ISSN : 0974 - 7486 Volume 9 Issue 4

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 9(4), 2013 [144-153]

Synthesis of silica sulphated zirconia binary oxide with improved acidic and textural properties

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ABSTRACT

Solid acid catalyst material has many advantages over homogeneous acid catalysts due to easy separation, reusability and environmental friendliness. The objective of this work is to synthesize non-ionic surfactant-templated, ordered mesoporous silica sulphated zirconia binary oxide with improved acidic and textural properties[1,2]. Attempts have been made to make synthesis methodology more economical by using cheaper raw materials like sodium silicate and zirconium oxy-chloride as source of silica and zirconia respectively[29]. A series of mesoporous SSZ materials were prepared using tri-block co-polymers as template by changing various parameters like the precursors used, the Si:Zr ratio, pH of the gel and the effect of the ageing time. The products were characterized by XRD, TEM, SEM, TPD, FTIR, nitrogen adsorption at liquid nitrogen temperature and by chemical analysis. Acidic properties of selected samples were determined by ammonia TPD technique. The catalytic activity of the prepared SSZ catalysts was evaluated for the synthesis of coumarone by Pechmann Reaction.

KEYWORDS

Homogeneous acid catalysts;
Surfactant templated;
Mesoporous;
Environment friendly;
Textural properties.

INTRODUCTION

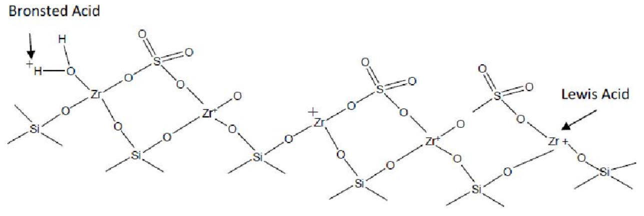
There is huge interest to synthesize an ordered mesoporous silica material of SBA-15 with good hydrothermal stability, large pore size and thick mesoporous walls in strongly acidic medium from triblock polymer surfactant but incorporation of catalytically active heteroatoms into purely siliceous walls is still quite challenging since the synthesis requires strongly acidic medium[1-3].

The amount of sulphate plays a significant role in stabilizing the mesostructure of SBA-15 and tuning the yield of tetragonal zirconia[2-4,14-18]. It is generally accepted that a tetragonal phase is needed for catalytically active samples and sulphated monoclinic zirconia exhibits poor activity in hydrocarbon isomerisation reaction. The final calcination temperature as well has an influence over the acid properties of sulphated zirconia[3,19-22].

Recently, several novel routes have been developed for direct synthesis of Zr-SBA-15 or sulphated Zr-SBA-15[4-7,23-27]. For example, Newalkar et al. reported direct synthesis of Zr-SBA-15 under microwave radiation[4,28], and Cheng et al. illustrated the synthesis of Zr-SBA-15 from zirconium precursor of $ZrOCl_2.8H_2O$ in the absence of HCl[5,29]. In these cases, the loading of Zr in the samples is relatively low, and the molar ratios of Si/Zr were not less than 10. Li et al. have reported direct synthesis of Zr-SBA-15 with extremely high Zr loading (Si/Zr at 0.43–∞), and Zr species in these samples were mainly crystalline ZrO_2 rather than isolated Zr^{4+} species[6]. Chen et al. have prepared sulphated Zr-SBA-15 from zirconium propoxide in the presence of ammonium sulphate[7,30,31] and it was found that the zirconium contents in the samples were strongly influenced by the amount of ammonium sulphate in the starting gel. Notably, the Zr-SBA-15 samples with high content of zirconium species usually gave excellent catalytic properties in esterifications.

Sulphated Zirconia Silica is a very important and a potential solid acid catalyst as both the type of acid sites: Bronsted and Lewis acid sites are present on its surface. The sulphate species are bonded with zirconium atom as bidentate chelating ligand and in presence of water molecule, the sulphate group behaves like ionic sulphate and generates Bronsted acid sites on the surface. Desorption of this water molecule converts ionic sulphate to covalently bonded sulphate group which generate Lewis acid site on zirconium atom. A logical surface structural model is suggested as shown in scheme 1[8,32,33].

