Acetone Condensation Over Sulfated Zirconia Catalysts

Mohammed H. Al-Hazmi · YongMan Choi · Allen W. Apblett

Received: 25 February 2013/Accepted: 30 April 2013/Published online: 15 May 2013 © Springer Science+Business Media New York 2013

Abstract The aldol condensation reaction over sulfated zirconia led to the production of diacetone alcohol, which was further dehydrated forming mesityl oxide. The sulfated zirconia was obtained from zirconium acetate ethane sulfonate as a single source precursor. Oxides were obtained by calcinations of the precursors at 550-650 °C, while the self-condensation reaction of acetone was carried out at 150 °C. The precursor and the produced oxides were characterized using various characterization techniques. The precursors were synthesized with different acetate to ethane sulfonate ratio, ranging from 1 to 3. The major products obtained from the condensation reaction over the resulted oxide were mesityl oxide, mesitylene isophorone, naphthalene, and pentamers. The selectivity of mesityl oxide was approximately 100 % at the initial time-onstream.

Keywords Sulfated zirconia · Ethane sulfonic acid · Aldol condensation · Acetone · Mesityl oxide

1 Introduction

The aldol condensation is an important reaction in fine chemicals and organic synthetic chemistry [1–5]. It involves the production of β -hydroxy aldehyde or β -hydroxy ketone by a condensation of aldehyde or ketone via a carbon–carbon

M. H. Al-Hazmi (🖂) · Y. Choi

SABIC Technology Center, Riyadh 11551, Saudi Arabia e-mail: HazmiMH@sabic.com

A. W. Apblett Chemistry Department, Oklahoma State University, Stillwater, OK 74078, USA

bond formation. The self-condensation of ketone is a wellestablished process, and important for the production of α , β unsaturated carbonyl compounds [6]. Such reactions are performed homogenously over a liquid base catalyst (i.e., soda or potash) [4, 7, 8] or a liquid acid catalyst (i.e., sulfuric acid) [9]. In addition, the reactions ordinarily require very long, complex, and hazardous procedures. Recently, efforts have been directed toward replacing the catalysts with more environmentally friendly heterogeneous solid catalysts [10-23]. For example, solid base catalysts, such as MgO and CaO, have been used [11-14, 24], while conventional solid acid catalysts used for the aldol condensation reaction include aluminum oxide, aluminum alkoxides, and zeolites [25, 26]. The aldol condensation of ketone is a complex reaction producing many products via the self-condensation of two ketone molecules or the cross condensation of one ketone with other ketone products formed. The reaction network and product distribution are controlled by catalyst's properties, reaction conditions, and the chemical nature of ketone. Acetone condensation has been widely studied over several solid acid catalysts along with accurate characterization using ¹³C nuclear magnetic resonance (NMR) and infrared (IR) spectroscopies [27–29]. The results from the condensation reaction of acetone over zeolites and alumina indicated that Lewis acid sites are mainly responsible active sites for the initial activation of acetone. It is known that base catalysts in adol condensation reactions are preferred [30], Hino and Arata [31–33] reported that remarkable enhancement of catalytic activities were observed by adding sulphate ions, leading to an increase in the surface acidity. Side reactions involved double bond migration, hydride transfer, oligomerization, and cracking can occur on catalyst surfaces. The influence of several factors (i.e., preparation methods, surface acidity, and physico-chemical properties of sulfated zirconia) on the catalytic activity and productivity was addressed. To the best of our knowledge, the transition metal coordination chemistry by sulfonates is poorly understood. The anions of sulfonic acids are believed to be bonded covalently with a zirconium metal forming salts (i.e., $[Zr(SO_3R)_n]^{+(4/n)}$). It is well known that sulfonate ions are an inefficient ligand, and they are weakly bound or non-bonded to most of the transition metals [34]. Generally, sulfated zirconia is synthesized by a precipitation of zirconium hydroxide from a variety of zirconium salts by aqueous ammonia solution, followed by sulfation using ammonium sulfate or sulfuric acid solutions [32, 33, 35–37]. The only single precursor source utilized for the synthesis of sulfated zirconia in the literature is zirconium sulfate. The thermal decomposition of zirconium sulfate leads to the formation of zirconium oxide and sulfur trioxide, which can be retained on the zirconia surface producing sulfated zirconia [38, 39]. However, the acid strength and the catalytic activity of the oxide obtained via this approach may be lower than those prepared by conventional procedures. This may be due to a decomposition of the oxide materials, which facilitates a rapid loss of sulfur species and reduces the surface acidity. To improve the catalytic activity and the acid strength of the oxide, it is imperative systematically to examine physical and chemical properties (i.e., specific surface areas, active sites, crystalline structures, and phase compositions) which are strongly influenced by preparation procedures, thermal treatment, starting materials, and sulfation agents [40, 41]. To date, no comprehensive studies describing the synthesis and characterization of sulfated zirconia from zirconium sulfonate complexes are available in the literature, which is crucial to design a better catalyst. In this study, we present a route to synthesize sulfated zirconia from zirconium acetate with different concentrations of the ethanesulfonic acid as a single source precursor. The synthesized zirconium oxide was evaluated for the aldol condensation reaction of acetone.

