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ZrO_2–SiO_2 Mixed Oxides Xerogel and Aerogel as Solid Acid Catalysts for Solvent Free Isomerization of α-Pinene and Dehydration of 4-Methyl-2-Pentanol

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Abstract Sulfated and non-sulfated ZrO_2–SiO_2 mixed oxide xerogel and aerogel samples having varied Zr/Si molar ratio were evaluated as solid acid catalysts for the isomerization of α-pinene and dehydration of 4-methyl-2-pentanol. Sulfation resulted into enhancement in the catalytic activity of both xerogel and aerogel samples towards the studied reactions. For example, sulfated catalysts showed 86–98% conversion of α-pinene and 8–35% conversion of 4-methyl-2-pentanol. The selectivity data for camphene and limonene indicated the requirement of moderate acidity. The correlation with cyclohexanol dehydration showed that isomerization of α-pinene is a Brønsted acid catalyzed reaction. The relationship of 4-methyl-2-pentanol conversion with acid site density and sulfur per unit area was found to be linear.

Keywords ZrO_2–SiO_2 mixed oxides · Xerogels · Aerogels · Pinene isomerization · Alcohol dehydration

1 Introduction

Zirconia as a catalyst or catalytic support has received considerable attention in recent years [1, 2]. However, relatively low surface area and weak acidity limited its extensive application in catalysis [3, 4]. In order to improve its surface area, zirconia can be combined with some materials possessing high surface area such as silica. Mixed metal oxides have been widely investigated since they have interesting catalytic properties [5–8]. The presence of a foreign element in the matrix of a pure metal oxide can greatly modify the structural, textural, acid–base and catalytic properties [9–11]. ZrO_2–SiO_2 mixed oxides have strong surface acidity and could be useful for diverse acid catalyzed reactions due to enhanced acidity as compared to less acidic individual zirconia or silica [11, 12]. The acidity of mixed oxides may further be modified by the use of sulfation [5, 10, 13]. The enhanced surface acidity and catalytic activity resulting from sulfation is extensively studied in the case of pure zirconia [11]. Influence of sulfation on the acidic properties of ceria–zirconia [10], zirconia–silica [5, 9, 13] and titania–silica [6, 14] mixed oxides has also been reported.

Monoterpenes like α-pinene are economically important compounds, which are extensively used in the

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pharmaceutical, cosmetic, food, fragrance and fine chemical industries [15]. α-pinene undergoes acid-catalyzed isomerization reaction resulting into valuable products such as camphene, limonene, mono-, bi- and tricyclic hydrocarbons, *p*-cymene, and oligomers [16]. Camphene is used in the production of camphor and limonene is widely employed in the synthesis of oxygenated compounds of perfumery industry [17]. The selectivity of various products strongly depends on the structural, textural and catalytic features of the catalyst along with the reaction conditions [18, 19]. Various solid acid catalysts such as zeolites, clays, zirconia and sulfated zirconia have been studied for the isomerization of α-pinene [20–25]. However, the selective isomerization of α-pinene to the desired isomers is still required.

Dehydration of alcohol is commercially important reaction to produce alkene as well as to identify acid and basic sites in heterogeneous catalysts [26, 27]. Isopropanol [28], 1-butanol [29], 4-methyl-2-pentanol [30, 31] and cyclohexanol [20, 32] are the most common alcohols studied for the dehydration reactions. Hexenes and skeletal rearranged products are reported during 4-methyl-2-pentanol dehydration [31]. Among these, hexenes such as 4-methyl-1-pentene and 4-methyl-2-pentene are major products, in which former has commercial values and is useful starting material for manufacturing thermoplastic polymers.

Recently, we have studied the effect of Zr/Si molar ratio, thermal and super critical drying methods, and sulfation on the structural, textural and catalytic properties of ZrO_2–SiO_2 mixed xerogel and aerogel samples [13]. In the present study, we have evaluated the catalytic activity of these materials for solvent free liquid phase isomerization of α-pinene and 4-methyl-2-pentanol dehydration. To the best of our knowledge, no report has been found so far in literature about isomerization of α-pinene and dehydration of 4-methyl-2-pentanol using sulfated or non-sulfated ZrO_2–SiO_2 mixed xerogels and aerogels.

