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THERMALLY EFFECTED STRUCTURAL AND SURFACE TRANSFORMATIONS OF SULFATED TiO_2, ZrO_2 and TiO_2–ZrO_2 CATALYSTS

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Abstract

Preparations were characterized by specific surface area, thermogravimetry, and X-ray diffractometry. Thermal effects observed were (a) sulfur loss, (b) sintering, (c) crystallization and transformation of the crystalline phase(s). Thermoanalytical curves indicate that decomposition of the sulfate occurs in two distinct steps. Decrease of surface area due to (b) and (c) is concomitant to decomposition of sulfate. Sulfate was found to hinder sintering, crystallization and phase transformations of ZrO_2 and TiO_2. In low-titania and -zirconia sulfated TiO_2–ZrO_2 the minor component enhances the effect of sulfate. In equimolar TiO_2–ZrO_2 sulfate decomposition is accompanied by rapid formation of crystalline $TiZrO_4$.

Keywords: catalysts, TiO_2–ZrO_2 systems

Introduction

Sulfated ZrO_2 and ZrO_2–TiO_2 mixed oxides are strong solid acids showing catalytic activity in different acid catalyzed reactions, such as, isomerization and cracking of alkanes, hydration and polymerization of alkenes [1, 2]. However, these catalysts are not commercialized yet, since higher activity and selectivity can be obtained using liquid acids in homogeneous processes. The relations between the number and strength of active sites, and the structure and composition of the sulfate-promoted metal oxide preparations were intensively studied [2–7]. Conditions of thermal treatment of the catalyst precursor was found decisive in determining catalytic properties, but, the nature of the structural and surface transformations taking place during the heat-treatment are not known in details. Present study shows that the favourable catalytic effect of sulfate promotion, in addition to generating strong acid sites, is to increase the thermal stability of high surface area amorphous and crystalline oxide phases.

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Experimental

Catalyst preparation

Metal hydroxides were precipitated by adding dropwise twice the stoichiometric amount of NH_4OH to aqueous solutions of $ZrOCl_2$ and $TiCl_4$ under continuous stirring. Starting solutions 0.2 molar for the metal salt were prepared from analytical grade $ZrOCl_2 \cdot 8H_2O$ (Reanal, Budapest, Hungary) and $TiCl_4$ (Fluka AG) of >97% purity. The NH_4OH solution contained 25 wt% ammonia. Metal hydroxide precipitates were filtered washed in distilled water, dried at 120°C contacted with 0.25 molar H_2SO_4 solution and dried again. For comparison sulfated zirconia was prepared also from precipitate obtained by the ambient temperature hydrolysis of Zr-*i*-propoxide with water. Hydrolysis was carried out by adding slowly to stirred, distilled water a solution containing 70 wt% $Zr(OC_3H_7)_4$ in isopropanol (Alfa Products).

Methods

Thermal studies

The TG, DTG and DTA curves of the preparations were determined. The instrument used was a type Q-1500D derivatograph (MOM, Budapest, Hungary). 400–600 mg of samples were heated up in air at a rate of 5 deg·min^{-1}. In some of the experiments to avoid extreme large exothermic effects samples were mixed with equal amount of α-Al_2O_3. α-alumina was also used as reference solid.

X-ray diffraction

X-ray powder diffraction data were recorded by a Seifert 350 DEBYFLEX 200 diffractometer using MoK$_\alpha$-radiation (λ=0.7093 nm).

Specific surface area

Adsorption isotherms of nitrogen were determined at –195°C. The surface area was calculated by the BET-method.