2 Experimental

2.1 Catalyst Preparation

All chemicals were purchased from Aldrich and used without further purification. The precursors were prepared by the reaction of zirconium acetate $((CH_3CO_2)_x \cdot Zr(OH)_y)$ and zirconium oxychloride $(ZrOCl_2 \cdot 8H_2O)$ with ethanesulfonic acid $(CH_3CH_2SO_3H)$ at variant mole ratios of the zirconium salt to ethanesulfonic acid, followed by drying. The ethanesulfonic acid solution was added slowly to the zirconium acetate ligands and produced acetic acid into the solution. The precursor was obtained by evaporation of water and the formed acetic acid, followed by drying under vacuum for 12 h. Based on the zirconium salt, the reaction yield was >95 %. The precursor is denoted as ZS-n(x:y), where ZS is a zirconium sulfonate complex, *n* is a serial number, *x* is a mole ratio of zirconium acetate, and y is a mole ratio of the ethanesulfonic acid. Oxides were obtained by calcinations of the precursors at 650 °C.

2.2 Catalyst Characterization

The prepared precursors and the oxides were characterized using various techniques. The specific surface area was obtained via a conventional Brunauer-Emmett-Teller (BET) multilayer nitrogen adsorption method using a Quantachrome Nova 1200 instrument. Thermogravimetric analyses (TGA) were performed using a Seiko EXSTAR 6000 TG/DTA 6200 instrument. A scanning electron microscope (JEOL JXM 6400 SEM) was used to examine the morphology of catalyst surfaces. Infrared spectra in the 4,000–400 cm^{-1} region were collected by diffuse reflectance of a ground powder diluted with potassium bromide on a Nicolet Magna-IR 750 spectrometer. Elemental analyses of carbon, hydrogen, and sulfur were performed by Desert Analytics. X-ray powder diffraction patterns were obtained by a Bruker AXS D8 advance diffractomer using copper K_{α} radiation with a wavelength of 1.5418 Å. XRD patterns were collected at ambient temperature, and the phases were identified using the ICDD database (ICDD# 42-1164 and #37-1484). The mean crystallite sizes of oxide samples were estimated using a line broadening method and Scherer's equation [42]. ¹³C NMR was also used for the characterization of the prepared zirconium complexes. ¹³C spectra were obtained with a Chemagnetics CMX-II solid-state NMR spectrometer operating at 75.694 MHz for ¹³C and a Chemagnetics 5 mm double resonance magicangle spinning probe. ¹³C cross-polarization/magic-angle spinning (CP/MAS) was carried out with a quasi-adiabatic sequence using two pulse phase modulation (TPPM) decoupling at 50–75 kHz. The ¹³C CP contact pulse of 1 ms length was divided into 11 steps of equal length with ascending radiofrequency field strength, while the ¹H contact pulse had constant radiofrequency field strength. At least 3,600 scans were acquired with a delay of 1.0 s between scans. The MAS sample spinning frequency was 6.0 kHz, maintained to within a range of ± 5 Hz or less with a Chemagnetics speed controller.

The acid strength of prepared sulfated zirconia powders was estimated using Hammett organic base indicators [43]. This determination is based on the ability of the oxide surface to change the organic base indicator into its conjugate acid due to proton transfer from Brønsted acid site on the surface to the indicator. The lower the Hammett acidity function (H₀) value is, the higher the acidity of the oxide surface. If the surface sites have an H₀ value less than the pKa value of the indicator, its color is changed as a result of the acid base reaction on the surface. The indicator solutions were prepared in 1 % (wt./wt.) concentration by dissolving of 0.5 g of the organic indicator in 50 ml of dry benzene since water can affect the results by rapid adsorption on the surface oxide. Before performing tests, sample surfaces were cleaned by heating under vacuum at 80 °C for 2 h. The acidity strength was experimentally determined by the addition of 0.1 g of the solid to 2 ml of dry benzene in a 20 ml test tube followed by an addition of 1 ml of the indicator solution. The tube was covered and left for 1 h to reach equilibrium before recording changed color. The pKa values of the conjugate acid of the indicators can be found in Ref. [38]. The total acidity measurement of catalyst samples was measured using the NH₃ temperature programmed desorption technique (NH₃-TPD) (Micromeritics AutoChem). Prior to NH₃ adsorption, the catalyst sample of 0.2-0.5 g was pre-treated in He (50 ml/min) at 500 °C for 45 min to remove pre-adsorbed species. Then it was cooled down to 100 °C, leading to a saturation with NH₃ (15 vol.% in He). Loosely bound NH₃ species were purged out in a He stream until the baseline of the integrator was stable. The samples were then heated to 550 °C at a heating rate of 10 °C/min in He (50 ml/min). The profile of ammonia evolved was monitored and recorded by the thermal conductivity detector (TCD) detector [44-46].

2.3 Catalytic Testing

The self-condensation reaction of acetone was carried out in an autoclave Teflon-lined batch reactor [47] in a constant temperature oil bath with a magnetic stirring. The reaction was carried out at 150 °C for 1–9 h. All of the experiments were carried out at ambient pressure. Samples were collected from the reactor at different reaction times for analysis. GC/MS (Hewlett Packard G1800A) equipped with a 30 m/0.25 mm HP5 column (crosslinked 5 % PhME silicone) was used to measure products.

