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PRECURSOR MEMORY EFFECT DETERMINING STRUCTURAL PROPERTIES OF SULFATED ZIRCONIA

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Properties of two catalysts tailored in the laboratory conditions by sulfation of commercial Zr–hydroxide and Zr–hydroxide of nitrate origin were compared with those of commercial SO_4–Zr–hydroxide. Equally thermally treated samples in the temperature interval 500–700°C, and having the same amount of sulfur, show different properties indicating memory effect of their solid parent materials. The catalyst obtained by sulfation of commercial Zr–hydroxide differs in amount of residual sulfates upon calcination from other two catalysts. The instability of sulfates in the previous case might be connected to the lowest surface area values of catalyst and the highest fraction of monoclinic phase observed at all applied calcination temperatures.

Keywords: *precursor memory effect, structural properties, sulfated-zirconia, textural properties, thermal properties*

Introduction

The usage of acids as catalysts is probably as old as catalysis itself [1]. Due to environmental and human health hazards, as well as equipment corrosion problems, traditionally used liquid acids have been replaced by their solid complements. Sulfated zirconia (SZ) is a potential candidate for many reactions requiring catalysts with acidic function, such as isomerization of *n*-chain paraffins, alkylation, etc. [2, 3]. The presence of sulfates increases zirconia stability, which can be manifested by steady surface area, as well as by higher content of tetragonal phase [4–8]. Generally speaking properties of SZ as a solid acid depend on preparation procedure, assuming precursor type of both zirconia and sulfates, preparation technique and activation process [5–19]. Nevertheless, there is no consensus in correlation of SZ origin and preparation procedure with its structural and textural properties. Thermal properties of sulfated-promoted and unpromoted zirconia, as well as mixed oxides including zirconia, have been studied in the past [5, 6, 8, 20]. Results indicate a process of phase transformation and sintering of catalysts being a function of method of their preparation, sulfates amount and their thermal history.

In the present study two SZ catalysts were synthesized from different precursors following the same procedure of preparation and calcination. Their thermal characteristics, correlated with textural and structural properties, were compared with properties of commercially sulfated catalysts with the same thermal history.

Experimental

Three types of SZ catalysts were prepared from different precursors following identical procedures for the equivalent steps required to obtain the particular sample in the sequence of synthesis: Catalyst 1 was obtained from commercial SO_4–$Zr(OH)_4$ (Aldrich) by its calcination; Catalyst 2 was obtained from $Zr(OH)_4$ (97%, Aldrich) by, first, its sulfation, and further calcination; and Catalyst 3 was obtained from $ZrO(NO_3)_2{\cdot}xH_2O$ (Aldrich) by precipitation with 25% NH_4OH to obtain an appropriate hydroxide, following the sulfation of the hydroxide and its further calcination. The sulfation step of both hydroxides (the commercial one – Catalyst 2 precursor, and one synthesized from nitrate – Catalyst 3 precursor) was done by wet-impregnation using 0.5 M H_2SO_4 to get initial sulfates content of 4%. As will be shown further in the text, this amount was precisely 4.2% and was also equal to the initial sulfates amount in the commercially sulfated sample (Catalyst 1). All three sulfated hydroxides were finally calcined at different temperatures for 3 h, using a temperature ramp of 30°C min^{-1} and 25 cm^3 min^{-1} flow of air. For the sake of clearness only samples after calcination will be considered as catalysts in the following text, while preceding materials will be denoted as precursors regardless the step of a particular catalyst preparation. Consequently, total of nine SZ-catalyst samples were obtained, denoted as (1), (2) and (3) depending on their precursors, followed by letter A, B or C depending on the applied calcination temperature: 500, 600 or 700°C,

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respectively. In addition, both unsulfated (2 and 3) and sulfated (2S and 3S) samples before calcination, were also considered as corresponding precursors for Catalysts 2 and 3.

Thermal properties by means of thermogravimetric analysis (TG) and differential thermal analysis (DTA) were investigated on a Baehr STA 503, in the controlled flow of air. The measurements were performed in the temperature range 30–1000°C using temperature ramp of 10°C min^{-1}. Textural characteristics of samples were investigated by means of surface area determined by BET, based on dynamic low temperature nitrogen adsorption/desorption (LTNA) using He as carrier gas on Micromeritics ASAP 2010.

