

Research Note

Preparation of a novel catalyst UDCaT-5: enhancement in activity of acid-treated zirconia—effect of treatment with chlorosulfonic acid vis-à-vis sulfuric acid

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Abstract

UDCaT-5, a zirconia-based catalyst, with high sulfur content (9% w/w) but preservation of the tetragonal phase of zirconia was synthesized for the first time, by using chlorosulfonic acid as a new source for sulfate ions. UDCaT-5 was characterized by using elemental analysis, FTIR, ammonia-TPD, XRD, and BET surface area. Its catalytic activity and stability were evaluated and compared with S-ZrO₂ in three different reactions. The characterization and reaction studies show that UDCaT-5 exhibits more superacidity vis-à-vis conventional sulfated zirconia prepared by using sulfuric acid.

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1. Introduction

Zirconia, when modified with sulfate ions, forms a highly acidic or superacidic material that exhibits superior catalytic activity than 100% sulfuric acid in many reactions [1–4]. It has been widely used to catalyze hydrocarbon isomerization, methanol conversion to hydrocarbons, alkylation, acylation, esterification, etherification, condensation, nitration, cyclization, etc. [5,6]. A variety of methods have been used to synthesize sulfated zirconia, which differ mainly in the type of precursors, precipitating agents, sulfation procedure, and calcination temperature. The catalytic activity of sulfated zirconia is mainly dependent on the precursor, type of sulfating agent, and calcination temperature. High sulfur content in the form of sulfate ions is introduced with H₂SO₄ as a sulfating agent in comparison with (NH₄)₂SO₄, (NH₄)₂S₂O₃, (NH₄)₂S, SO₃, SO₂, H₂S, etc. [6]. Different methodologies are used to increase the sulfur content in zirconia with crystalline stability toward the tetragonal phase of zirconia but only a maximum of 4% w/w sulfur content was achieved (Table 1) [7–14]. Some control of sulfate loading

can be achieved by changing the calcination temperature but another property, noticeably crystallinity of zirconia, also is affected [7,8]. Wender [8] reported that sulfated zirconia, derived from impregnation with 0.25 M sulfuric acid and calcined at 600 °C for 3 h, possessed 2.5% w/w sulfur content (in the form of sulfate ions). It is also reported that “percolation” with sulfuric acid of concentrations varying from 0.05 to 2 M led to about the same amount of sulfur in sulfated zirconia after calcination [9]. Morterra et al. [10] have studied the effect of sulfate concentration on the Brønsted acidity of the catalyst. Their results suggest an increase in the Brønsted acidity with an increase in sulfate concentration up to a certain maximum, after which the amount of Brønsted acidity remains constant. This trend has also been reported by Nascimento et al. [11]. Thus, sulfur in the form of sulfate present above 4% w/w is lost during the thermal activation and represents a thermally more labile fraction.

Fârcașiu and co-workers [12] reported that the sulfur content could be controlled and zirconia with high sulfur loading can be achieved. Their report suggests that zirconia exhibits a pure tetragonal phase at low values of sulfur content but at a higher value (S > 4%), its crystallinity is strongly affected and a monoclinic phase of zirconia is formed in addition to the tetragonal phase. In another study [13], sulfated zirconia was prepared by different procedures using a colloidal sol-

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Table 1
Preparation procedure of S–ZrO₂

Sulfating agent	Preparation method	Sulfur content (% w/w)	Calcination temperature (°C)	Nature of the phases ^a	Ref.
0.25 M H ₂ SO ₄	Impregnation method	2.5	600	T	[8]
0.05 to 2 M H ₂ SO ₄	Percolation	1.48	620	T	[9]
(NH ₄) ₂ SO ₄	Percolation	0.81	620	T	[9]
(NH ₄) ₂ S ₂ O ₃	Percolation	0.45	620	T	[9]
(NH ₄) ₂ S	Percolation	0.16	620	T	[9]
0.5 M H ₂ SO ₄	Controlled impregnation	1.43	580	T	[12]
0.5 M H ₂ SO ₄	Controlled impregnation	3.42	580	T	[12]
0.5 M H ₂ SO ₄	Controlled impregnation	5.64	580	T + M	[12]
0.5 M H ₂ SO ₄	Colloidal-sol-gel (using CH ₃ COOH peptizing agent + 3 weeks aging)	4.6	650	T+M + Zr(SO ₄) ₂	[13]
0.5 M H ₂ SO ₄	Colloidal-sol-gel (Zr(OH) ₄ reflux in H ₂ SO ₄)	2.2–3.7	650	T + M + Zr(SO ₄) ₂	[13]
0.5 M H ₂ SO ₄	Immersing Zr(OH) ₄ in 0.5 M H ₂ SO ₄	4%	650	T	[14]
0.5 M solution of chlorosulfonic acid and ethylene dichloride	Immersing Zr(OH) ₄ in 0.5 M solution of chlorosulfonic acid and ethylene dichloride	9%	650	T	This work