Results and discussion

Zirconia and sulfated zirconia

Curves given in Fig. 1 show distinct differences between the thermoanalytical properties of the pure and the sulfated zirconia samples. Weight loss below

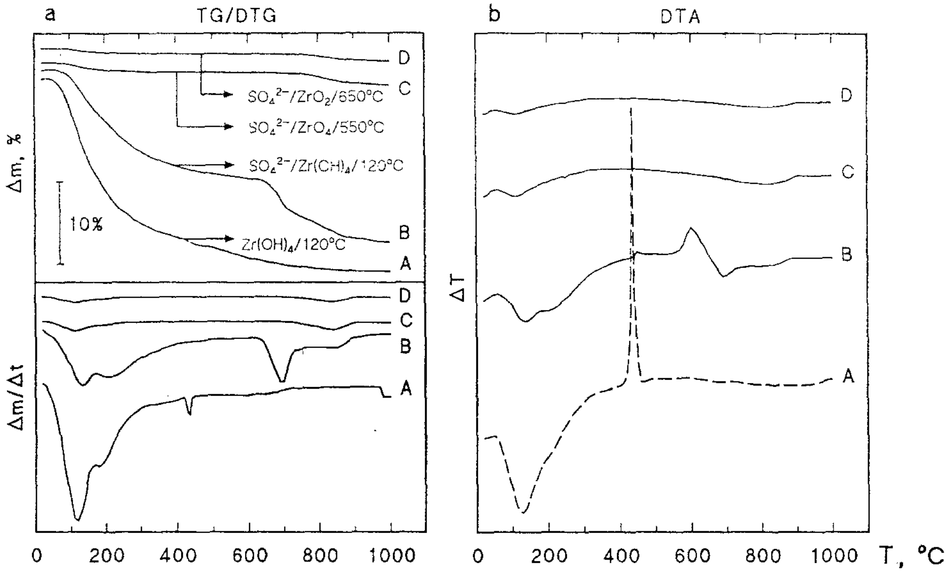

Fig. 1 TG, DTG (a) and DTA (b) curves of $Zr(OH)_4$ (A), sulfated $Zr(OH)_4$ (B) and sulfated $Zr(OH)_4$ air-calcined for 3 h at 550°C (C) and 650°C (D). Samples were prepared from $ZrOCl_2$

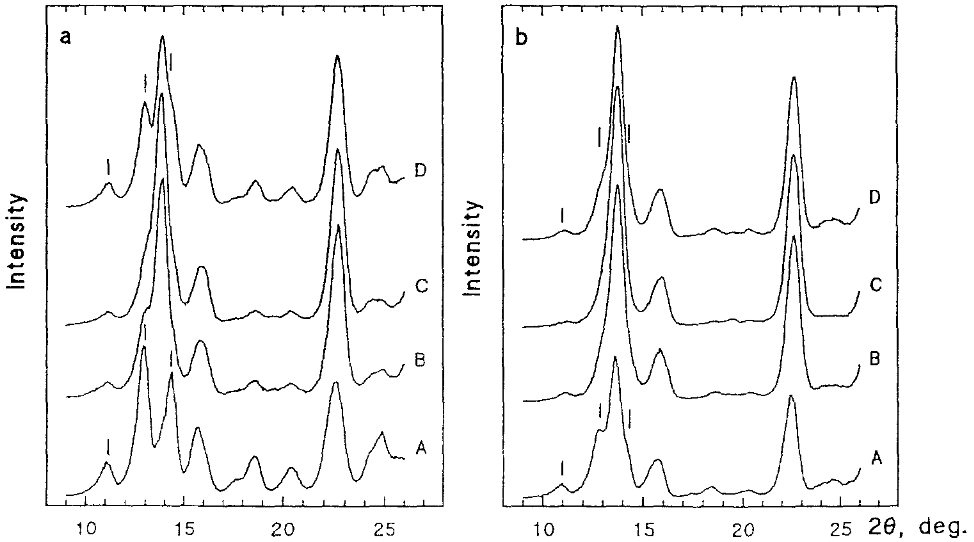

Fig. 2 X-ray patterns of ZrO2 (A) and SO_4^{2-}/ZrO_2 (B,C,D) samples prepared from $ZrOCl_2$ (a) and $Zr(OC_3H_7)_4$ (b). Hydroxide and sulfated hydroxides were air-calcined for 3 h at 550°C (A, B), 600°C (C), and 650°C (D). Bars above peaks indicate diagnostic reflections of monoclinic ZrO_2