Post-synthesis grafting method used for synthesis of sulphated silica zirconia may destroy the mesostructure and block channels. In the present study, we have attempted to synthesize mesoporous sulphated zirconia silica using a direct synthesis method to incorporate zirconia into mesoporous SBA-15 under acidic condition. Studied on effect of source of silica, zirconia and sulphate has been carried out along with the effect of concentration of Zr and $SO_{4,}$ pH, time and temperature of reaction on the final properties of the ssz SBA-15.



Scheme 1 : Proposed surface model and superacidic species

EXPERIMENTAL SECTION

Catalyst preparation

A series of mesoporous SiO_2–SZ material were synthesized by using $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich) as a template. In a typical synthesis 1 g of P123 was dissolved in 30 cc water along with 5.3 cc of 35% wt. HCl. When a clear solution was obtained, 0.3412 g of $(NH_4)_2SO_4$ was added. Then Zirconium propoxide (1.2 cc) and Tetra ethyl orthosilicate (TEOS) (2.3 cc) were added to the above solution. The pH of this solution when measured was found to be less than zero. The reaction mixture was kept at room temperature for 20 hours while stirring. The reaction mixture was transferred to Teflon lined autoclave and kept in oven at 100 ºC for 24 h. Finally, the precipitate was centrifuged from the solution, washed well, dried at 100 ºC for 8 h and was then calcined at 600 ºC for 6 h. The product was designated as ssz 1. Similarly three products ssz 2, ssz 3 and ssz 4 were prepared by changing source of Zr with $ZrOCl_2$, source of Si with sodium silicate (SiO_2 = 28.97 % w/w, Na_2O = 9.16 % w/w, H_2O = 61.87 % w/w) and source of sulphate as sulphuric acid respectively as shown in TABLE 1.

Further synthesis were carried out by keeping all the synthetic parameters same as that in ssz 4 except that for Zr/Si molar ratio, and was named as ssz 5a (Zr/Si = 0.67), ssz 5b (Zr/Si = 1). The effect of pH on the composition and properties of final products was studied by adjusting the pH of the gel with ammonia solution to pH 2 (ssz 61) and 2.2 (ssz 64). In ssz 71 all parameters were same as that of ssz 61, except for the amount of water that is used during synthesis. While in ssz 61, the total water used was 9500 mmole (171 ml), water used during synthesis of ssz 71 was 11167 mmole (201 ml).

Catalytic reaction

Sulphated silica zirconia was employed as catalyst for Pechmann reaction to obtain coumarone. For the reaction 5 mmol resorcinol and 10 mmol EAA were heated for 4 h. at 160 ºC using 10 wt% catalyst. The main product obtained was 7-Hydroxy-4-methyl coumarone. To the reaction mixture 72 µl of hexadecane was added as an internal standard. Small amounts of the reaction mixture was collected and submitted for

GCMS. After the reaction was over 15-20 cc of methanol was added and the crude product was dissolved in it. The catalyst was separated by centrifuge and the supernatant liquid was characterized by GCMS.

RESULTS AND DISCUSSIONS

EDX analysis was carried out to know the chemical composition of the surface of the samples. Bulk chemical analysis of the samples was carried out by digestion of the sample in HF followed by wet chemical analysis for Zr and SO_4 by gravimetric analysis as ZrO_2 and $BaSO_4$ respectively. S was also analyzed by ICPES (inductively coupled plasma emission spectroscopy) using Perkin Elmer Instruments, optima 2000 DV to know the bulk sulphur content. In TABLE 1 the condition and composition of the gel and product and the effect of precursors, pH of gel, different input of zirconia on the composition of the catalyst is presented.

TABLE 1 : Experimental conditions, composition of gels and products analyzed by EDX and wet chemical analysis.