^a T, tetragonal phase, M, monoclinic phase.

gel technique and impregnation. The colloidal sol-gel technique leads to the formation of sulfated zirconia with a high amount of sulfur content along with mono and polynucleate sulfate species as well as supported sulfuric acid. All previous literature suggests that S–ZrO₂ has been prepared so far with a maximum 4% w/w of sulfur with preservation of the tetragonal phase of zirconia and above this value the tetragonal phase is strongly affected. Thus, it will be most advantageous to synthesize sulfated zirconia with a high sulfur content particularly above 4% with a pure tetragonal phase to exhibit high superacidity. We report, for the first time, a preparation of sulfated zirconia with a high sulfur content (9%), possessing better activity including preservation of its tetragonal phase by using chlorosulfonic acid as a new source for sulfate ions. This new catalyst is designated as UDCaT-5 and the conventional sulfuric acid-treated catalyst as S–ZrO₂ in this investigation.

2. Experimental

2.1. Chemicals

Zirconium oxychloride, aqueous ammonia solution, sulfuric acid, toluene, and benzyl chloride were procured from M/s. s. d. Fine Chemicals (India). *p*-*tert*-Butylcyclohexanol (PTBCH) and chlorosulfonic acid were purchased from Lancaster and Spectrochem (India), respectively. *n*-Hexane was procured from Merck (Germany).

2.2. Catalyst preparation

Zirconium hydroxide was prepared by hydrolysis of aqueous zirconium oxychloride (ZrOCl₂·8H₂O) with aqueous

ammonia at room temperature at a pH of 9–10. The precipitated zirconium hydroxide was washed with deionized water until a neutral filtrate; the absence of chlorine ion was detected by phenolphthalein and AgNO₃ tests. A material balance on Cl before and after precipitation and washing shows no retention on the solid. Zirconium hydroxide was dried in an oven for 24 h at 100 °C and was crushed to 100 mesh size.

Three catalysts, UDCaT-5a, UDCaT-5, and UDCaT-5b, were synthesized: (i) UDCaT-5a, Zr(OH)₄ immersed in 6 cm³/g of 0.5 M solution of chlorosulfonic acid and ethylene dichloride solution; (ii) UDCaT-5, Zr(OH)₄ immersed in 15 cm³/g of 0.5 M solution of chlorosulfonic acid and ethylene dichloride; (iii) UDCaT-5b, Zr(OH)₄ immersed in 50 cm³/g of 0.5 M solution of chlorosulfonic acid and ethylene dichloride. All materials were immersed for 5 min in the solution and then without allowing moisture absorption were kept in an oven and the heating was started to evaporate the solvent and then to a temperature of 120 °C after about 30 min. These materials were kept in oven at 120 °C for 24 h and calcined at 650 °C for 3 h to get the active catalysts.

Sulfated zirconia (S–ZrO₂) was prepared by immersing Zr(OH)₄ in 15 cm³/g of 0.5 M of sulfuric acid followed by drying at 120 °C for 24 h and calcination at 650 °C for 3 h [14].

The molarity of solution of chlorosulfonic acid in ethylene dichloride used to get UDCaT-5 was the same as that of aqueous solution of sulfuric acid used to get S–ZrO₂.