The crystal structure was resolved by means of X-ray diffraction analysis (XRD) using Philips APD-1700 diffractometer with Cu-anticathode and monochromator, at 40 kV and 55 mA. The crystallite size was estimated from the full width at half-maximum using Scherrer's equation. Volume fractions of tetragonal/monoclinic phases were calculated from XRD lines using Eq. (1) [21]:

$$X_{\text{m}}=\frac{I_{\text{m}}^{28.25}+I_{\text{m}}^{31.31}}{I_{\text{m}}^{28.25}+I_{\text{m}}^{31.30}+I_{\text{t}}^{30.30}}\ \text{and}\ V_{\text{m}}=\frac{1.311X_{\text{m}}}{1+(1.311-1)X_{\text{m}}} \qquad (1)$$

where $I_{\text{t(m)}}^{2\theta}$ stands for intensities of tetragonal (*t*) and two monoclinic (*m*) zirconia phases, at angles 2θ=30.30°; 2θ=28.25 and 31.30°, respectively. The value 1.311 is a constant equivalent to the system [21].

Results and discussion

Thermal properties of unsulfated precursor samples 2 and 3 with skipped calcination step are presented in Fig. 1. Two distinct processes characterize TG and DTA profiles for both samples. The first occurring from room temperature to about 120°C is due to loss of surface water and amounts to mass loss of about 5%. The second process is completed up to about 450°C and is attributed to split out of coordinated water and condensation of hydroxyl groups. The corresponding mass loss of the second process amounting to additional 17 and 18% indicates a slightly higher constitutional water content in the case of the commercial zirconium hydroxide (catalyst presursor 2). In DTA curves of both precursors the loss of water ends with exothermal effects in the temperature interval from 425–450°C. These exothermal effects followed by no mass change are typical for phase transformation from amorphous zirconium–hydroxide into a monoclinic crystalline phase [5, 22]. The shift of the exothermal effect to somewhat higher temperature (443°C) in the case of the precursor sample of nitrate origin (catalyst precursor 3) indicates crystallization process being slightly postponed in that particular case. The same magnitude of these effects for both samples, however, points out identical mechanisms of crystallization process of chemically equivalent materials regardless of their origin.

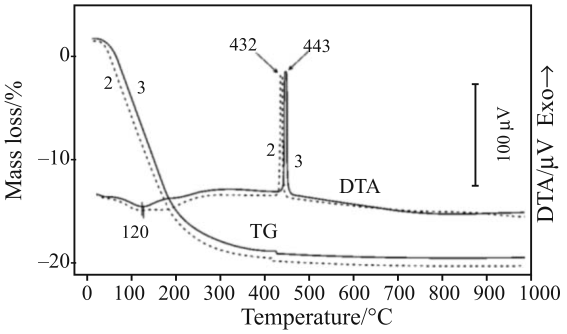

Fig. 1 Thermal properties of catalyst precursors - - - – 2 and —– 3 (unsulfated and thermally untreated zirconium hydroxides of different origin)

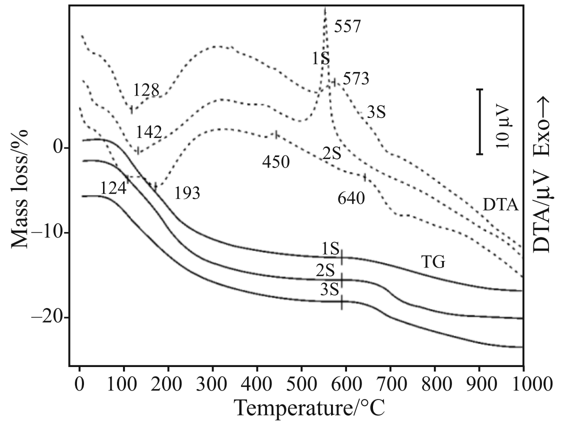

Fig. 2 Thermal properties of sulfated but still uncalcined precursor samples 1S, 2S and 3S