300°C is associated with the release of weakly bound water and partial dehydroxylation of the hydroxide (Fig. 1, A and B). Water desorbed amounts to about 23.3 and 13.1 wt% for the pure and the sulfated $Zr(OH)_4$ sample, respectively. Decomposition of surface sulfate takes place above 600°C in two characteristic steps (Fig. 1, B). Upon a 3 h static calcination at 550°C sample loses the more weakly bound sulfate only. Slightly more sulfur can be removed by treatment at 650°C (Fig. 1, C and D).

Water release and sulfate decomposition are endothermic processes. At about 430°C zirconia undergoes an exothermic transformation without weight change (Fig. 1b, A). According to the X-ray diffractometric results shown in Fig. 2 the DTA peak at about 430°C corresponds to the exothermic crystallization of the amorphous zirconia into a monoclinic crystalline phase. Characteristic reflections of the monoclinic ZrO_2 are at $2\ \Theta=12.8°$ (d=3.16) and $2\Theta=14.4°$ (d=2.83) (Fig. 2a, A). Exothermic phase transformation and endothermic sulfate decomposition of the SO_4^{2-}/ZrO_2 preparation occurs simulta neously as indicated by the superimposed peaks of the thermoanalytical curve in the 550–650°C temperature range (Fig. 1b, B). On the X-ray pattern of the sulfated zirconia precalcined at 550°C the intense peak at $2\Theta=13.8$ (d=2.96) is a reflection of the tetragonal ZrO_2 phase (Fig. 1a, B). The tetragonal-to-monoclinic transition occurs without significant thermal effect above 600°C (Fig. 2a, C and D). The exact temperature of this transformation depends on the properties of the hydroxide precursor of the SO_4^{2-}/ZrO_2 catalyst. Tetragonal phase is thermally more stable in the catalysts obtained from $Zr(OC_3H_7)_4$ than in those prepared from $ZrOCl_2$ (cf. Fig. 2a and b).

Table 1 Specific surface area ($m^2 \cdot g^{-1}$) of preparations[a] pretreated at different temperatures[b]

Catalyst[c]	Pretreatment temp./°C			
	450	550	600	650
ZrO_2	–	50.6	–	–
ZrO_2/SO_4	–	101.1	97.6	63.4
ZrO_2/SO_4[d]	–	114.5	108.7	77.1
$(Ti/Zr)O_2/SO_4$ (1/9)	–	147.2	–	86.7
$(Ti/Zr)O_2/SO_4$ (1/1)	244.4	171.4	–	82.1
$(Ti/Zr)O_2/SO_4$ (9/1)	102.5	87.3	–	57.1
TiO_2/SO_4	126.5	–	–	38.1

(a) Preparations were obtained from $ZrOCl_2$ or $TiCl_4$ solutions or from the mixture thereof.

(b) Samples were calcined in air at the temperature indicated for 3 h. Specific surface area was calculated by the BET-method from adsorption isotherms of nitrogen.

(c) Identification defines first the dioxide of the metal component(s), SO_4 indicates that preparation was sulfated, and finally the Ti to Zr atomic ratio is given for the mixed oxides.

(d) Preparation was obtained from $Zr(OC_3H_7)_4$.

( ) Atomic ratio

Results suggest that surface sulfate increases the thermal stability of the amorphous and tetragonal crystalline phases. As an important consequence sulfated preparations retain high specific surface area at elevated temperatures. The formation of the monoclinic phase proceeds at temperatures where sulfate can decompose. Latter process is accompanied by significant loss of surface area (Table 1).