2.3. Reaction procedure and analysis

Vapor-phase isomerization of *n*-hexane was conducted in a downflow fixed-bed reactor at WHSV of 3 h⁻¹ at 250 °C

using H_2 as carrier gas and the effluent stream was analyzed online by GC (GC1000 Chemito) equipped with a capillary column and FID detector. Liquid-phase reactions were conducted in a glass reactor of 5 i.d. and 10 cm height with four glass baffles and a four-bladed disk turbine impeller located at a height of 0.5 cm from the bottom of the vessel and mechanically agitated with an electric motor. In a typical alkylation reaction, 0.5 mol toluene was reacted with 0.05 mol benzyl chloride with a catalyst loading of 0.018 g/cm^3 , 1000 rpm, and 90°C . Esterification reactions were conducted with 0.02 mol PTBCH and 0.60 mol acetic acid with a catalyst loading of 0.025 g/cm^3 at a speed of 1000 rpm at 90°C and analyzed by a Chemito gas chromatograph equipped with a stainless-steel column (diameter 1/8 inches and length 4 m) packed with liquid stationary phase of 10% OV-17 on Chromosorb WHP, and a FID detector.

3. Results and discussion

3.1. Characterization

3.1.1. Ammonia-TPD

Temperature desorption using ammonia as a probe has been proposed as a measurement of the total acidity and acid strength distribution in solids [15]. It has been reported that

other compounds may evolve from the surface than just the original probe molecule. In some cases probe or the sulfate decomposes when acidity of metal ion promoted $S\text{-ZrO}_2$ is determined by ammonia-TPD [16,17]. However, decomposition of sulfate is observed above 600°C during TPD analysis for unpromoted sulfated zirconia by using NH_3 as a probe [18,19]. We used ammonia-TPD (Autochem 2920, Micromeritics) to determine the acid strength of the conventional sulfuric acid-treated zirconia ($S\text{-ZrO}_2$) and chlorosulfonic acid-treated zirconia materials, UDCaT-5a, UDCaT-5, and UDCaT-5b. Fig. 1A depicts that $S\text{-ZrO}_2$ exhibits two peaks, one at 180°C and another at 450°C corresponding to intermediate and strong acid strengths. Similar types of intermediate and strong acid strengths are reported for $S\text{-ZrO}_2$ by others [18,19]. Corma et al. [20] have reported generation of a superacidic peak at 550°C in ammonia-TPD for $S\text{-ZrO}_2$ calcined at 550°C for 3 h. It is well known that the calcination temperature is a very important parameter and $S\text{-ZrO}_2$ calcined at 550°C has a different acid strength distribution than that calcined at 650°C . Thus $S\text{-ZrO}_2$ synthesized and calcined at 550°C by Corma et al. exhibits superacidic centers at 550°C in ammonia-TPD. The total number of acid sites of $S\text{-ZrO}_2$ ($0.433 \text{ mmol g}^{-1}$) prepared by our procedure was almost the same as that of $S\text{-ZrO}_2$ ($0.420 \text{ mmol g}^{-1}$) prepared by Corma et al. [20]. This confirms that the acid strength of $S\text{-ZrO}_2$ prepared by us also possesses the same type of acidity reported in the literature.