2 Experimental

2.1 Catalyst Synthesis

ZrO_2–SiO_2 mixed oxides having varied molar ratio of Zr to Si (1:1, 1:2 and 2:1, respectively) have been prepared and characterized as reported earlier [13]. ZrO_2–SiO_2 xerogel samples obtained after conventional thermal drying followed by calcination at 600 °C are designated as X-ZSi-R and aerogel samples were obtained after supercritical drying using *n*-propanol as a solvent are designated as A-ZSi-R (where, $R = 1{:}1$, 1:2 and 2:1 representing ZrO_2:SiO_2 molar ratio). Both xerogel and aerogel samples were sulfated using 1 N H_2SO_4 followed by calcination at 600 °C and are designated as SX-ZSi-R and SA-ZSi-R, respectively.

2.2 Characterization

Sulfated and non-sulfated ZrO_2–SiO_2 mixed xerogel and aerogel samples, before and after calcination were analyzed using X-ray powder diffractometer (Philips X'pert) using CuKα radiation ($\lambda = 1.5405$ Å). Specific surface area, pore volume and pore size distributions of samples were determined from nitrogen adsorption–desorption isotherms at 77.4 K (ASAP 2010, Micromeritics, USA). The bulk sulfur (wt%) loading in sulfated ZrO_2:SiO_2 aerogel and xerogel samples before and after calcination at 600 °C was analyzed by CHNS/O elemental analyzer (Perkin–Elmer, 2400, Sr II, USA). Total surface acidity measurement by Temperature Programmed Desorption (TPD) of NH_3 was carried out using Micromeritics Pulse Chemisorb 2720 instrument [13].

2.3 Catalytic Activity for α-Pinene Isomerization

Typically, α-pinene (2 mL) and catalyst (0.1 g) mixture was heated at 150 °C under constant magnetic stirring for 2 h. Precautions were taken to maintain the temperature and to check the vapor loss of the products. The reaction products were analyzed by a gas chromatograph-mass spectrometer (Shimadzu, GC–MS QP 2010, Japan) with Petrocol DH 50.2 capillary column, programmed oven and ion source at 200 °C using He as a carrier gas. The conversion and selectivity values were calculated as below:

$$\begin{aligned}&\text{Conversion of }\alpha\text{-pinene(wt \%)}\\&\quad = 100 \times [\text{Initial wt \%} - \text{Final wt \%}]/[\text{Initial wt \%}]\end{aligned}$$

Selectivity for camphene (wt%) $= 100 \times$ [GC peak area % of camphene]/[Σ Total peak area of all the products].

2.4 Catalytic Activity for 4-Methyl-2-Pentanol Dehydration

Dehydration of 4-methyl-2-pentanol was studied in a fixed bed reactor. The catalyst (0.2 g) was packed in a glass reactor bed and activated in situ at 450 °C for 2 h under N_2 flow. 4-methyl-2-pentanol (2 mL) was delivered by a syringe pump injector (Cole Parmer, 74900 series) with a flow rate of 1 mL h^{-1} under N_2 (15 mL min^{-1}) at 145 °C. The product samples were collected after 1 h and analyzed by a gas chromatograph (HP 6890) having HP5 capillary column, FID detector and programmed oven and N_2 as carrier gas. The conversion of 4-methyl-2-pentanol and selectivity for each product was calculated following the procedure similar to that described above for α-pinene.