In Fig. 2, DTA and TG curves of the same precursors upon sulfation (2S and 3S), together with the commercially sulfated precursor 1S, but all of them still not calcined, are presented. For two samples having sulfates tailored in the laboratory conditions (precursors 2S and 3S) DTA profiles indicate dehydration of the surface water takes place in two steps pointing out their inhomogeneous structure. This is particularly in the case of the precursor 2S having an additional endothermal maximum at 193°C next to the one at 124°C. These trends are similar to DTA profiles of both samples without sulfates (Fig. 1), although effects are not so obvious due to magnitude of the following exothermal effects present in both thermograms. Water dehydration of commercial $Zr(SO_4)_2\cdot 4H_2O$, occurring up to 400°C even in four steps, was reported recently indicating the importance of precursor type used for catalyst preparation [23]. Obviously, incorporation of sulfates into the zirconium–hydroxide matrix used in this work did not bring much change in the mechanism of water elimination regardless of the precursor origin. In contrast, dehydration of surface water for the sulfated sample 1S performs in one step, with an endothermal maximum at 142°C on DTA curve (Fig. 2). The position of the maximum representing the surface water removal at higher temperature in comparison to other two precursors, as well as the clear shape of the peak, might be the result of thermal history of the sulfated precursor 1S, which might have been thermally stabilized previously under unknown conditions (data were not delivered by the producer). DTA curves of all three precursors in the interval 200–450°C are similar and can be explained by coordinated water removal and condensation of hydroxyl groups. Their broad shoulder-like shapes with an exothermal character differ, however, from rather small endothermal effects in the same temperature range claimed earlier in the case of sulfated zirconia catalysts obtained by sol–gel method starting from an alkoxide [6]. Finally, exothermal effects due to the phase transformation from amorphous to more crystalline phase occur in DTA curves at different temperatures for every particular sulfated sample and are shifted to higher values comparing to their counterparts on Fig. 1. These are effects at 557 and 573°C for precursors 1S and 3S, respectively, and two effects in the case of the precursor 2S: at 450 and even 640°C. The shift of the formation of crystalline zirconia phase to higher temperatures in literature is usually connected with impurity content, i.e. with the incorporated sulfur in the particular case [6, 22]. Occurrence of two exothermal peaks in the case of sample precursor 2S speaks in favor of its inhomogeneity. Its phase transformation starts at the lowest temperature compared to other precursors, i.e. 450°C, however the process is not smooth but rather distorted up to 640°C. The characteristic shape of DTA curve of the sulfated precursor 2S is obviously the result of a specific manner of sulfates incorporation into the particular zirconium-hydroxide matrix, which is slightly richer with water.

Exothermal effects on DTA curves around 600°C on Fig. 2 coincide with sinking of TG curves for all three samples representing mass loss due to sulfates removal. According to literature sulfates decomposition is followed by evolution of SO_3 and/or SO_2–SO together with O_2 and O, depending on the gas environment, and occurs above 550°C [24, 25]. This effect is endothermal by its nature, however the total effect represents the balance between strong exothermal effect due to crystallization and the heat needed for sulfates decomposition. TG curves presented in Fig. 2 show mass loss of about 4.2% in the temperature interval 550–1000°C and accomplishment of plateaus at the final temperature proves that the process of degradation is finished. Assuming that these effects represent sulfates decomposition, and knowing from the literature that above 800°C almost all of the sulfates have been lost [25, 26], it appears that there is the same S quantity in all three catalyst precursor samples, amounting to 1.4 mass%.

In Fig. 3 X-ray diffraction profiles for sulfated and calcined catalyst samples are presented. Obviously, the incorporation of sulfates into the zirconia matrix postponed phase transformation, since all XRD patterns of the series A show the presence of only tetragonal SZ phase despite the catalyst precursor type. Values at $2\theta=30.30$; 28.25 and 31.25° corresponding to SZ calcined at 600 and 700°C (series B and C), however, indicate a mixture of both tetragonal and monoclinic phases. The last prevails at the highest calcination temperature but its relative fraction differs depending on catalyst precursor type (series C on Fig. 3.). Ratios of volume