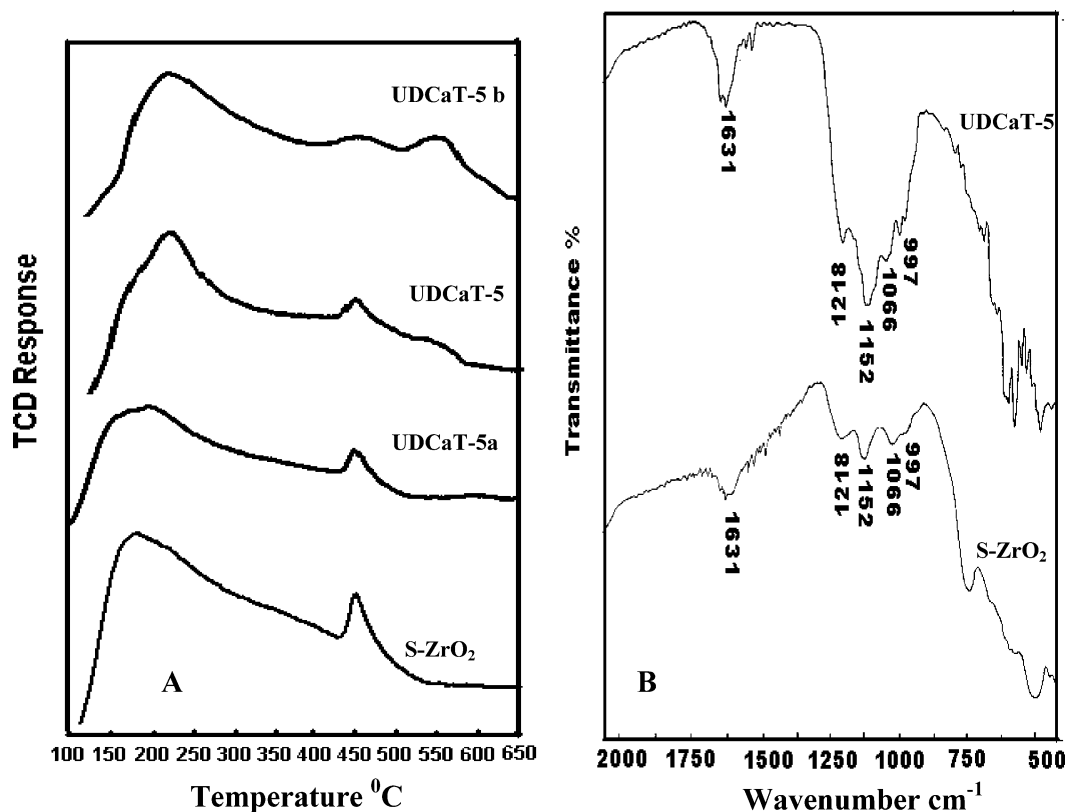


Fig. 1. (A) Ammonia-TPD of $S\text{-ZrO}_2$ and UDCaT-5. (B) FTIR of $S\text{-ZrO}_2$ and UDCaT-5.

In the case of UDCaT-5a well-defined peaks were obtained at 210 and 450 °C which indicate that it possesses strong and very strong acid strength, respectively. Further, the total number of acid sites of UDCaT-5a was 0.403 mmol g⁻¹ which was about 7% lower than that for S-ZrO₂ (0.433 mmol g⁻¹). However, UDCaT-5a possesses a higher acid strength than S-ZrO₂ which is evident from the higher NH₃ desorption temperature for the former. It should be noted that a lower volume (6 cm³/g) of 0.5 M solution of chlorosulfonic acid and ethylene dichloride was used to treat Zr(OH)₄ for preparation of UDCaT-5a than the volume (15 cm³/g) of 0.5 M sulfuric acid use to treat Zr(OH)₄ for preparation of sulfated zirconia (S-ZrO₂). A completely different type of spectra was obtained for UDCaT-5 and UDCaT-5b vis-à-vis S-ZrO₂. The most striking feature of the spectra of the UDCaT-5 and UDCaT-5b is the generation of an additional peak at 550 °C in both. Corma et al. [20] assign this peak to superacidic centers of S-ZrO₂ calcined at 550 °C. It is thus inferred here that there is a generation of superacidic centers in UDCaT-5 and UDCaT-5b, even though they were calcined at 650 °C for 3 h and the same peak is not observed in S-ZrO₂ calcined at 650 °C. The total acid sites of each UDCaT-5 (0.584 mmol g⁻¹) and UDCaT-5b (0.623 mmol g⁻¹) are much higher than that of S-ZrO₂ (0.433 mmol g⁻¹) prepared by us and by Corma et al. (0.420 mmol g⁻¹). The acidity of both UDCaT-5 and UDCaT-5b is dependent on the molar strength of chlorosulfonic acid and is more superacidic than S-ZrO₂. Hence, it was thought desirable to characterize UDCaT-5 through FTIR, XRD, BET surface area, pore-size analysis, and elemental analysis and its activity was compared with that of S-ZrO₂.