3 Results and Discussion

3.1 Catalyst Characterization

The detailed characterization of sulfated and non-sulfated ZrO_2–SiO_2 mixed xerogel and aerogel samples have been mentioned in our earlier report [13]. It was observed that the ZrO_2:SiO_2 molar ratio and drying method has significant effect on the structural and textural properties in terms of crystallinity, surface area, pore volume and pore diameter. Xerogel samples were found to be amorphous in nature indicating the uniform mixing and homogeneity of mixed oxides, whereas, supercritical drying at high temperature and pressure resulted into crystalline aerogel samples having predominantly tetragonal zirconia. Both xerogels and aerogels, though having different structural and textural features, were found to have the total number of acid sites per unit surface area (0.0021–0.0029 mmol NH_3 m^{-2}) and the catalytic activity for cyclohexanol conversion (31–41 wt%) in the similar range (Table 1). Sulfation resulted into remarkable enhancement of catalytic activity for cyclohexanol conversion (91–99%) for both sulfated xerogel and aerogel samples, though the surface area and pore volume decreased significantly. Sulfated xerogel samples showed higher acid sites density (0.0074–0.013 mmol NH_3 m^{-2}) compared to sulfated aerogel samples (0.0027–0.0082 mmol NH_3 m^{-2}) (Table 1) due to the higher sulfur loading in xerogel samples (5.10 to 7.57 wt%) compared to aerogel samples (1.58 to 2.65 wt%) [13] and therefore resulted into higher cyclohexanol conversion (>99%).

3.2 Isomerization of α-Pinene

The isomerization of α-pinene over sulfated and non-sulfated ZrO_2–SiO_2 xerogel and aerogel samples resulted mainly into bicyclic camphene, tricyclene and monocyclic limonene and α-terpinene under the experimental conditions studied. The reaction parameters namely temperature, time and substrate to catalyst ratio for the isomerization of α-pinene were optimized over one of the catalysts, i.e., A-ZSi-1:1**.** Initially, the reaction was carried out at different temperatures in the range of 110–150 °C (Fig. 1). The conversion of α-pinene was found to increase from 14 to 36% with increasing the reaction temperature from 110 to 150 °C. There was no significant variation observed in camphene (~36%) and α-terpinene (~2%) selectivity. However, limonene selectivity was found to increase from 36 to 45% with an increase in the temperature from 110 to 150 °C. It suggested that formation of limonene was more affected by temperature changes than those of the formation of camphene and α-terpinene.

The kinetic study was carried out at 150 °C over A-ZSi-1:1 catalyst (Fig. 2). It was observed that conversion of α-pinene increased from 26 to 36% till 90 min and remained nearly constant between 120 and 180 min. Hence, we have taken 120 min as optimized reaction time for further study. No significant variation was observed in camphene and tricyclene selectivity with increase in time. However, the formation of limonene increased from 39 to 45% with increasing time from 10 to 120 min**,** whiles other products such as terpinolene, iso-terpinolene, γ-terpinene, etc., were observed to decrease from 26 to 17% with increasing reaction time.

The effect of substrate to catalyst ratio was studied in the range of 10–40 by varying the amount of catalyst and by keeping α-pinene amount constant (2.0 g) over A-ZSi-1:1 catalyst at 150 °C. The conversion of α-pinene was observed to decrease by increasing substrate to catalyst ratio from 10 to 40. The maximum conversion of α-pinene (53%) was observed with substrate to catalyst ratio of 10, which decreased to 36 and 34% with substrate to catalyst

Table 1 Characterization of sulfated and non-sulfated ZrO_2–SiO_2 xerogel and aerogel catalysts [13]

Sample	BET surface area (m^2/g)	Acid sites conc. (mmol NH_3/g)	Acid sites/Surface area (mmol NH_3/m^2)	% S/Surface area (% S/m^2)	Cyclohexanol conversion (%)
X-ZSi-1:1	266	0.78	0.0029	–	39
X-ZSi-1:2	300	0.67	0.0022	–	31
X-ZSi-2:1	290	0.78	0.0027	–	41
SX-ZSi-1:1	105	1.20	0.0114	0.048	>99
SX-ZSi-1:2	160	1.19	0.0074	0.039	93
SX-ZSi-2:1	126	1.64	0.013	0.060	>99
A-ZSi-1:1	475	1.31	0.0028	–	34
A-ZSi-1:2	678	1.46	0.0021	–	32
A-ZSi-2:1	335	0.93	0.0028	–	35
SA-ZSi-1:1	194	0.99	0.0051	0.011	92
SA-ZSi-1:2	285	0.78	0.0027	0.005	91
SA-ZSi-2:1	160	1.31	0.0082	0.016	97