3 Results and Discussions

3.1 Characterization of Synthesized Precursors and Sulphated Zirconium Oxides

TGA profiles of zirconium sulfonate precursors derived from the reaction of zirconium salts with different concentrations of the ethanesulfonic acid are shown in Fig. 1. The TGA curve of the ZS-3(1:1) sample was slightly different from the ZS-4(1:2) sample. The TGA profile of ZS-3(1:1) exhibited a stepwise thermal decomposition with three distinct regions. A weight loss observed between room temperature and 150 °C is due to the evolution of the coordinated water molecules on the surface. A gradual



Fig. 1 TGA curves for the prepared zirconium ethane sulfonate hydroxide precursors of ZS-3(1:1) and ZS-4(1:2)

decomposition was observed between 150 and 350 °C, which can be attributed to the decomposition of the organic sulfate ligands and the hydroxy group. The weight loss between 350 and 600 °C is attributed to the decomposition of the acetate ligands. The TGA curve for the ZS-4(1:2) sample, however, showed a sharp weigh loss between 350 and 450 °C due to the loss of the additional ethane sulfonate ligands. Table 1 shows the CHS elemental analyses and detail information of the precursors obtained from the reaction of zirconium acetate and zirconium oxychloride with the ethanesulfonic acid in different mole ratios. The possible proposed formulas were made based on the elemental analyses and the TGA data. Table 2 and Fig. 2 show the stretching frequencies of the carboxylate carbonyl group $v_{COO(sym.)}$ and $v_{COO(asym.)}$ and the splitting (Δv) between the asymmetric and symmetric carbonyl stretching frequencies of several synthesized zirconium acetate ethyl sulfonate complexes, which were prepared by the reaction of zirconium acetate with a variant amount of the ethanesulfonic acid. The carboxylate's stretching frequencies of zirconium acetate complexes are between 1,400 and $1,700 \text{ cm}^{-1}$. The results clearly show that the asymmetric carboxylate absorption stretching frequencies v_{COO(asym.)} and the Δv values decrease dramatically with an increase of the number of ethylsulfonates on the precursors. This is indicative of a change of the coordination mode of the bridging acetate group to either a wider angle or a higher delocalization to the double bond. Additionally, ¹³C NMR spectra of the zirconium sulfonate precursors are shown in Fig. 3. The NMR spectra show that the intensity of the ${}^{13}C$ acetate peaks at 24 and 178 ppm is decreasing, while that of the ethylsulfonate at 8.8 and 45.7 ppm is increasing with an increasing amount of ethylsulfonate until the acetate peaks are completely disappeared. This observation supports the findings using IR spectroscopy, and clearly suggests that the ethane sulfonate gradually replaces the

Sample ^a	Elemental analysis (%)			ZrO ₂ (%) ^b	Proposed precursor formula ^c	Expt. MW	Theo. MW
	С	Н	S				
ZS-1(1:0.25)	12.3	3.29	2.62	55.4	[Zr(O) _{0.9} (OH) ₁ (OAC) ₁ (ESA) _{0.2}]·0.8H ₂ O	222	219
ZS-2(1:0.5)	13.5	3.40	6.33	50.5	[Zr(O) _{1.25} (OAC) ₁ (ESA) _{0.5}]·0.5H ₂ O	243	247
ZS-3(1:1)	12.1	3.54	9.52	44.5	[Zr(O) _{1.3} (OAC) _{0.6} (ESA) _{0.8}]·2H ₂ O	276	272
ZS-4(1:2)	14.6	3.61	16.91	34.0	[Zr(O) _{0.9} (OAC) _{0.4} (ESA) _{1.8}]·2.2H ₂ O	361	367
ZS-5(1:3)	15.7	3.49	18.50	26.4	[Zr(O) _{0.6} (ESA) _{2.8}]·3H ₂ O	465	464

Table 1 The structures and properties of synthesized zirconium sulfonate complexes obtained from the reaction of zirconium salts and the ethanesulfonic acid

^a Zirconium sulfonate complexes with different concentrations of the ethanesulfonic acid (ESA)

^b Calcination was done at 650 °C

^c Based on the results of TGA and elemental analysis

 Table 2 IR stretching frequencies of the asymmetric and symmetric carbonyl groups in the synthesized zirconium acetate ethyl sulfonate complexes containing a different amount of the ethanesulfonic acid

Sample	$v_{COO} (cm^{-1})$	$\Delta v (cm^{-1})^{b}$	
	Asym.	Sym.	
ZrA ^a	1573	1450	123
ZS-2(1:0.5)	1575	1456	119
ZS-3(1:1)	1557	1455	102
ZS-4(1:2)	1540	1459	81

^a Zirconium acetate hydroxide

^b $\Delta v = v_{COO(asym.)} - v_{COO(sym.)}$



Fig. 2 IR spectra of the zirconium sulfonate precursors obtained from the reaction of 1 mol of zirconium acetate with a different mole ratio of ESA. **a** zirconium acetate, **b** ZS-2(1:0.5), **c** ZS-3(1:1), **d** ZS-4(1:2), and **e** ZS-5(1:3). The *arrow* corresponds to an asymmetric stretching of COO



Fig. 3 ¹³C NMR spectra of the zirconium precursors obtained from the reaction of 1 mol of zirconium acetate with different mole ratios of ethanesulfonic acid (ESA). **a** zirconium acetate, **b** ZS-3(1:1), **c** ZS-4(1:2), and **d** ZS-5(1:3)

acetate ligands. The complete replacement was observed when the zirconium acetate precursor reacts with three mole equivalents of the ethanesulfonic acid (ZS-5(1:3)). The XRD pattern of the precursor derived from ZS-3(1:1) precursor at different temperatures is shown in Fig. 4. It is known that hydroxyl ions available on the surface of zirconium oxide stabilize the tetragonal phase and delay the transformation to the monoclinic phase [48]. As shown in Fig. 4, the tetragonal phase started to appear at approximately 500 °C. As temperature increases, more crystalline tetragonal phases are developed without the appearance of the monoclinic phase until about 950 °C. The comparison of these data with that from zirconium acetate shown in Fig. 4 revealed that the zirconium sulfonate precursors produce a thermally stable tetragonal phase due to the presence of the sulfate ions. Sulfate ions are believed to increase the thermal energy required to remove the hydroxyl ions during the thermal dehydroxylation process [49]. The phase composition results also show a degree of a dependency on the nature of the sulfated zirconia single