Titania and sulfated titania

Curves E in Fig. 3a and b are DTA curves of titania and sulfated titania, respectively. In contrast with zirconia, a fraction of the dried $Ti(OH)_4$ samples is crystalline (Fig. 4a, A1). Exothermic crystallization of the amorphous fraction is indicated by the peak at about 300°C (Fig. 3a, E). Both pure and sulfated titania release about 13 wt% water below 300°C. Decomposition of sulfate takes place above 450°C. Beside the broad endothermic peak of sulfate decomposition no crystallization peak is discernible (Fig. 3b, E). The X-ray diffractometric examination of sulfated titania shows that samples calcined below 550°C are in the anatase form, but, upon calcination at 550°C the rutile form also appears (Fig. 4a, A2 and A3). In samples treated at 650°C the rutile phase is present already in considerable fraction (Fig. 4a, A4).

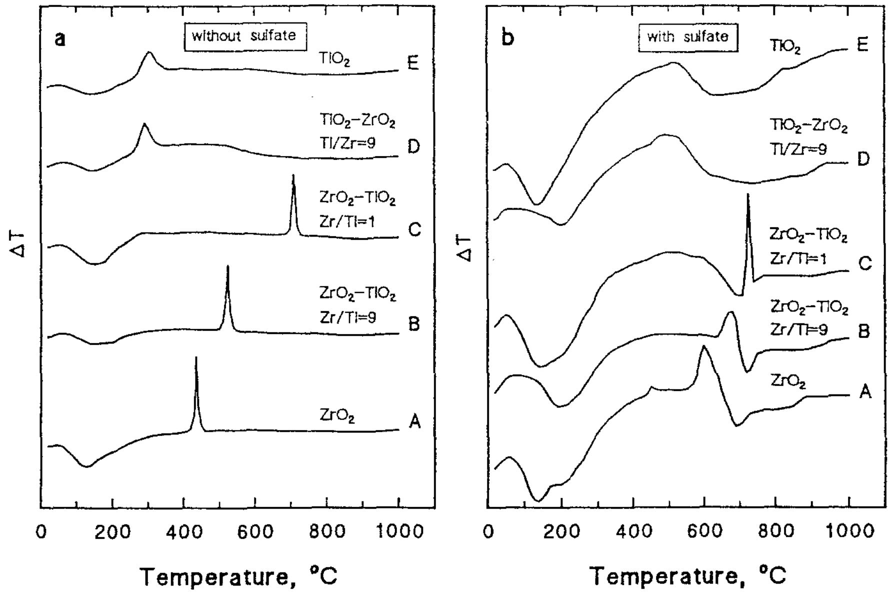

Fig. 3 DTA curves of pure (a) and sulfated (b) $Zr(OH)_4$ (A), binary titania–zirconia co-precipitates with Ti/Zr atomic ratio of 1/9 (B), 1/1 (C), 9/1 (D) and $Ti(OH)_4$ (E). Samples were precipitated from the aqueous solution of $ZrOCl_2$, $TiCl_4$ or the mixture thereof