Sample (ssz)	Sources & quantity				SiO_2+ ZrO_2+ SO_4^{2-}		% Loss	Zr/Si (M/M)			pH of gel	$SO_4^{2-/}$/Zr(M/M)			S wt% SiO_2 ICP
	SiO_2 ICP Mmol	ZrO_2 Mmol	SO_4^{2-} mmol	Water (mmol)	Total Input (g)	Total Output (g)		Gel	Product			Gel	Product		
									EDX	Chemical analysis			EDX	Chemical analysis	
1	TEOS 10.3	$Zr(OPr)_4$ 2.576	$(NH_4)_2SO_4$ 2.576	1670	1.827	-	-	0.25	0.013	0.148	0	1	0	0	-
2	TEOS 51.5	$ZrOCl_2$ 12.88	$(NH_4)_2SO_4$ 12.88	8300	5.913	3.8168	35.46	0.25	0.03	0.035	0	1	0	0	-
3	Na_2SiO_3 51.5	$ZrOCl_2$ 12.88	$(NH_4)_2SO_4$ 12.88	7860	5.913	2.507	57.61	0.25	0.015	0.05	0	1	0	0	1.3
4	Na_2SiO_3 51.5	$ZrOCl_2$ 12.88	H_2SO_4 12.88	7860	5.913	2.82	52.31	0.25	0.03	0.07	0	1	0	0	1.6
5a	Na_2SiO_3 51.5	$ZrOCl_2$ 34.3	H_2SO_4 34.3	7680	10.61	4.44	58.13	0.66	0.075	0.16	0	1	0.06	0.24	4.02
5b	Na_2SiO_3 51.5	$ZrOCl_2$ 51.5	H_2SO_4 51.5	7560	14.38	5.165	64	1	0.08	0.28	0	1	0.07	0.39	5.4
61	Na_2SiO_3 51.5	$ZrOCl_2$ 12.88	H_2SO_4 18.632	9500	6.466	4.53	23.34	0.25	0.21	0.24	2	1.45	0.04	0.07	1.32
64	Na_2SiO_3 51.5	$ZrOCl_2$ 12.88	H_2SO_4 18.632	9500	6.466	-	-	0.25	0.15	0.23	2.2	1.45	0.05	0	-
71	Na_2SiO_3 51.5	$ZrOCl_2$ 12.88	H_2SO_4 18.632	11167	6.466	4.84	25.19	0.25	0.13	0.21	2	1.45	0.02	0	-

In ssz 1, ssz 2, ssz 3, ssz 4, various precursors were altered in order to see if there is any change in the incorporation of zirconia and sulphur. It was observed that when TEOS in ssz 2 was replaced by Na_2SiO_3 in ssz 3, chemical analysis results revealed that there was an improvement in the Zr/Si ratio (TABLE 1). Similar observation was noticed in EDX report when $Zr(OPr)_4$ in ssz-1 was replaced by $ZrOCl_2$ in ssz 2. This was also very well proved that sulphuric acid is a better sulphating agent than ammonium sulphate as when $(NH_4)_2SO_4$ in ssz 3 was replaced by H_2SO_4 in ssz 4, the sulphur content improved from 1.3 wt% to 1.6 wt% as observed in ICP (TABLE 1).

It can be observed from the results of TABLE 1 that with an increase in pH of the gel from 0 to 2, the Zr/Si ratio in the product increased though the initial ratio in gel of sample ssz 61, 64 and 71 is less than that of ssz 1 to 5b. This effect is also reflected in the results of the material balance. (TABLE 1; column of % wt loss) This may be attributed to a very low pH condition of the gel of samples prepared without adjusting the pH with ammonia solution. Due to incomplete hydrolysis of zirconia, at low pH condition there appeared lower zirconia content in ssz1 to ssz 4.

It was also observed from the results of TABLE 1 that with the increase in Zr/Si ratio in the gel from 0.25 to 1 the Zr/Si ratio in the product increased. It can also be seen from the results that change in SO_4 content of the product is associated with Zr content. Results of TABLE 1 indicate that there is a relation between the sulphate in the product and the water content of the gel. In the case of ssz 1 and ssz 2 sulphate was not detected by any methods of analysis, while in ssz 3 and ssz 4 sulphur could be detected by ICP.

In samples ssz1 to ssz 5b prepared under similar pH conditions, it was observed that as the sulphur content in the product increased from 1.3 to 5.4 wt % (ICP), the Zr/Si ratio in the product also improved from 0.05 to 0.28 (chemical analysis). EDX results also showed similar trends. This is due to the fact that under strong acidic conditions, the zirconium centre exists in the cationic form. This may form a polyoxo ion with the sulphate which then interacts strongly with the silicate species in the solution. Thus the greater sulphur content in the product, better is the zirconia loading in the sample.