Fig. 4 X-ray diffraction pattern for the zirconium sulfonate single precursor derived from the reaction of 1 mol of zirconium acetate with 1 mol of ethanesulfonic acid (ZS-3(1:1)) at **a** 550 °C, **b** 700 °C, **c** 850 °C, **d** 950 °C, **e** 1,050 °C, and **f** zirconium acetate at 800 °C



Fig. 5 Average crystallite size of the ZS-5(1:3) precursor calcined at different temperatures

Fig. 6 a Sulfated zirconia from pyrolysis of zirconium sulfonate precursors at 650 °C of ZS-3(1:1), ZS-4(1:2), and ZS-5(1:3). **b** IR spectra of the **a** zirconia obtained from zirconium acetate heated at 720 °C, **b** zirconium sulfonate precursor ZS-1(1:3) dried at 100 °C, and c sulfated zirconium oxide obtained from calcination of ZS-5(1:3) calcined at 650 °C precursor and on the amount of sulfur species formed on the surface. The crystallite size measurements obtained from the X-ray diffraction for the thermally treated single precursor (ZS-5(1:3)) at different calcination temperatures are shown in Fig. 5. For the sample calcined at 550 °C, a small average crystallite size of about 4 nm was observed. The crystallite size is increased by raising the temperature, and reached a 12 nm average size when the sample was calcined at 850 °C due to a sintering and an agglomeration of the particles during the thermal treatment. IR spectra of the oxide from the ZS-5(1:3) precursor are shown in Fig. 6. Three peaks in the IR region from 1,000 to $1,250 \text{ cm}^{-1}$ were observed $(1,029 \text{ to } 1,069 \text{ cm}^{-1}, 1,143 \text{ cm}^{-1}, \text{ and}$ 1,222 to 1,243 cm⁻¹). These bands are considered as characteristic peaks for the S-O stretching modes of the coordinated SO_4^{2-} species on the surface. They are characteristic peaks for the chelating bidentate sulfate species coordinated to the zirconium metal ion [50]. Furthermore, the peak observed at about 1.389 cm^{-1} is corresponding to the SO stretching frequency of sulphate species adsorbed on the metal oxide surface [50, 51]. The broad peak observed at $3,375 \text{ cm}^{-1}$ is attributed to the hydrogen bonding of adsorbed water on the zirconia surface. Additionally, the peak at $1,627 \text{ cm}^{-1}$ is attributed to the OH bending mode of adsorbed water [51]. Based on the IR studies (Fig. 6), the oxide obtained from the ZS-3(1:1) and ZS-4(1:2) precursors are similar to each other with slight differences in the relative intensities of the peaks. This implies that the sulfate group adsorbed on the surface have similar structures. The characteristic peak for the $v_{S=O}$ of the ZS-3(1:1) sample was observed at 1,376 cm⁻¹, but it is shifted to a higher position $(1,389 \text{ cm}^{-1})$ than that of ZS-4(1:2). This increase may occur due to the increase of the surface sulfate group. As shown in Fig. 6, the oxide with high sulfate contents (ZS-5(1:3)) has a different IR spectrum in the v_{S-O} region with appearance of new strong bands at about $1,065 \text{ cm}^{-1}$ and $900-1,000 \text{ cm}^{-1}$. This change may result from the formation of polynuclear



sulfate compounds [51, 52]. Furthermore, the degree of hydration of the crystalline sulfate groups may also influence the structure of the adsorbed sulfate group on the surface [51]. Figure 7 shows the influence of the sulfate concentration on the phase composition and thermal stability. All samples were calcined at 950 °C for 8 h. It was reported that the acetate/zirconium stoichiometry in the zirconium acetate complex precursors has a negligible effect on crystallite phases and crystallization temperatures [53]. Therefore, the observed variation in the phase composition may be directly attributed to the presence of the sulfate group on the final oxide surface. Zirconium acetate itself showed a complete transformation of the tetragonal phase to the monoclinic phase at this temperature. However, the results showed that by the addition of 0.1 mol ratio of ESA to zirconium acetate (Fig. 7a), the tetragonal phase was highly stable and resisted the transformation into a monoclinic phase. The presence of the tetragonal phase was ~ 56 %. Even a small amount of sulfate may create defect sites on the zirconium oxide crystals, affecting the stability of the tetragonal phase. By increasing the mole ratios of ESA, the structure retained more in the tetragonal phase. It has been reported that sulfates stabilized the tetragonal phase by a contribution to the rigidity of the structure, leading to an elongation of the Zr-Zr bond distance [40]. Active sites and vacancies on the zirconium oxide surface that adsorbs oxygen species can facilitate the transformation from tetragonal to monoclinic phases [37]. However, the sulfate ions linked to the surface cover the sites and impede the phase development from both amorphous to crystalline phases and from tetragonal to monoclinic phases. Interestingly, beyond the 1:1 mol ratio of