Table 1 Specific surface area, phase composition, zirconia crystallite size and amount of remaining sulfates as a function of calcination temperature

Sample	Surface area/ $m^2\,g^{-1}$	Volume fraction of tetragonal/ monoclinic phases/%	Crystallite size/nm		Amount of remaining sulfates after calcination[4]/%
			[2]t	[3]m	
1S[1]	145	/	/	/	/
1A	130	100	10.3	–	4.2
1B	103	93.3 / 6.7	11.8	11.7	3.9
1C	70	48.3 / 51.7	12.7	13.7	2.0
2S	100	/	/	/	/
2A	82	100	16.5	–	2.3
2B	68	69.1 / 30.9	20.6	18.2	2.3
2C	45	27.3 / 72.7	23.5	20.5	1.8
3S	222	/	/	/	/
3A	144	100	8.2	–	3.0
3B	117	80.3 / 19.7	12.7	9.1	2.9
3C	89	37.5 / 62.5	13.7	10.2	2.6

[1]S – sulfated and uncalcined; [2] tetragonal phase; [3] monoclinic phase; [4] measured from TG taking T of previous calcination as the T for beginning of sulfate removal in TG analysis

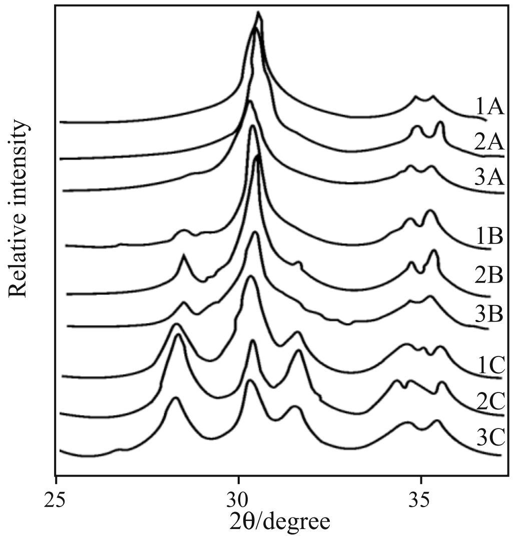

Fig. 3 XRD patterns of catalysts of different origin (1, 2 and 3) previously calcined at A – 500°C, B – 600°C and C – 700°C

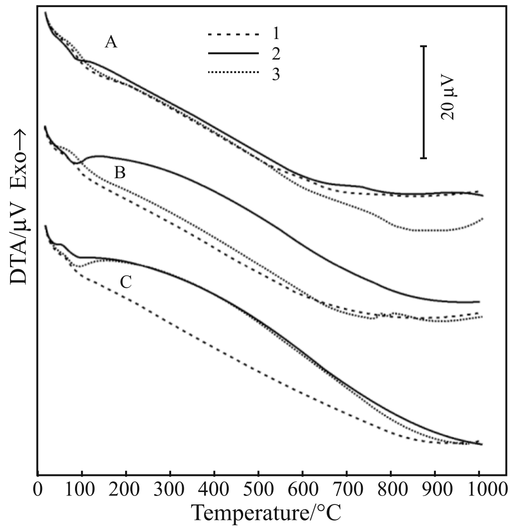

Fig. 4 DTA curves of sulfated zirconia samples of different origin (1, 2 and 3) previously calcined at A – 500°C, B – 600°C and C – 700°C

fractions of tetragonal to monoclinic phases, as well as crystallite sizes for both phases as a function of calcination temperature are summarized in Table 1. The results of phase structure of both series A and B, as well as the entire results of their textural characteristics [17], are in line with results of some recent investigation on unsulfated zirconia catalyst [20], pointing out to the importance of sulfates presence in order zirconia to keep certain characteristics. It is foremost related to the pure monoclinic phase structure of sulfate-free-zirconia and its textural properties characterized by low surface area and pores of large diameter for the sample calcined at only 550°C [20] In contrast, catalysts investigated in this work and exposed to 600 and 700°C have such a textural characteristics [17] and significant fraction of tetragonal phase that are beneficial for their activities in *n*-hexane isomerization reaction [18, 19].