The sulphated zirconia silica (ssz) samples were characterized by powder X-ray diffraction analysis for the phase identification and determination of crystalline size of zirconia/sulphated zirconia using X'pert MPD system, Philips, Holland. It is desirable to have homogeneous mixing of Zr in silica structure for the generation of surface acid sites. According to the hypothesis of Tanabe and co-workers[9] the acidic properties of mixed metal oxide is associated with the "charge imbalance" that develops due to heterolinkage (M-O-M') whereas in this work in case of Zr-O-Si it is due to the mismatch in coordination number. In order to have better acidic properties the Zr atoms should be well dispersed at atomic level in this mixed-oxide material. When incorporation of Zr increases, phase separation is expected to occur and that is reflected in the PXRD pattern as crystalline zirconia. The degree of dispersion of the zirconia can be explained in terms of crystallite size of the crystalline phase of the Zirconia. Smaller the crystallite size better the dispersion and hence the acidic properties. If the crystalline phase is absent the dispersion of the Zr is very high[9].

The crystalline phase formed and crystallinity of ssz after calcinations at 600 ºC was measured by X ray powder diffractometer using Cu K-alpha radiation (λ=1.540598 Å). The samples were scanned in 2θ range of 20º - 80º. Crystallite size of tetragonal phase was determined from the characteristic peak ($2\theta = 30º$) for the (111) reflection by using Scherrer formula with a shape factor (K) of 0.9 as below,

Crystallite size = $K\lambda/W \cos\theta$

Where $W=W_b - W_s$; W_b is the broadened profile width of the experimental sample and W_s is the standard profile width of reference silicon sample. W_b is the FWHM (full width at half maxima) of the broadened diffraction line on the 2θ scale. All diffraction lines have a measurable width, even when the crystallite size exceeds 1000 Å due to divergence of incident beam, size of the sample or width of the X-ray source. However, the W_b refers to the extra width or broadening, due to the crystallite size alone. In other words, W_b is essentially zero when crystallite size exceeds 1000 Å. The width of the diffraction curve increases as the thickness of the crystal decreases i.e. the crystallite size decreases[10-12].

Powder X-ray diffraction patterns of the ssz samples along with pure sulphated zirconia (sz 125 and sz 75) are depicted in Figure 1. The wide angle XRD patterns show three prominent peaks at 2θ ~30º, ~50º and ~60° which correspond to the 111, 220, 311 reflections respectively of tetragonal crystalline zirconia phase. A small hump at 35° corresponds to 200 reflection of monoclinic phase of zirconia[11,12]. Pure sulphated zirconia having two different Zr/SO_4 ratio (Zr/SO_4 = 1/0.75 and 1/1.25) were found to be highly crystalline materials with very intense characteristic peaks of tetragonal zirconia phase. In the case of sulphated zirconia silica samples it is observed that as the concentration of zirconia increases the crystallinity of the sample increases. This is also evident from the results of the peak intensity of the 111 plane of tetragonal phase depicted in TABLE 2. As the FWHM decreases from ssz 3 to ssz 5a, the crystallite size increases. XRD pattern (Figure 1) of ssz 3 with only 0.19% Zr (atom%) the material was found to be almost amorphous as no diffraction lines were observed which signifies that zirconia is distributed uniformly within the structure with little phase separation. This further indicates that for catalyst with Zr content > 0.19% phase separation of zirconia occurs and zirconia crystals were formed. The characteristic broad peak of amorphous silica in the 2θ range of 20° - 30º was observed in all the samples except samples sz 125 and sz 75.

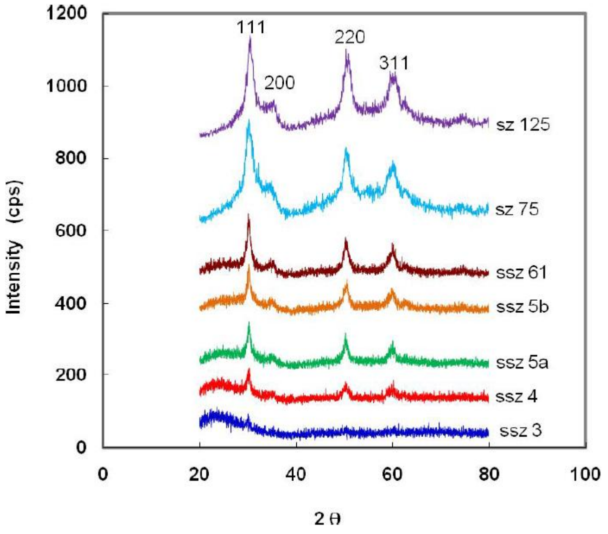


Figure 1 : PXRD pattern of mesoporous sulphated zirconia silica materials with various Zr loading in wide-angle region.