Fig. 7 Effect of the sulfate concentration on the phase composition and thermal stability. **a** Zirconium acetate, **b** with 0.1 ESA, **c** ZS-1(1:0.25), **d** ZS-2(1:0.5), **e** ZS-3(1:1), **f** ZS-4(1:2), and **g** ZS-5(1:3). The sulfated zirconium oxides were calcined at 950 °C

zirconium acetate to ESA (Fig. 7e), a decrease in the stability of the tetragonal phase was observed. It may reflect a very different decomposition pathway leading to sulfated zirconia particles with varying microstructures, resulting in the tetragonal to monoclinic phase transformation. This may also be due to the observed change of the nature of the sulfate group coordinated to the zirconium surface. For example, zirconia with a 91.9 % monoclinic phase was obtained from the three mole equivalents of the ESA precursor (Fig. 1g). Therefore, based on the characterization, we found that there is a maximum in the amount of the sulfate group necessary for the stabilization of the tetragonal phase at high temperature, and its maximum phase stability is obtained when the oxide surface has a certain ratio of $SO_4^{2-}/O\overline{H}$. Beyond that ratio, the sulfate group replaces a large amount of the hydroxyl group from the surface, and appears to be abundant on the surface. This affects its coordination nature and facilitates the evolution of sulfate species in the form of SO₂ gas at elevated temperatures. Figure 8 shows the specific surface area of sulfated zirconium oxides obtained from different precursors by varying the ESA mole ratios. The mole ratio of the ESA is proportional to the amount of the sulfate group on the surface area of final oxides. All samples were calcined at 650 °C for 8 h. We observed a dramatic increase in the oxide surface area as the sulfur content arises. This can be attributed to the interaction of the sulfate group on the oxide surface. It is assumed that the surface area increase may be due to the presence of bridging sulfate SO_4^{2-} ions on the surface. The bridging sulfate ions replace hydroxyl species on the surface, resulting in a more rigid and stable structure. Furthermore, the bridging sulfate ions elongate the Zr–Zr separation from about 3.4–4.3 Å [39, 54], which facilitates the dispersion of the oxide particles, and accordingly, increases the surface area. Figure 9 shows representative SEM images of the zirconium acetate



Fig. 8 Effect of ESA mole ratios on the surface area of the sulfated zirconium oxide calcined at 650 $^{\circ}$ C

starting material and the zirconium ethyl sulfonate precursor (ZS-5(1:3)). They were recorded for both the precursor itself and the oxide obtained from the pyrolysis of the precursor. The SEM image of zirconium acetate shows smooth spherical particles with holes on the particles, whose sizes are in the range from 2 to about 20 µm (Fig. 9a). Heating of the zirconium acetate at 650 °C yielded the zirconium oxide (Fig. 9b), and the SEM images clearly shows that it became more polished spherical particles. The morphology of the zirconium sulfonate precursor (ZS-5(1:3)) (Fig. 9c) shows uniformly shaped crystals sticks with an average diameter of about 0.5 µm. By calcination at 650 °C, the morphology was completely changed to form rod-like zirconia with an average diameter of about 200 to 500 nm and with several microns in length. This is due to the sintering of the particles during the thermal transformation of the precursor to the oxide. The uniaxial growth may be a reflection of the formation of the tetragonal phase with preferred growth in the C axis.

The general proposed pathway for the thermal decomposition of the zirconium sulfonate precursors to form sulfated zirconium oxide is shown in Scheme 1. To study the decomposition behaviour of the precursor, the precursor derived from the reaction of zirconium acetate with ethanesulfonic acid was heated in a sealed glass tube using a tube furnace at various temperatures in the range of 250-450 °C. The decomposition process was initiated at about 200 °C–300 °C by the β -hydride elimination reaction to evolve ethylene. Ethylene presumably further undergoes the dimerization and trimerization over the acid surface at high temperatures generating a mixture of C_4 – C_6 olefins. Sulfur dioxide (SO₂) was also formed at this stage. Hydrogen sulfide (H₂S) and more SO₂ were also released as by-products at higher decomposition temperatures (above 350 °C). The C₄ and C₆ olefins directly reacted with H₂S via a cyclization reaction and produced a mixture of thiophene. It is well known that the reaction of alkanes or olefins with SO₂ or H₂S at high temperature in an inert gas environment can produce thiophene [55, 56]. In our experiments, the formation of thiophene and H₂S started at about 400 °C. At <400 °C, the reaction mainly produced SO_2 , water, and ethylene. Figure 10 shows a schematic diagram for the possible products formed from the thermal decomposition of ZS-5(1:3). Due to a smaller amount of O₂ than that for zirconium acetate, thiophene was produced when a larger amount of the sample was placed in the sealed tube. Thiophene may also be formed as a result of the reaction of sulfur with ethylene producing a



Fig. 9 SEM images of **a** zirconium acetate before heating, **b** zirconium acetate prepared at 650 °C, **c** ZS-5(1:3) before heating, and **d** ZS-5(1:3) prepared at 650 °C. The *scale bar* is 1 μm

Scheme 1 Thermal decomposition of zirconium sulfonate precursors to sulfated

zirconium oxides







conjugated thiodiethylene intermediate, which further reacts with ethylene followed by an intramolecular cyclization. The formation of diethyl sulfide and dithiolanes also suggests that the reaction follows a free radical mechanism. Other products obtained, such as elemental sulfur (S_8) , carbonyl sulfide (COS), diethyl disulfide, 1,4dithiane, and 2-methyl-1,3-dithiolane were also detected as a result of the reduction pyrolysis of the precursor. Elemental sulfur, which was observed at a high decomposition temperature (above 450 °C), apparently was formed as a result of the decomposition of H₂S or thiophene under the reduction conditions. The sulphur was, then, deposited on the surface of the decomposed precursor. When the pyrolysis was conducted in a larger volume sealed tube with more O₂, CO₂ and SO₂ were produced more than thiophene and other products. This implies that thiophene, alkylated thiophene products, and other possible aromatic products are oxidized to SO₂ and CO₂. When the precursor was pyrolyzed in O_2 rich environment in an open vessel at 450 °C followed by extraction with methylene chloride, no S_8 was deposited, indicating that all the sulfur species were oxidized to SO_2 or the surface sulfate group [55]. Three main steps were observed during the thermal decomposition of the zirconium acetate sulphonate precursors: (i) the evolution of SO₂ at a temperature below 300 °C, (ii) the evolution of the H₂S and thiophene at a temperature range between 300 and 450 °C, and (iii) the formation of elemental sulfur at a temperature above 450 °C. The amount of SO₂, S₈, and H₂S purely depend on the pyrolyzed precursor. This clearly implies that upon the formation of the zirconia lattices as a result of the thermal treatment, different sulfate group's structures may be present on the surface and be decomposed at different temperatures. The preparation methods and the nature of the zirconium sulfonate precursor strongly influence the sulfate content, the nature and the structure of the sulfate group on the surface.