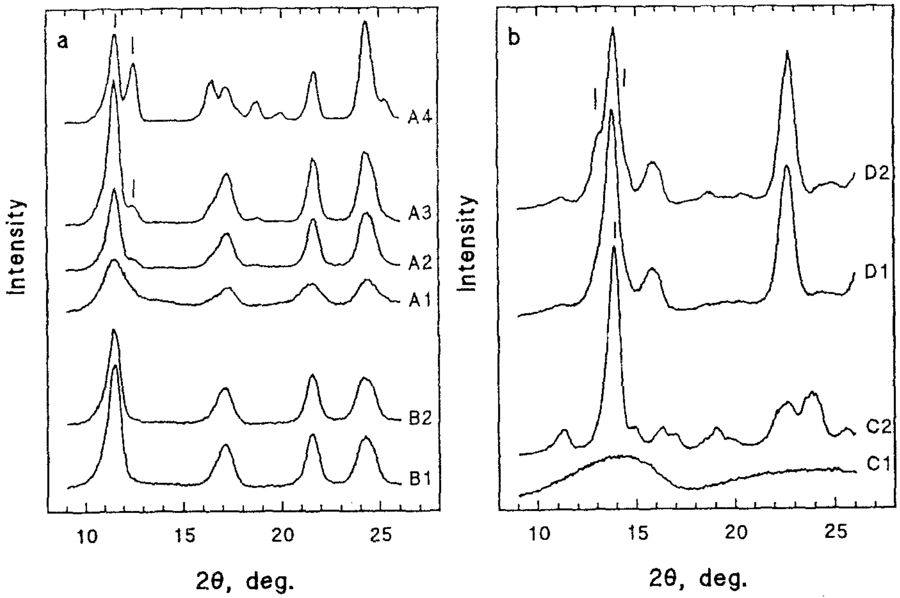

Fig. 4 X-ray powder patterns of sulfated titania and TiO_2·ZrO_2 mixed oxides with high titania content (a), and sulfated TiO_2–ZrO_2 mixed oxides with high zirconia content (b). Diffractograms were recorded following a 3 h heat treatment of $Ti(OH)_4$ at 120°C (A1), 450°C (A2), 550°C (A3) and 650°C (A4); of titania-rich (Ti/Zr=9) co-precipitates at 450°C (B1) and 550°C (B2), of equimolar (Ti/Zr=1) co-precipitates at 550°C (C1), and 650°C (C2); and of zirconia-rich (Zr/Ti=9) co-precipitates at 550°C (D1) and 650°C (D2). Bars above peaks indicate diagnostic reflections of rutile (A3, A4), $TiZrO_4$ (C2) and monoclinic zirconia (D2)

Thermochemical properties of titania samples were studied since sulfated titania have significance as acid catalyst and also due their relevance to the catalytically important TiO_2–ZrO_2 systems [4, 6, 7].

Titania-zirconia and sulfated titania-zirconia

DTA curves of mixed titanium – zirconium hydroxides are shown in Fig. 3a, B, C and D. The effect of titania on the temperature of amorphous-to-crystalline transformation of zirconia is similar to that of sulfate, i.e., the temperature of the phase transformation is increased. This change was observed up to the atomic ratio of Ti/Zr=1 (Fig. 3a, A–C). At Ti/Zr=9 the peak at about 300°C can be attributed to the crystallization of titania. This process is only slightly influenced by the presence of zirconia (Fig. 3a, cf. D and E).

Thermoanalytical curves of sulfated binary TiO_2–ZrO_2 oxides are shown in Fig. 3b, B, C and D. In general, the curve of the sample rich in zirconia (Zr/Ti=9) resembles that of zirconia (Fig. 3b, A and B), and the curve of the sample rich in titania (Ti/Zr=9) is similar to that of titania (Fig. 3b, D and E).

We have shown that surface sulfate can hinder the crystallization of zirconia. In mixed oxides with low titania content the temperature of both sulfate decomposition and crystallization is higher than in SO_4^{2-}/ZrO_2 (Fig. 3b, cf. A and B). As a result this sample retains high surface area after treatment of elevated temperature (Table 1).

Part of the sulfated and dried titania-rich sample (Ti/Zr=9) is in the anatase form. Comparison of the DTA curve of this sample with that of sulfated titania does not show that co-precipitated zirconia would be of any significant effect on the thermoanalytical properties (Fig. 3b, cf. D and E). However, X-ray diffractometric examination indicates that the presence of zirconia hinders the anatase-to-rutile transformation at 550°C where pure titania was partly converted to rutile (Fig. 4a, cf. B2 and D3). The tetragonal-to-monoclinic transformation of zirconia is effected similarly by the presence of titania in the zirconia-rich sample (Zr/Ti=9) (cf. Fig. 2a, B and Fig. 4b, D1).

The DTA curve of the sulfated TiO_2–ZrO_2 sample with the atomic ratio of Ti/Zr=1 shows that sulfate decomposition is followed by a very fast crystallization process (Fig. 3b, D). In this respect sample differs from mixed oxides of both low and high titania content. The crystalline phase was identified as $TiZrO_4$.