Thermal properties of SZ catalyst samples of different origin, previously calcined at desired temperatures, are presented in Fig. 4 by means of their DTA curves. The same can be correlated with surface area, phase composition, and size of crystallites given in Table 1. Shapes of DTA curves of Catalyst 1 series are very similar despite the applied calcination temperature, indicating once more the postulation of some thermal pretreatment (stabilization), which have been done before the calcination procedure applied in the laboratory. The ratio of volume fraction of tetragonal to monoclinic phase for the Catalyst 1 maintains its high value even after calcination at 700°C, i.e. there is still almost half of the volume fraction of tetragonal zirconia in the Catalyst 1C, as can be seen from Table 1. This is in accordance with a relatively small increase of crystallite size for the series of Catalysts 1 as result of calcination temperature increase (from 1A to 1C). Namely, the crystallite size in the particular cases is still in the range of the critical particle size responsible for inducement of the fast phase transformation, which was found to be about 10 nm in the case of unsulfated zirconia [27]. Consequently sintering is delayed and that can be traced by very slow decay of specific surface area with increase of calcination temperature (Table 1). The stability of tetragonal phase of sulfated zirconia exposed to 600°C due to the presence of very small crystallite size of 1.0–1.4 nm was proved recently [28]. Smooth and very much ordered phase transformation of Catalyst 1 series is also evidenced on Fig. 5 presenting TG profiles of all calcined catalysts. Both remaining water and sulfates contents, the last being also presented in the last column of Table 1, are smaller as higher is the calcination temperature. In addition sulfates incorporated in the Catalyst 1 are very stable; the complete initial amount of sulfates is still present in the sample calcined at 500°C (Table 1).

Among catalyst samples previously calcined at 600°C (set B of DTA curves in Fig. 4) only Catalyst 2 differs by a broad shoulder from about 200–600°C. This shoulder is similar by its shape (but not by its intensity) to the shape of DTA curves in Fig. 2 assigned to the structural water removal. That indicates that catalyst sample 2B after being exposed to 600°C might have a structure differing from structure of both Catalysts 1B and 3B. Indeed, Catalyst 2B having still the predominant but at the same time the smallest fraction of tetragonal phase among all samples in B series, is characterized with crystallites bigger than 20 and 18 nm for tetragonal and monoclinic phase, respectively (Table 1). These might be large enough to

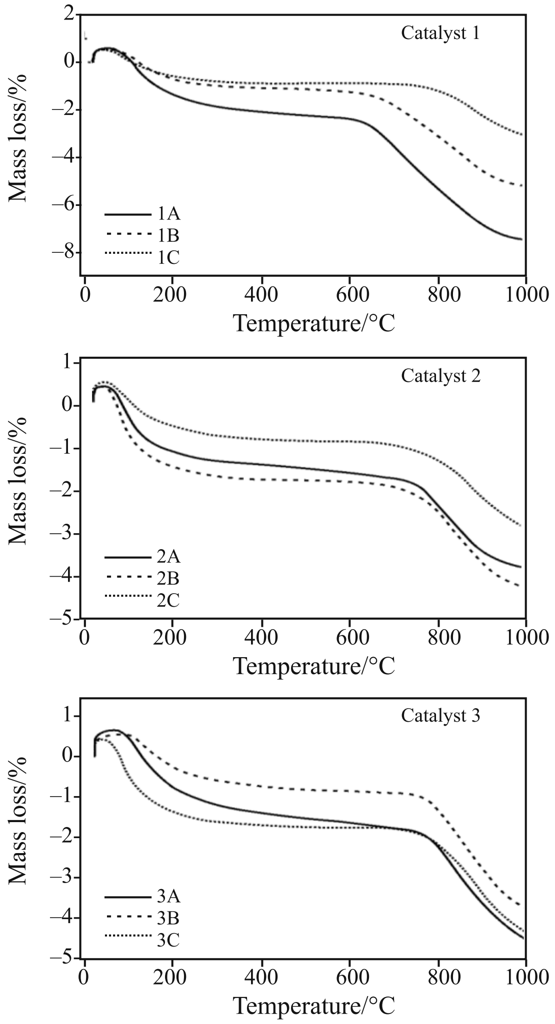

Fig. 5 TG curves of sulfated zirconia samples of different origin (1, 2 and 3) previously calcined at —— – 500°C, - - - – 600°C and · · · – 700°C