The total acidity measurements of several sulfated zirconium oxides obtained from different zirconium sulfonate precursors are listed in Table 3. The total acidity was measured using the NH_3 -TPD technique, while the acid strength data was estimated using different Hammett indicators. Table 3 indicates that the surface acidity of the sulfated zirconia obtained from different precursors has a wide variety of total acidities and acid strengths. The dissimilar acidic properties can be mainly attributed to: (i) the variations in specific surface area of the oxide, (ii) the availability and concentration and distribution of the acid

Table 3 Acidity measurements of sulfated zirconia catalytic systems utilized for acetone condensation reaction

Catalyst ^a	$S_{BET} (m^2/g)$	Total acidity NH ₃ desorption (mmol/g)				Acidity strength (pKa)
		400-800 K	800–950 K	Total	Acid density (µmol/m ²)	
ZrO ₂	2.5	_	_	_	-	> +3.3
ZS-2(1:0.5)	20.1	1.87	0.28	2.65	131.8	From -5.7 to -8.2
ZS-3(1:1)	23.9	2.72	0.46	3.18	133.0	From -8.2 to -11.4
ZS-4(1:2)	27.5	3.33	0.52	3.85	140	< -11.4
ZS-5(1:3)	49	3.85	0.62	4.47	91.2	< -11.4

^a Sulfated zirconia obtained from precursors that were synthesized from zirconium acetate with different mole ratio of ethane sulfonic acid. All samples were calcined at 650 °C. (For samples description, please refer to Table 1)

sites, and (iii) the structure of sulfate species on the surface. This confirms that the coordinated surface sulfate group affects the strong acidity. Moreover, the total acidity measurements of the oxide series obtained from the reaction of zirconium acetate with different mole ratios of ethanesulfonic acid demonstrated that the acidity increased with the increase of the sulfate concentration on the surface. As shown in Table 3, the acid strength measured by Hammett indicators showed that the strength increased with an increase of the sulphonate group to reach the maximum at pKa higher than -11.4, which then protonated 4-nitrotouluene. The surface of the oxide turned to yellow. This may be attributed to the generation of more Brønsted acid sites. It is expected that the initial decomposition of the zirconium sulfonate precursor during the thermal treatment in air at low temperature may proceed by the β hydride elimination forming ethylene and water. Adsorbed water may then react with the adjacent sulfate groups to yield adsorbed bisulfates (HSO₄) and the hydroxyl group. As proposed by Ecormier et al. [57], at low sulfate concentration the surface may be rich in hydroxyl and bridge the hydroxyl group with the bisulfate group. Upon further heating to higher temperature (>600 °C), the bisulfate undergoes a condensation reaction with the adjacent hydroxyl group evolving water and forms a bridging bidentate sulfate group on the surface with a concurrent formation of weak and strong Lewis acid sites. Water molecules were evolved during the thermal decomposition of the precursor, or it could be re-adsorbed on Lewis acid sites to form weak Brønsted acid sites. The formation of the tetragonal phase with a low sulfate concentration and the thermal stability of this phase at higher temperature may be delayed by the presence of a high concentration of the stabilized hydroxyl group on the surface. In addition, by a further increase in the concentration of sulfur species, the bisulfate group on the oxide surface can be increased, and polynuclear sulfate compounds (i.e., pyrosulfate) may be formed. As discussed above, XRD data showed that the

Scheme 2 Schematic for the formation of pentamer product from acetone. *Bullet* is the position of ¹³C

sample with high sulfur species undergoes a rapid transformation of the tetragonal to monoclinic phases upon calcination at higher temperature. This may be either due to the different microstructure (nanocrystalline) of zirconia or a non-facile loss of sulfate due to the different mode of coordination. On the other hand, the total acidity measured by the NH₃–TPD adsorption technique showed that there are two regions (400–800 K and 800–950 K), representing the strength of mild and strong acids, respectively. The total acidity density showed an increase by a rise of ethane sulphonate in the oxide precursor to a maximum density at ZS-4(1:2), and then, was declined. In addition, we found that the strong acid site's density was also increased by increasing the sulphone group on the surface at an optimum value, and then, a dramatic decline was observed (ZS-5(1:3)).

3.2 Acetone Condensation Reaction

The reaction of acetone over the solid acids follows several pathways leading to numerous products. The acetone condensation reaction was performed at 150 °C with 10 wt./wt.% (catalyst/ketone). It is well known that the acetone condensation reaction starts with a protonation of acetone over the solid surface to form a conjugate acid. The next step involves an electrophilic addition of a carbonium ion of the conjugate acid with the enol form of another acetone molecule via a well-known aldol reaction to yield diacetone alcohol (DAA). Dehydration of DAA occurs readily over sulfated zirconia acid sites to form mesityl oxide (MO). Another acetone enol reacts further with the mesityl oxide following the similar mechanism mentioned above to produce linear phorone. The cyclization of phorone to isophorone mainly arises through the Michael addition mechanism which involves the conjugate addition of the enolate nucleophile anion to the β -carbon of an α , β unsaturated carbonyl electrophile double bond [57, 58]. Mesitylene [59] may be formed as a result of the dehydration and rearrangement of isophorone over acid sites.