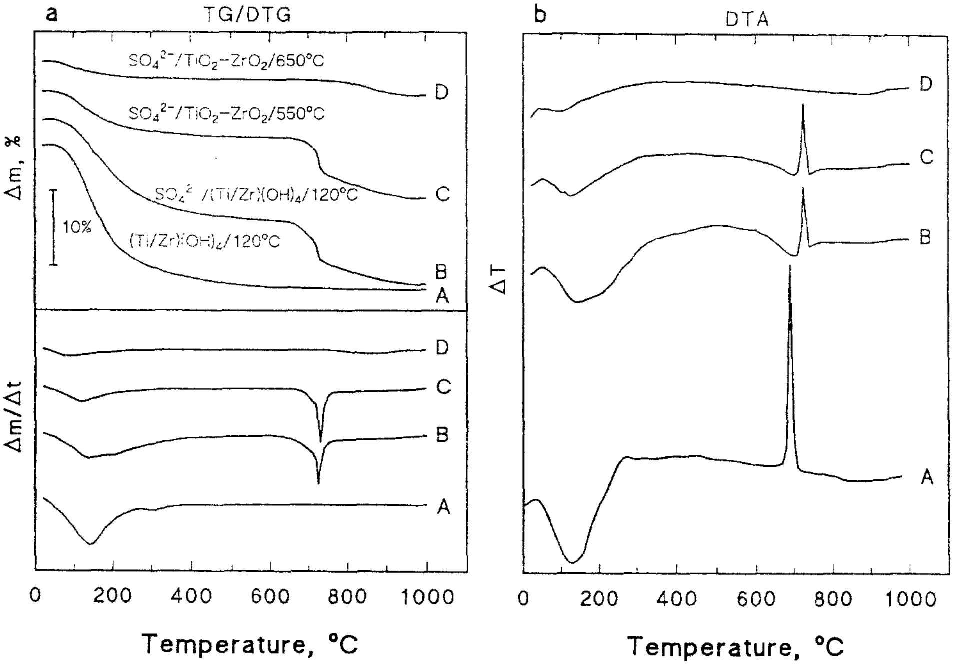

Fig. 5 TG, DTG (a) and DTA (b) curves of equimolar titania–zirconia co-precipitate dried at 120°C (A), sulfated and dried again (B), air-calcined at 550°C (C), 650°C (D) for 3 h

$TiZrO_4$ and sulfated $TiZrO_4$

Sulfated, equimolar TiO_2–ZrO_2 mixed oxides precalcined at 550°C are amorphous (Fig. 4b, C1). The crystalline phase formed upon treatment at 650°C shows strong reflection at $2\Theta=13.95$ (Fig. 4b, C2). Reflection $2\Theta=13.95°$ ($d=2.92$) which is diagnostic for the $TiZrO_4$ phase can not be distinguished from the most intensive 111 reflection of the tetragonal ZrO_2. Nevertheless, the lack of the 65% intensity 202 ZrO_2 peak suggests that the peak at $2\Theta=13.95°$ can not be reflection of tetragonal zirconia, but indicates crystalline $TiZrO_4$. thermoanalytical curves in Fig. 5 shows that crystallization in the sulfated catalyst proceeds at higher temperatures than in the pure mixed oxide and is parallelled by the two-step decomposition of sulfate.

Conclusions

In addition to known effect of creating strong acidic sites on the surface of solids studied surface sulfate is increasing the thermal resistance of high surface area amorphous and crystalline phases against sintering. In the TiO_2–ZrO_2 mixed oxides not only the surface sulfate hinders the aggregation of the main oxide component, but also the second oxide. In TiO_2–ZrO_2 compositions crystalline $TiZrO_4$ can be formed. The surface properties and the catalytic significance of pure and sulfated $TiZrO_4$ is not known in details yet. The present work shows that surface, textural and structural properties of the solids studied do not change independently on thermal effects. For optimizing catalytic properties all these factors has to be considered.

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