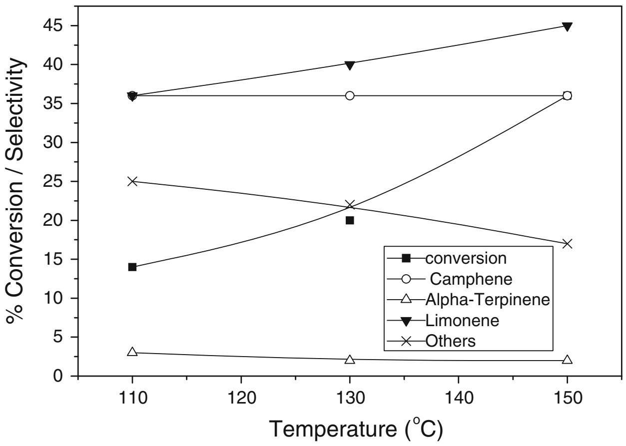

Fig. 1 Isomerization of α-pinene over A-ZSi-1:1 catalyst at different temperatures. *Reaction conditions* Catalyst = 0.1 g, α-Pinene = 2.0 g, time = 2 h, (others: terpinolene, iso-terpinolene, γ-terpinene, etc.)

ratio 20 and 40, respectively. However, camphene selectivity was found to be maximum (36%) with substrate to catalyst ratio of 20 and was lower (32%) with substrate to catalyst ratio of 10 and 40. Similarly, limonene selectivity was also observed to increase from 41 to 45% with an increase in substrate to catalyst ratio from 10 to 20 and decreased to 39% on further increasing the substrate to catalyst ratio to 40. Hence, substrate to catalyst ratio of 20 was selected as optimized ratio on the basis of the selectivity of the desired products rather than the conversion of α-pinene.

The isomerization of α-pinene over a series of sulfated and non-sulfated ZrO_2–SiO_2 mixed xerogel and aerogel samples (Table 2) showed the formation of mainly bicyclic camphene and monocyclic limonene, α-terpinene and terpinolene. Pure zirconia (ZrO_2) and sulfated zirconia (SO_4–ZrO_2) samples prepared by sol–gel method were also studied for comparison.

ZrO_2 showed no activity for the isomerization of α-pinene, while SO_4–ZrO_2 resulted into 100% conversion of α-pinene, however, the selectivity for the desired products such as camphene (24%) and limonene (nil) was less and the formation of side products was more (62%). It suggested the necessity of the moderate acidity to obtain the desired products during the isomerization of α-pinene. ZrO_2–SiO_2 xerogel samples with varied molar ratio showed the conversion of α-pinene in the wide range of 8–79%, while aerogel samples showed the conversion in the range of 36–56%. However, the selectivity for camphene (32–36%) and limonene (34–45%) was observed in the similar range for both xerogel and aerogel samples. The increase in the conversion of α-pinene compared to ZrO_2 and increase in the selectivities for the desired products compared to SO_4–ZrO_2 observed over ZrO_2–SiO_2 samples indicated that the presence of a foreign element in the matrix of a pure metal oxide can significantly modify the catalytic properties.

Sulfated ZrO_2–SiO_2 samples showed significant enhancement in the conversion of α-pinene (86–98%). Among the products, formation of tricyclene was observed to be significantly increased over sulfated samples (14–36%) compared to non-sulfated samples (1–2%). On the contrary, formation of camphene and limonene was higher over non-sulfated samples. The formation of α-terpinene could not be observed linear. It indicated that formation of camphene and limonene requires moderate acidity, whereas tricyclene and α-terpinene need higher acidity.