Pentamers

Furthermore, another possible route for the formation of mesitylene is the condensation of three acetone molecules to produce the trialcohol intermediate, followed by a rapid dehydration on the acid sites to release three water molecules and mesitylene. Among all these products, mesityl



Fig. 11 Acetone conversion over sulfated zirconia samples at 150 °C



Fig. 12 Product distribution resulted from acetone condensation over the sulfated zirconia samples calcined at 650 °C. After **a** 1 h, **b** 3 h, and **c** 9 h of reaction time. In the x axes, only mole ratios were shown for clarity (Table 1)

oxide, isophorone, and mesitvlene are commercially important products obtained from the acetone condensation reaction [18, 60]. These products are mainly applicable in polymerization and separation of heavy metals. Naphthalene products such as pentamers are also formed in considerable amount via a proposed mechanism shown in Scheme 2. The pentamer was identified using mass spectrometry, which indicated a molecular mass fragmentation at m/e = 200 involving five ¹³C atoms. This suggests that it is formed as a result of the condensation of five acetone molecules. Most likely, this product was formed directly from the reaction of isophorone with mesityl oxide producing an intermediate, followed by a rapid dehydration to evolve two water molecules and products. Figure 11 shows the conversion of acetone versus a reaction time over the sulfated zirconia samples. The results clearly showed that the conversion is enhanced by the oxide obtained from the increase of the ethane sulfonic acid/acetate molar ratio in the precursor, ZS-1(1:0.25) shows the least conversion over time. On the other hand, the conversion over ZS-5(1:3) was



Springer

rapidly increased to its maximum after only 3 h of the reaction time (about 80 % conversion). Then, the conversion remained constant. Obviously, the high initial activity of the ZS-5(1:3) sample is attributed to its high surface area and dispersion of the active sites on the surface. The product distribution results are summarized in Fig. 12, which demonstrates that the aldol condensation reaction of acetone initially produced mesityl oxide during the first 3 h of the reaction time with a high selectivity. However, mesityl oxide was not observed in this condition due to the high acidity of the catalyst surface. It was reported that the alcohol dehydration process requires low acidic strength sites with +0.8 of pKa [61]. However, when the reaction was performed at room temperature for 12 h with 10 wt.% (catalyst/acetone), primary condensation products were observed (i.e., diacetone alcohol and mesityl oxide). The acetone conversion in this condition was very low (approximately 92 % selectivity for diacetone alcohol and 8 % selectivity for mesityl oxide). It clearly indicates that the selectivity toward the diacetone alcohol is sensitive to the reaction temperature. The high selectivity for diacetone alcohol observed at room temperature is presumably owing to dehydration steps, and a further condensation of ketone to higher molecular-weight products has a high activation energy and occurs quite slowly at room temperature. As shown in Fig. 12, more condensation products can be formed when the reaction was performed at 150 °C for a longer time. These products are generally formed as a result of self and cross condensation of mesityl oxide with acetone. When the reaction proceeds for a longer time or over stronger acidic surfaces, the concentration of mesityl oxide was decreased since it was consumed during the cross-condensation reaction with acetone producing isophorone, mesitylene, and pentamer. The selectivities towards these products were increased by the reaction time. The selectivity of isophorone is much lower than other products due to its instability, resulting in the decomposition over strong acid sites producing mesitylene or a further reaction with mesityl oxide forming pentamers. It was found that more self- and cross-condensation reactions take place on a stronger acid site.

4 Conclusions

We demonstrated that the reaction of zirconium acetate with different concentrations of the ethanesulfonic acid provides a successful method for controlling of sulfur content on the surface of the final sulfated zirconium oxide obtained from the pyrolysis of single precursors. This was achieved by the sequential and gradual displacement of the acetate ligands by the sulfonate ions. Sulfated zirconium oxide powders prepared by the thermal treatment of the zirconium sulfonate single source precursors exhibited a strong surface acidity and relatively high surface areas. On the basis of various characterization techniques, we verified that the surface sulfate structure and the surface acidity strongly depend on the concentration of the sulfates on the surface. The total surface acidity, acid strength, and surface area showed an increase by the arising of the amount of sulfate groups on the surface.

The zirconium sulfonate complexes used in this study yielded the highly stabilized tetragonal phase sulfated zirconia with a small crystallite size after pyrolysis.

The obtained sulfated zirconium oxides catalyzed acetone self-condensation reactions. The catalytic activity and product selectivity were strongly influenced by catalyst properties and the surface acidity of the employed sulfated zirconia catalyst. Our systematic examination showed that acidity is critical in the dehydration of the intermediate alcohol to the corresponding α , β -unsaturated carbonyl compounds, and accordingly, mesityl oxide was produced with a high selectivity from the acetone self-condensation reaction.

To support our proposed mechanism based on ex situ techniques, in situ experiments (i.e., time-resolved XRD approaches) may need to obtain more detailed information to understand the mechanism. In addition, more fundamental studies on acid sites at the molecular level may provide more detailed information about the elemental steps to more accurately elucidate the reaction mechanism.

Acknowledgments We highly appreciate the financial support by SABIC.