3.1.2. Elemental analysis

It was expected that during the thermal treatment of UDCaT-5, chlorosulfonic acid would decompose to sulfuryl chloride, pyrosulfuryl dichloride, sulfuric acid, sulfur dioxide, chlorine, and water [21]. The elemental analysis showed a complete absence of Cl species and that 9% w/w S as sulfate was retained on the surface of UDCaT-5. This implied that sulfuryl chloride and pyrosulfuryl dichloride were not formed on the surface of the UDCaT-5. In contrast, only 4% of S in the form of sulfate ion is retained on S-ZrO₂ when sulfation of zirconia is done through sulfuric acid.

3.1.3. FTIR

The IR spectra (Shimadzu) of UDCaT-5 shows a pattern of four bands assigned to bidentate SO₄²⁻ ions in C_{2v} symmetry with ν₃ at 1218, 1152, and 1066 and ν₁ at 997 cm⁻¹ coordinated to zirconia (Fig. 1B). The absence of a band at 1400 cm⁻¹ indicates that there is no formation of polynuclear sulfates S₂O₇²⁻ on the surface of UDCaT-5. The band at 1631–1642 cm⁻¹ is attributed to δ_{O-H}-bending frequency of water molecules associated with the sulfate group [22], suggesting that chlorosulfonic acid is decomposed during calcination of the UDCaT-5. An additional broad band at

3400 cm⁻¹ (not shown) corresponds to the stretching vibration ν_{OH} of the hydroxyl group. IR bands between 700 and 415 cm⁻¹ are characteristics of crystalline zirconia. It may thus be concluded that during the calcination at 650 °C, condensation of the hydroxyl group of Zr(OH)₄ occurs leading to a crystalline zirconia without any change of the nature of sulfate species. The IR spectra of the S-ZrO₂ show a similar pattern as UDCaT-5, indicating the presence of the bidentate chelating sulfate group coordinated to zirconia [6,14]. IR spectra confirm that chlorosulfonic acid is decomposed during calcination at 650 °C and sulfate ions are retained on the surface of the UDCaT-5.

3.1.4. X-ray diffraction

Powder XRD (Phillips PW1729) was used to elucidate the crystalline phase of sulfated zirconia and UDCaT-5 (Fig. 2A). It is generally observed that pure zirconia transforms into a monoclinic phase from a tetragonal phase above the calcination temperature of 600 °C [6]. This transformation is prevented in both S-ZrO₂ and UDCaT-5 due to doping of SO₄²⁻. Preservation of the tetragonal crystalline phase, which is essential for catalytic behavior in sulfated zirconia, has been well explained in earlier literature [6] but this phenomenon was also evident in the case of UDCaT-5. The crystal structure of the sulfated zirconia is also affected by the sulfur content and the low or medium sulfate content zirconia crystallizes only in the tetragonal form, whereas for sulfate content zirconia (S > 4%), it exists in a monoclinic form, in addition to the major tetragonal form [12]. However, the crystal structure of the zirconia is not affected due to the high sulfur content in UDCaT-5 and the quantity of the tetragonal phase of zirconia in UDCaT-5 is the same as that in S-ZrO₂.

3.1.5. BET surface area and pore-size analysis

The BET surface area (ASAP 2010, Micromeritics) of UDCaT-5 is lower than that of S-ZrO₂ (Table 2, S. No. 2). Fărcașiu et al. [12] had observed that the surface area of S-ZrO₂ gradually increases at a low sulfate content up to 4% w/w (119 m²/g) but it decreases abruptly at the maximum sulfate content of 5.64% (71 m²/g) due to migration of sulfate ions to the bulk phase of zirconia. A similar reason could have been ascribed in our case. However, XRD results indicate that the tetragonal phase of zirconia, which is essential for exhibiting superacidity, is retained even after high sulfate ions were introduced on the surface of the UDCaT-5. Furthermore, migration of the sulfate group into the bulk phase of the zirconia would have resulted in extensive formation of a monoclinic phase of zirconia and zirconium sulfate [12], but it was not observed in the XRD. Therefore, the retention of high sulfate ions on the surface of the UDCaT-5 without changing the crystalline phase of the zirconia must follow a different mechanism. It is reported that the precursor Zr(OH)₄ should be made more reactive to obtain a high sulfate ion content on zirconia and it is accomplished by prolonged heating of suspension containing