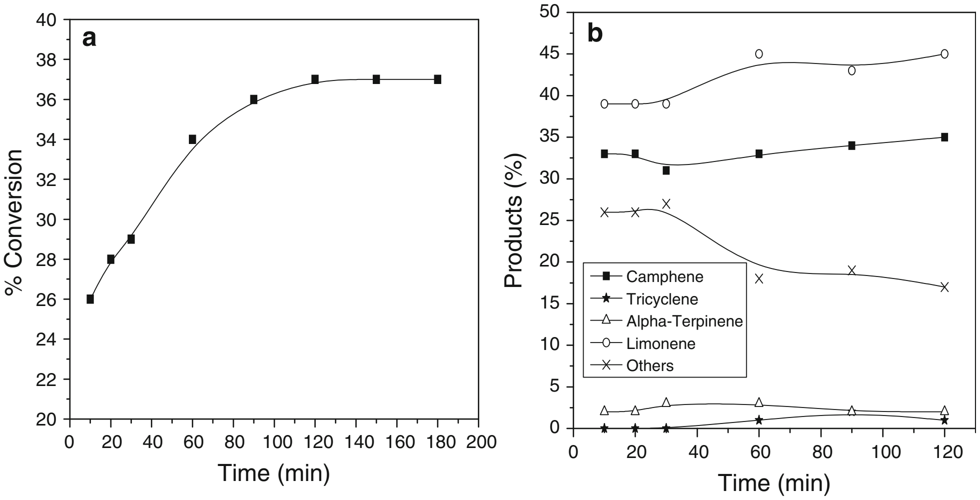

Fig. 2 **a** Variation in α-Pinene conversion and **b** various products formation with time over A-ZSi-1:1 catalyst. *Reaction conditions* Catalyst = 0.1 g, α-pinene = 2.0 g, temperature = 150 °C, time = 2 h (others: terpinolene, iso-terpinolene, γ-terpinene, etc.)

Table 2 Isomerization of α-pinene and selectivity for various products over sulfated and non-sulfated ZrO_2–SiO_2 xerogel and aerogel catalysts

Catalyst	% Conversion	% Selectivity				
		Camphene	Tricyclene	α-Terpinene	Limonene	Others
ZrO_2	Nil	–	–	–	–	–
SO_4–ZrO_2	100	24	14	–	–	62
X-ZSi-1:1	8	32	–	–	34	34
X-ZSi-1:2	29	32	1	6	42	19
X-ZSi-2:1	79	35	2	7	34	22
SX-ZSi-1:1	89	24	23	8	26	19
SX-ZSi-1:2	93	31	17	22	3	27
SX-ZSi-2:1	93	29	18	22	2	29
A-ZSi-1:1	36	36	1	2	45	16
A-ZSi-1:2	56	33	1	4	42	20
A-ZSi-2:1	39	32	1	3	40	24
SA-ZSi-1:1	93	32	19	2	31	16
SA-ZSi-1:2	98	34	14	16	2	34
SA-ZSi-2:1	86	28	36	10	3	23

Reaction conditions Catalyst = 0.1 g, α-Pinene = 2.0 g, temperature = 150 °C, time = 2 h (others: terpinolene, iso-terpinolene, γ-terpinene, etc.)

The formation of various mono-, bi- and tricyclic products by the isomerization of α-pinene occurred through the carbocation formation by the interaction of the proton of the acid catalyst with the double bond of α-pinene [17]. It is reported that in the presence of high acidic conditions, camphene and isomeric bi- and tricyclic compounds are transformed to monocyclic compounds [17]. This may be the reason that we found lower camphene selectivity with sulfated samples having higher acid site density compared to non-sulfated samples having lower acid site density. It further confirmed with sulfated xerogel and aerogel samples having varied acidity. For example, sulfated xerogel samples having higher sulfur and acid site density (Table 1 and Sect. 3.1) resulted into 24 to 31% of camphene selectivity, whereas, sulfated aerogel samples having lower sulfur and acid site density resulted into higher camphene selectivity (28 to 34%). These results were in good agreement with Encormier et al. [23], who observed that low sulfur of SO_4–ZrO_2 catalyst favoured the camphene formation.

The formation of other side products was greatly reduced in sulfated ZrO_2–SiO_2 samples (16–34%) compared to pure SO_4–ZrO_2 (62%), though the values for the conversion of α-pinene and camphene selectivity were comparable. Non-sulfated ZrO_2–SiO_2 samples also showed the reduced formation of other side products. It clearly suggested that the acidity of the catalyst and the selectivity for the desired products can be tunable with mixed oxides as compared to pure metal oxides.

Furthermore, the correlation between the conversion of α-pinene and cyclohexanol dehydration reaction over sulfated xerogel and aerogel samples (Fig. 3) clearly showed that isomerization of α-pinene is a Brønsted acid catalyzed reaction. Similar result was also observed using acid treated montmorillonite clays [20].

