1/1 mixture

Table 2
THE CATALYTIC PERFORMANCES OF THE CATALYSTS OBTAINED FROM DIFFERENT PRECURSORS WHILE USING DIFFERENT PRECIPITATION AGENTS

$Zr(OH)_4$ Precursor	Precipitation agent	Solvent	Conversion *n*-C_4H_{10}* (%)	r_i (mmoles *iso*-$C_4H_{10}/g_{cat} \cdot s$)	Selectivity (%)
$ZrOCl_2 \cdot 8H_2O$	NH_4OH	methanol-ethanol	21.88	$4.93 \cdot 10^{-4}$	91.00
$ZrOCl_2 \cdot 8H_2O$	NH_4OH	*iso*-propanol	17.04	$4.05 \cdot 10^{-4}$	96.00
$ZrOCl_2 \cdot 8H_2O$	$N_2H_4 \cdot H_2O$	water	40.87	$6.89 \cdot 10^{-4}$	84.04
$ZrCl_4$	NH_4OH	ethanol	31.5	$5.31 \cdot 10^{-4}$	61.5
$ZrCl_4$	$N_2H_4 \cdot H_2O$	ethanol	55.73	$8.37 \cdot 10^{-4}$	62.81
$ZrCl_4$	$(NH_2)_2CO$	ethanol	38.3	$6.2 \cdot 10^{-4}$	65.4

* testing conditions: 250 °C; reaction time: 10 minutes; reaction mixture flow : 5 mL/min.; catalysts activated by pretreatment in air flow at 250 °C during 30 minutes, then cooled to the reaction temperature in argon flow.

-tri-dimensional grown crystals, with sizes varying in the range microns – tens of microns;

-the sulfated sample shows a bimodal size distribution with crystallites of 1-2μ (fig. 2) and 10-20μ (fig. 3). The large crystallites have well defined shapes but their

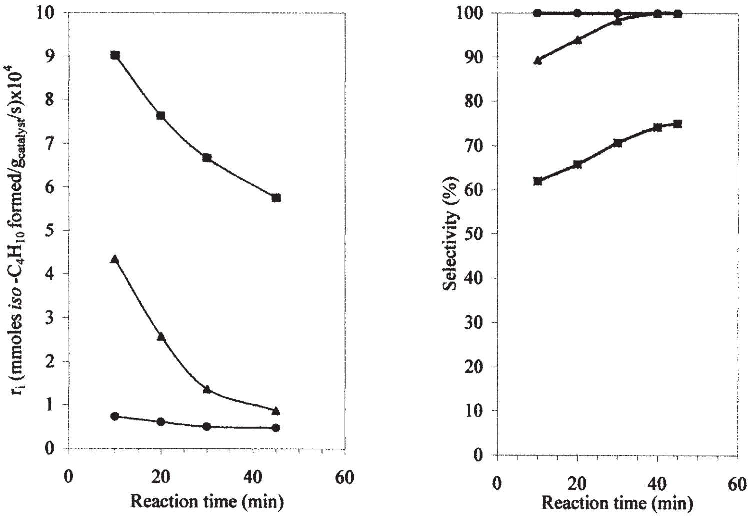

Fig. 5. The catalytic performances at different reaction temperatures for ZrO_2/SO_4^{2-} obtained from $ZrCl_4$, precipitated with $N_2H_4{\cdot}H_2O$, pretreated in air flow as a function of the reaction time: • - 100°C; ▲ -150 °C;■ - 250 °C; (a – rate of isomerization); (b- selectivity to isobutane)

Table 3

CATALYTIC PERFORMANCES OF ZrO_2/SO_4^{2-} OBTAINED FROM $ZrOCl_2 . 8H_2O$ PRECIPTATED WITH $N_2H_4 . H_2O$ PRETRATED IN AIR AND HYDROGEN FLOW, RESPECTIVELY

Catalyst	Temperature (°C)	Reaction time (min.)	Conversion of *n*-C_4H_{10}* (%)	r_i (mmoles *iso*-$C_4H_{10}/g_{cat}{\cdot}s$)	Selectivity (%)
ZrO_2/SO_4^{2-} pretreatment in air flow	150	10	17.7	$3.82{\cdot}10^{-4}$	90.7
		20	8.7	$1.95{\cdot}10^{-4}$	89.8
		30	4.3	$9.66{\cdot}10^{-5}$	87.5
	250	5	49.1	$8.08{\cdot}10^{-4}$	83.9
		10	40.9	$6.89{\cdot}10^{-4}$	84.0
		15	30.0	$5.71{\cdot}10^{-4}$	83.1
		20	21.5	$4.46{\cdot}10^{-4}$	76.6
		30	21.1	$4.39{\cdot}10^{-4}$	68.0
ZrO_2/SO_4^{2-} pretreatment in hydrogen flow	150	10	3.8	$7.81{\cdot}10^{-5}$	100
		20	1.3	$3.00{\cdot}10^{-5}$	100
		30	0.8	$2.00{\cdot}10^{-5}$	93.6
		45	0.7	$1.76{\cdot}10^{-5}$	83.1
	250	10	35.8	$7.2{\cdot}10^{-4}$	81.0
		20	30.9	$5.88{\cdot}10^{-4}$	81.2
		30	26.9	$5.30{\cdot}10^{-4}$	78.4
		45	25.9	$4.85{\cdot}10^{-4}$	77.3

Reaction conditions: temperature: 150 and 250 °C; flow rate of the reaction mixture 5 mL/min; 0.5 g catalyst

surfaces are covered by sub-micronic up to amorphous formations. Partially these formations have lamellar shape and they are probably grown on the surface of the crystallites;

-their presence is indicated in the XRD only by an increase of the amorphous background. Due to the fact that in the XRD analysis only the first crystalline planes are implied the amorphous phase deposited on the surface of the crystals may mask the crystalline structure of their core.

d) DTA/TG Analysis

The results of the DTA/TG analysis for the precursors $Zr(OH)_4$, $Zr(OH)_4/SO_4^{2}$ are displayed in figure 4.