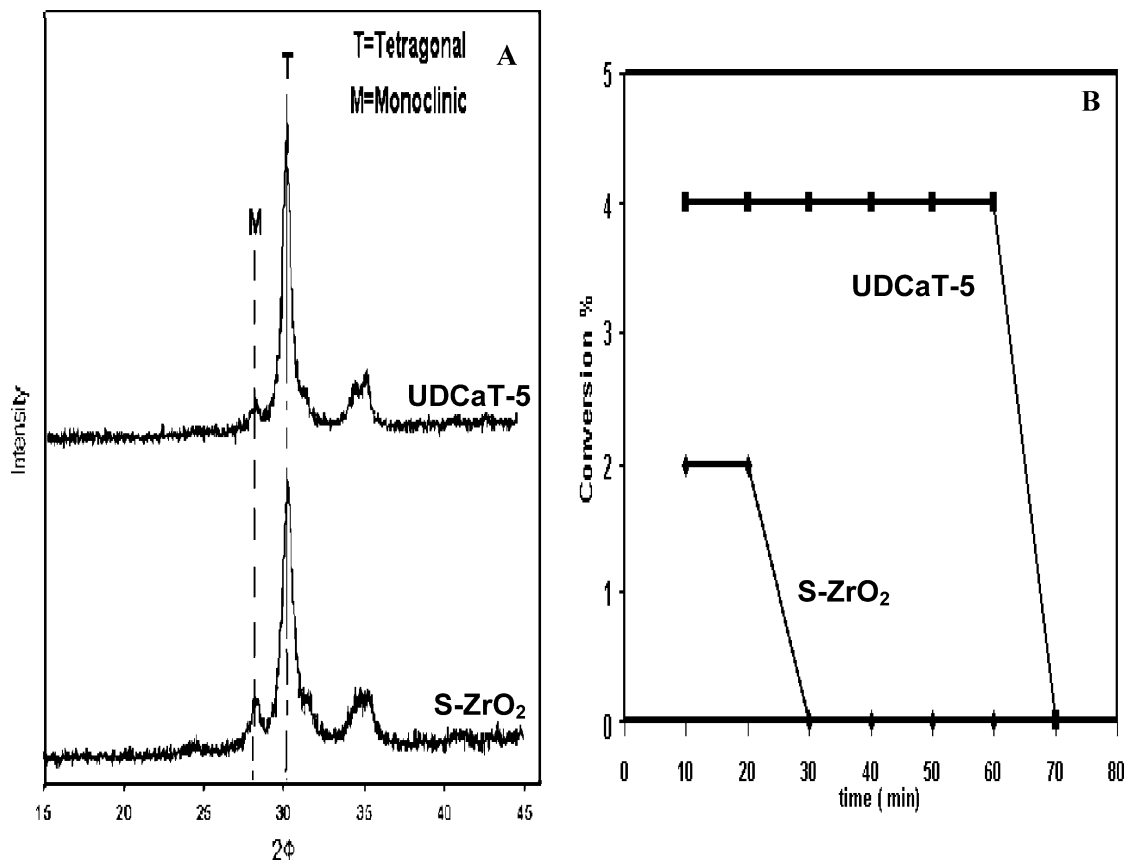


Fig. 2. XRD of S-ZrO₂ and UDCaT-5. (B) Time stream of isomerization of *n*-hexane on S-ZrO₂ and UDCaT-5.

Table 2
Acidity and activity of catalysts

S. No.	Parameters	Catalysts			
		S-ZrO ₂	UDCAT-5a	UDCAT-5	UDCAT-5b
1	Acidity by NH ₃ -TPD (mmol g ⁻¹)	0.433	0.403	0.584	0.623
2	BET surface area (m ² g ⁻¹)	103	—	83	—
3	Isomerization of <i>n</i> -hexane, conversion % (after 20 min)	2	—	4	—
4	Benylation of toluene, initial activity × 10 ⁶ (mol s ⁻¹ g ⁻¹)	8	—	15	—
5	Benylation of toluene, conversion of BzCl % after 1 h	79	—	97	—
6	Esterification of PTBCH, conversion of PTBCH % after 4 h	53	—	76	—