additionally accelerate process of phase transformation for the sample exposed to 700°C, resulting in the dramatic decrease of surface area and further crystallite size enlargement due to sintering (Table 1). An early monoclinic zirconia phase appearance in the case of the catalyst sample 2B might be connected to its low amount of remaining sulfates, as can be followed by TG analysis presented in Fig. 5. Namely, the amount of sulfates remaining after calcination of the sample 2B is equal to the amount remained in the catalyst sample 2A (Table 1). That is to say all of not strongly bonded sulfates, i.e. more than half of the initial sulfates amount, were released yet during calcination at 500°C. The consequence of that is seen in the rapid increase of monoclinic phase fraction, decrease of surface area and increase of crystalline size. Further treatment at 600°C did not bring any additional sulfates elimination, but when the highest calcination temperature was applied an additional amount equal to 0.5 mass% of sulfates was removed (Table 1). Consequently, the sample 2C is left with the lowest sulfates contents in comparison to other catalyst samples calcined at the highest temperature. This fact points out to the presence of sulfates of the lowest stability in the sample 2C, but also coincides with its highest monoclinic phase fraction and the poorest textural properties (Table 1). Similarly to these findings the tetragonal zirconia phase was also found to coincide with formation of labile sulfates prepared by sulfation using SO_3, the active sites responsible for high *n*-butane isomerization activity [15].

DTA curves on Fig. 4 indicate position of Catalyst 3 somewhere between other two catalysts; shapes of DTA curves of Catalyst 3 obtained at 500 and 600°C (3A and 3B) are close to that one of Catalyst 1 having the maximum stability. After the precursor of Catalyst 3 was thermally treated at the highest temperature (sample 3C) the shape of its DTA curve matches these of Catalysts 2B and 2C. Applying the same logic as in the case of other two catalysts it seems that the emphasized sintering of Catalyst 3 is postponed up to the point when the highest calcination temperature was applied. Indeed, for the sample 3B, having still the substantial part of tetragonal phase and a low value of crystallite size for both phases, i.e. 12.7 and 9.1 nm (Table 1), sintering process is retarded as can be proved by still high surface area value of the sample 3B. Once it was thermally treated at 700°C (sample 3C) a sharp decline of tetragonal/monoclinic ratio, as well as the low value of specific surface area can be observed (Table 1). The prevailing monoclinic phase in the case of the sample 3C might be sensitive to water readsorption. Figure 5 showing the biggest mass loss up to 200°C exactly in the case of catalyst sample 3C confirms this.

The above observations undoubtedly show the influence of a parent material on rate of process of sintering and outcome differences in properties of sulfated zirconia. Obviously the memory effect of solid materials, defined as catalytic properties dependence on the history of catalyst preparation [29], can be extended to the precursor memory effect [30]. Indeed, DTA effects assigned to phase transformation occur at higher temperature in the case of precursor 3 than for precursor 2 (Fig. 2). It seems that the later is phase transformation from amorphous to crystalline phase, the more postponed is the following sintering process that coincides with monoclinic zirconia phase presence. Again, the Catalyst 1 precursor completely tailored in commercial conditions, showing exothermal maximum at somewhat lower temperature comparing to that one of Catalyst 3 precursor, i.e. 557°C for 1S *vs.* 573°C for 3S (Fig. 2), can be excluded from the previous conclusion. This is because of its perfectly uniform structure resulting from a likewise stable structure of the parent material.

Conclusions

Zirconium–hydroxide matrix of different origin is not a unique host for sulfates incorporation resulting in different thermal, structural and textural properties of sulfated zirconia catalysts. This indicates a memory effect of their solid parent material influencing different properties among catalysts with the same thermal history. It is difficult to conclude whether poorly bounded sulfates influence instability of the particular zirconium–hydroxide, and the instability of the outcome zirconia which is subjected to sintering, or the fast phase transformation of the host following with dramatical changes of its textural and structural properties, induces easy removal of guest sulfates ions.

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