3.3 Dehydration of 4-Methyl-2-Pentanol

The dehydration of 4-methyl-2-pentanol over ZrO_2–SiO_2 samples leads to a mixture of 4-methyl-1-pentene and 4-methyl-2-pentene; along with skeletal isomers of C_6-alkenes and dehydrogenation to 4-methyl-2-pentanone

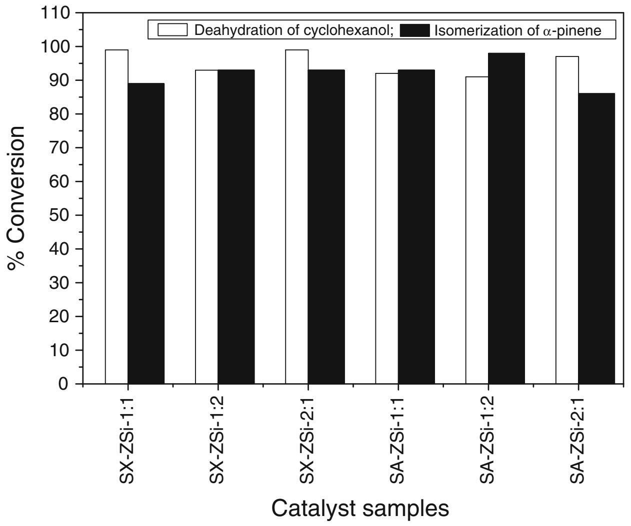

Fig. 3 Correlation between conversion values of α-pinene isomerization and cyclohexanol dehydration reaction over sulfated ZrO_2–SiO_2 xerogel and aerogel samples

Table 3 Conversion (%) of 4-methyl-2-pentanol dehydration and selectivity (%) for various products over sulfated and non-sulfated ZrO_2–SiO_2 xerogel and aerogel catalysts

Samples	% Conversion	% Selectivity			
		4-Methyl-1-pentene	4-Methyl-2-pentene	C_6 Alkene isomers	4-Methyl-2-pentanone (MIBK)
X-ZSi-1:1	1	55	45	–	–
X- ZSi-1:2	1	51	49	–	–
X- ZSi-2:1	2	60	33	–	7
A-ZSi-1:1	Nil	–	–	–	–
A-ZSi-1:2	Nil	–	–	–	–
A-ZSi-2:1	Nil	–	–	–	–
SX-ZSi-1:1	25	68	–	32	–
SX-ZSi-1:2	8	75	12	13	–
SX-ZSi-2:1	35	67	14	12	7
SA-ZSi-1:1	7	36	15	49	–
SA-ZSi-1:2	4	36	27	32	5
SA-ZSi-2:1	14	42	18	33	7

Reaction conditions Catalyst 0.2 g, reaction temperature = 145 °C under N_2, vaporizer temperature = 150 °C, flow rate = 1 mL/h

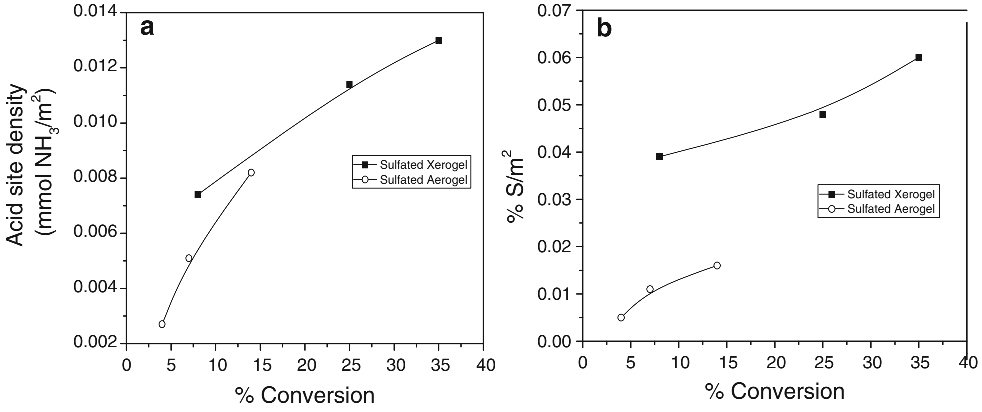

Fig. 4 Correlation of 4-methyl-2-pentanol conversion with **a** acid site density and **b** % S per unit surface area of ZrO_2–SiO_2 sulfated xerogel and aerogel

(Table 3). The xerogel samples showed a very low conversion (1–2%) of 4-methyl-2-pentanol, whereas, aerogel samples did not show any activity for 4-methyl-2-pentanol conversion.