In the temperature range 130-300°C the DTA curves present a wide and intense endothermic peak due to the dehydration and dehydroxilation.

The zirconium hydroxide sample (fig. 4a) has an intense exothermic peak at 420°C, characteristic to the crystallization of ZrO_2.

Meanwhile, the sulfated zirconium hydroxide sample presents a wider exothermic peak with low intensity at 615 °C.

In this temperature range the TG curve indicates a small but continuous loss of weight related to the partial decomposition of sulphate groups (fig. 4b).

e) Catalytic test results

The catalytic test results showing the activity and selectivity of ZrO_2/SO_4^{2-} obtained from different precursors while using different precipitation agents are displayed in table 2.

The data presented in table 2 revealed that:

-the preparation method applied for obtaining the $Zr(OH)_4$ precursor influences the catalytic performances. The catalysts obtained from $ZrCl_4$ are more active but less selective than those obtained from $ZrOCl_2{\cdot}8H_2O$ when the same precipitation is used.;

-the method using iso-propylic alcohol as solvent for the zirconium source leads to a catalyst with relatively low activity but extremely selective for *iso*-C_4H_{10} obtained even at 250 °C;

-the catalysts obtained by precipitation with hydrazine hydrate followed by aging are very active, showing the highest conversions of *n*-butane, but the selectivities to *iso*-C_4H_{10} do not exceed 84 %;

-the catalyst prepared from $ZrCl_4$ using NH_4OH as precipitation agent lead to lower conversion of *n*-butane compared to the one prepared by precipitation with hydrazine hydrate while the selectivities to *iso*–butane are similar;

Taking into account the high conversion levels reached at 250 °C with the catalyst obtained from $ZrCl_4$ precipitated with $N_2H_4{\cdot}H_2O$ and aged during 72 h, this catalyst has been also tested at different reaction temperatures at the same flow rate of the reaction mixture. The results are presented in figure 5 (a, b).

The catalytic activity (r_i) decreases linearly in time, with different slopes f or each reaction temperature. Over 150 °C the formation of by-products resulting from cracking side-reactions which compete the main reaction of isomerisation were evidenced. The selectivity to *iso*-C_4H_{10} at 100°C, is 100% and it does not decrease in time; it exceeds 90 % at 150°C, all along the 45 min reaction time while sightly increasing as the catalytic activity (r_i) decreases. The selectivity to *iso*-C_4H_{10} at 250°C, is not higher than 72-74 %.

The catalyst obtained from $ZrOCl_2{\cdot}8H_2O$ by precipitation with $N_2H_4{\cdot}H_2O$ followed by aging has been tested at 150 and 250°C. For these temperatures, the selectivity for *iso*-C_4H_{10} formation is affected by parallel or successive reactions which lead to the deactivation of the catalyst. These operating conditions have been adopted aiming to evaluate the stability of the catalyst under severe operating conditions.

In a series of experiments, prior to the catalytic test, the catalyst has been submitted to a pretreatment in hydrogen flow at 250°C during 30 min, followed by cooling in argon flow to 150°C and purging with argon at this temperature during 30 min.

The reactions at 150 and 250°C respectively, were performed during 30 min.

Another series of experiments consisted of catalytic tests performed with the same catalyst pretreated in air flow at 250 °C during 30 min, while the cooling in argon flow was performed in the above-mentioned conditions.

The catalytic tests results are presented in table 3.

It has been noticed that the catalytic activity is always higher for the catalyst that suffered the pretreatment in air flow compared to the one pretreated in hydrogen flow. This effect is much more intense at 150°C.

The selectivity to *iso*-C_4H_{10} is higher at 150°C than at 250°C and it is decreasing in time along with the decrease of the catalytic activity expressed as *n*-butane conversion.

At both reaction temperatures, the sample pretreated in hydrogen flow is more selective than the one pretreated in air flow.

The pretreatment in hydrogen flow may reduce some superficial sulfate groups, leading to the modification of the acid strength of the active sites and subsequently to the decrease of their ability to generate reaction intermediates carbenium ions.

Conclusios

The catalytic activity of ZrO_2/SO_4^{2-} catalysts depends in high extent of the preparation method used for the obtaining of $Zr(OH)_4$, as well as of the activation procedure applied to the catalyst before the reaction.

The catalysts obtained from $ZrCl_4$ are more active but less selective than those obtained from $ZrOCl_2{\cdot}$ $8H_2O$ when the same precipitating agent is used.

The most active catalysts are those obtained by precipitation with hydrazine hydrate followed by aging even if the selectivity to *iso*-butane does not exceed 84%.

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