Zr(OH)₄ at reflux in H₂SO₄ [13]. Also a prolonged contact of Zr(OH)₄ with sulfuric acid and use of peptizing agent such as acetic acid for 3 weeks are reported to result in a high sulfate content [13]. We reasoned that to introduce a higher sulfate content, chlorosulfonic acid could be used as the sulfating agent since it would be more strongly adsorbed on the Zr(OH)₄ than sulfuric acid and it would be possible to avoid the use of a peptizing agent with extensive heating under reflux conditions. Further, chlorosulfonic acid would be decomposed during calcination into sulfuryl chloride, pyrosulfuryl dichloride, sulfuric acid, and higher polyacids leaving more sulfur in the samples than that in sulfuric

acid-treated zirconia. In fact, preparation of UDCaT-5 using chlorosulfonic acid showed that there was no formation of the polynucleate sulfate ion and also there was no Cl residue in the sulfate ions of UDCaT-5, which was confirmed by the FTIR spectra and elemental analysis. Thus, we infer that this decomposition process occurs with a corresponding decrease in surface area and not due to migration of sulfate ions into the bulk phase of zirconia. Another argument in favor of this supposition is that the XRD of both catalyst S-ZrO₂ and UDCaT-5 contain monoclinic and tetragonal phases. The diffractograms show the same amount of tetragonal phase of zirconia in both samples.

3.2. Catalytic activity and stability of UDCaT-5

3.2.1. Isomerization of *n*-hexane

The initial activity of UDCaT-5 was twice that of S–ZrO₂ in *n*-hexane isomerization (Table 2, S. No. 3 and Fig. 2B). Although UDCaT-5 deactivates completely after 1 h, its deactivation is much slower than that of S–ZrO₂ which deactivates completely in 20 min. The high catalytic activity of UDCaT-5 in the isomerization of *n*-hexane is due to the high acid strength of UDCaT-5. The selectivity of 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane is together 77% for both catalysts. The acidic catalysts require metal doping in isomerization reactions to overcome deactivation and it is a matter of a separate study.

3.2.2. Benzylation of toluene with benzyl chloride

It was observed that the initial rate of reaction with UDCaT-5 was almost twice than that with S–ZrO₂ (Table 2, S. Nos. 4 and 5). The reusability of the catalyst was also tested thrice in the case of the benzylation of toluene. It was observed that UDCaT-5 shows the same activity after the third use which confirms the stability of the UDCaT-5 even in the presence of the corrosive HCl generated in situ.

3.2.3. Esterification of *p*-tert-butylcyclohexanol with acetic acid

The stability of S–ZrO₂ is susceptible where water is generated as a coproduct. When fresh S–ZrO₂ is mixed with water, the pH of the suspension decreases quickly due to hydrolysis of the sulfate groups, which is confirmed by the identification of sulfate ions in the aqueous phase [19]. The same test was conducted for UDCaT-5 for fresh and reused catalyst by pH measurement and it was found that there was no leaching of sulfate ions from UDCaT-5. PTBCHA is widely used in perfumery along with ionones, cedarwood products, and floral and nonfloral perfume chemicals and is a very versatile perfume material for soap and fragrance [23]. Thus, esterification of *p*-tert-butylcyclohexanol with acetic acid was chosen to study the efficacy and stability of the UDCaT-5 in the presence of water generated in situ. UDCaT-5 displayed higher catalytic activity in comparison to S–ZrO₂ (Table 2, S. No. 6) for this reaction. In order to study the stability of the UDCaT-5 the catalysts was reused thrice and it was found that UDCaT-5 retained its activity in all three experiments. Thus, there was no leaching of the sulfate ion from UDCaT-5 and it is a stable catalyst in comparison with S–ZrO₂. These activity studies further bolster the assumption drawn from the spectroscopic studies.

4. Conclusion

We report, for the first time, that chlorosulfonic acid treatment of zirconia resulted into formation of a novel catalyst, named UDCaT-5 which is superior to sulfuric acid-treated S–ZrO₂. Despite the fact that the same strength and volume of chlorosulfonic acid was used to get UDCaT-5 as those used for sulfuric acid to get S–ZrO₂, UDCaT-5 contains more sulfate ions, is more stable, and also is more active in comparison with S–ZrO₂. The characterization and reaction tests support the above results.

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