References

- 1. Veloso O, Monteiro F, Sousa-Aguiar F (1991) Stud Surf Sci Catal 84:1913
- 2. Wierzchawski T, Zatorski W (1991) J Catal 9:411
- 3. Rode J, Gee E, Marquez N, Uemura T, Bazagani M (1991) Catal Lett 9:103
- 4. Reichle WT (1980) J Catal 63:295
- 5. Hoelderich WF (1988) Stud Surf Sci Catal 41:83
- 6. Colonge J (1931) Bull Soc Chem Fr 49:426
- 7. Zhang G, Hattori H, Tanabe K (1988) Appl Catal A-Gen 36:189
- 8. Lippert S, Baumann W, Thomke K (1991) J Mol Catal 69:199
- 9. Baigrie L (1985) J Am Chem Soc 107:3640
- 10. Wang YH, Wang GJ, Xiao JH, Ma J (1993) Chem J Chin 14:1448
- Di Cosimo JI, Díez VK, Apesteguía CR (1996) Appl Catal A-Gen 137:149
- Di Cosimo JI, Díez VK, Apesteguía CR (1998) Appl Clay Sci 13:433
- 13. Luo SC, Falconer JL (1999) J Catal 185:393
- Wang FZ, Yang K, Chai YM, Gao PC (2008) Chin J Inorg Chem 24:1417
- 15. Stevens MG, Chen D, Foley HC (1999) Chem Comm 275
- Thomas L, Tanner R, Gill P, Wells R, Bailie JE, Kelly G, Jackson SD, Hutchings G (2002) J Phys Chem 4:4555
- 17. Canning AS, Jackson SD, McLeod E, Vass EM (2005) Appl Catal A-Gen 28:959

- 18. Philippou A, Anderson MW (2000) J Catal 189:395
- Zamora M, López T, Gómez R, Asomoza M, Melendrez R (2005) Catal Today 289:107
- 20. Ma C, Liu G, Wang Z, Li Y, Zheng J, Zhang W, Jia M (2009) React Kinet Catal Lett 98:149
- 21. Rodrigues ACC, Monteiro JLF (2009) Appl Catal A-Gen 362:185
- 22. Waters G, Richter O, Kraushaar-Czarnetzki B (2006) Ind Eng Chem Res 45:5701
- 23. Bej SK, Thompson LT (2008) Appl Catal A-Gen 264:141
- 24. Komatsu T, Misuhashi M, Yshima T (2002) Stud Surf Sci Catal 142:667
- 25. Muzart J (1982) Synthesis 60
- 26. Jerry M (1992) Advanced organic chemistry, 4th edn. Wiley, New York
- 27. Bell V, Gold H (1983) J Catal 79:286
- 28. Xu W, Raftery D (2001) J Catal 204:110
- 29. Biaglow A, Sepa J, Gorte R, White D (1995) J Catal 151
- Casale MT, Richman AR, Elrod MJ, Garland RM, Beaver MR, Tolbert MA (2007) Atmos Environ 41:6212–6224
- 31. Hino M, Arata K (1979) Chem Lett 8:477-480
- 32. Hino M, Arata K (1980) J Chem Soc Chem Commun 851
- 33. Hino M, Kobayashi S, Arata K (1979) J Am Chem Soc 101:6439
- 34. Kuznetsov V (1940) J Appl Chem 13:1257
- 35. Arata K (1990) Adv Catal 37:165
- 36. Gillespie R, Peel T (1972) Adv Phys Org Chem 9:1
- 37. Davis B, Keogh R, Srinivasan R (1994) Catal Today 20:219
- 38. Arata K, Hino M, Yamagata N (1990) Bull Chem Soc 63:244
- 39. Escalona E, Penarroga M (1995) Catal Lett 30:31
- 40. Song S, Sayari A (1996) Cat Rev Sci Eng 38:329

- 41. Yadav G, Nair J (1999) Micro Meso Mat 33:1
- 42. Kooli F, Sasaki T, Watanabe M (1999) Langmuir 15:1090
- 43. Hammett L, Deyrap A (1932) J Am Chem Soc 54:2721
- 44. Yadav GD, Murkute AD (2004) Adv Synth Catal 346:389
- Benitez VM, Yori JC, Vera CR, Pieck CL, Grau JM, Parera JM (2005) Ind Eng Chem Res 44:1716
- 46. Chen WH, Ko HH, Sakthivel A, Huang SJ, Liu SH, Lo AY, Tsai TC, Liu SB (2006) Catal Today 116:111
- Garnweitner G, Antonietti M, Niederberger M (2005) Chem Commun 21(3):397–399
- 48. Gomez R, Lopez T (1998) J Sol Gel Sci Technol 11:309
- Wang J, Valenzyela M, Salmon J, Vazquez A, Garcia-Ruiz A, Boxhimi X (2001) Catal Today 68:21
- 50. Ganapathy D, Jayeshi J (1999) Micropor Mesopor Mat 33:1
- 51. Morterra C, Cerrato G, Emanule C, Bolis V (1993) J Catal 142:349
- 52. Bensitel M, Saur O, Lavally J, Morrow B (1988) Mater Chem Phys 19:147
- 53. Geiculescu A, Specncer H (1999) J Sol Gel Sci Tech 16:243
- 54. Corma A, Martin-Aranda M (1991) J Catal 130:130
- 55. Ryashentseva M (1994) Rev Heter Chem 10:23
- 56. Ryashentseva M, Minacher K, Afanas'eva Y (1964) USSR
- 57. Ecormier M, Wilson K, Lee A (2003) J Catal 215:57
- 58. Aiken W, Matijevic E (1996) J Mater Sci 38:329
- Salvapati GS, Ramanamurty KV, Janardanarao M (1989) Selective catalytic self-condensation of acetone. J Mol Catal 54:9–30
- 60. Lelkar C, Schutz A (1998) Appl Clay Sci 13:417
- 61. Delannay F (1984) Chemical industries (V-15), characterization of heterogeneous catalysis. Marcel Dekker, New York