Sulfated samples showed enhanced activity in terms of increased conversion of 4-methyl-2-pentanol (8–35%) and selectivity for 4-methyl-1-pentene (67–75%). Silica rich sulfated xerogel sample (SX-ZSi-1:2) showed the minimum conversion of 8%. The conversion was found to increase from 8 to 35% with increase in Zr content. Sulfated aerogel samples showed lower conversion of 4-methyl-2-pentanol (4–14%) and selectivity for 4-methyl-1-pentene (36–42%) as compared to sulfated xerogel samples. However, sulfated aerogel samples also showed the similar trend of lower conversion with silica rich samples (4%), which increased (7 to 14%) with increasing Zr content, without showing significant effect on the selectivity for 4-methyl-1-pentene (36–42%). 4-methyl-2-pentene (12–14%) and other C_6-alkene isomers (12–32%) along with a little dehydrogenated product i.e., 4-methyl-2-pentanone (7%) were also found with both sulfated xerogel and aerogel samples, however, sulfated aerogel samples showed higher amount of these side products as compared to sulfated xerogel samples (Table 3). The conversion of 4-methyl-2-pentanol increased linearly with increasing the amount of acid sites and sulfur per unit area (Fig. 4). Higher alcohol conversion was observed in xerogels samples compared to aerogel samples due to the presence of higher sulfur and thus higher acid site density in sulfated xerogel samples compared to aerogel samples. These results suggested that higher surface acidity is required to achieve significant conversion of 4-methyl-2-pentanol as well as for higher selectivity for the desired product, i.e., 4-methyl-1-pentene.

It is reported that during secondary alcohol dehydration, alcohol molecule first gets adsorbed on the surface of metal oxide catalysts followed by a two-step mechanism involving intermediate carbocation formation (E1), a concerted pathway (E2) or via carbanion formation mechanism (E1cB), which resulted into the different products such as 1-alkene, 2-alkene etc. [31, 33]. E1cB mechanism favors the formation of 1-alkene (Hofmann projection), while E1 and concerted E2 mechanisms result into 2-alkene (Saytzeff projection) as a major product. The results of the present study showed that sulfated xerogels and aerogels samples formed 4-methyl-1-pentene in the range of 67–75% and 36–42%, respectively. Additionally, the significant formation of 4-methyl-2-pentene (12–27%) and slight formation of 4-methyl-2-pentanone (5–7%) is observed. However, it is difficult to unambiguously comment on the operating mechanism based on the data collected in the present study.

4 Conclusions

Sulfated and non-sulfated ZrO_2–SiO_2 mixed xerogel and aerogel samples having varied Zr/Si molar ratios were evaluated as heterogeneous acid catalysts for solvent free isomerization of α-pinene and dehydration of 4-methyl-2-pentanol. Sulfated samples showed significant enhancement in the catalytic activity for both the reactions studied. Sulfated samples exhibited higher conversion of α-pinene (86–98%) compared to non-sulfated samples; however, the selectivity for camphene and limonene were comparable or slightly lower indicating that the formation of camphene and limonene requires moderate acidity. The results clearly suggested that the acidity of the catalyst and the selectivity for the desired products can be tunable with ZrO_2–SiO_2 mixed oxides as compared to pure metal oxides. The correlation with cyclohexanol dehydration showed that isomerization of α-pinene is a Brønsted acid catalyzed reaction.

For 4-methyl-2-pentanol dehydration, ZrO_2–SiO_2 mixed xerogel and aerogel catalysts resulted into lower conversion (4–35%); sulfated xerogel samples showed higher conversion and selectivity for 4-methyl-1-pentene compared to sulfated aerogel samples. The correlation of 4-methyl-2-pentanol conversion with acid site density and sulfur per unit area was found to be linear, which suggested that higher surface acidity is required to achieve significant conversion of 4-methyl-2-pentanol as well as for higher selectivity for the desired product, i.e., 4-methyl-1-pentene.

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