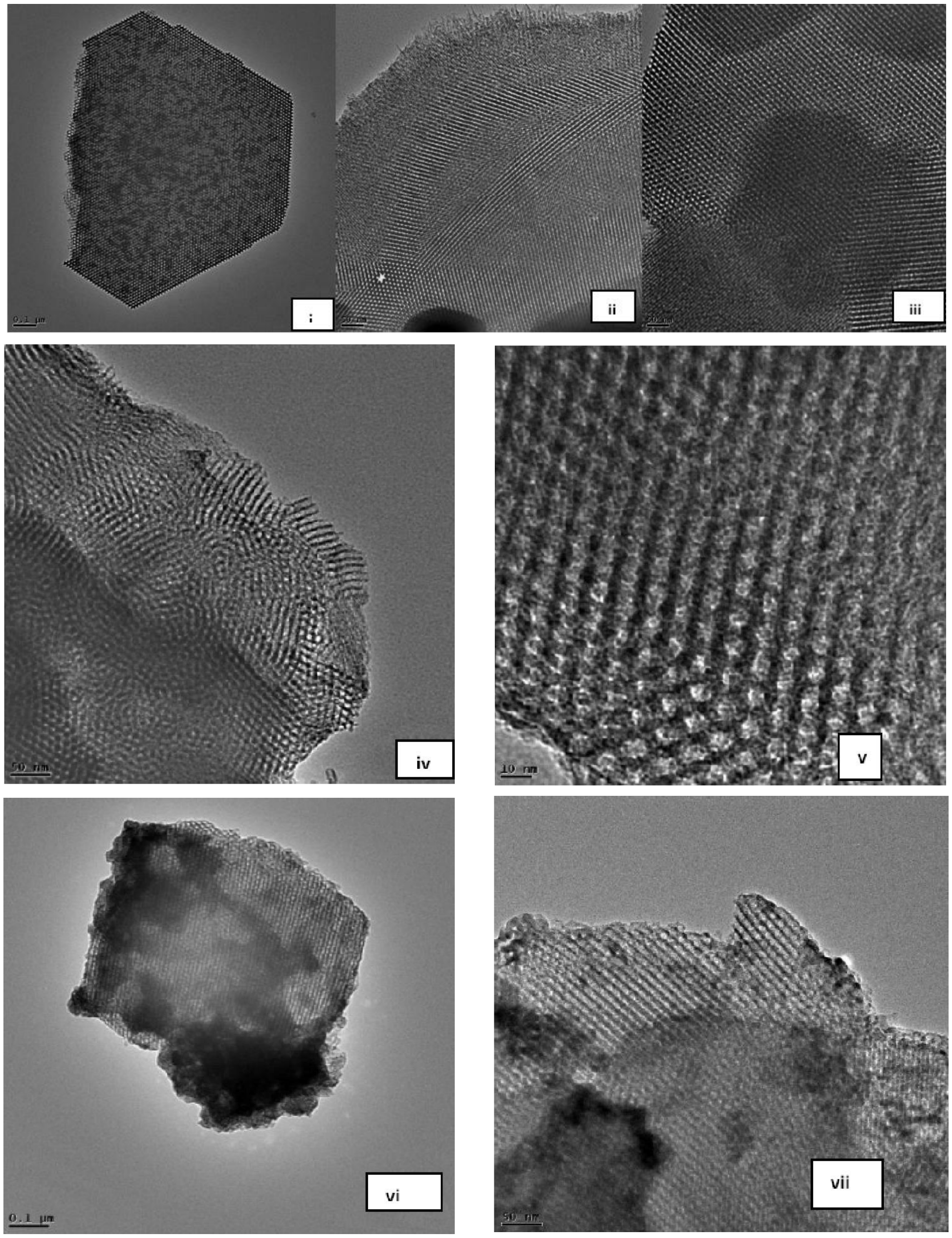


Figure 2 : TEM images of samples ssz 3 (i, ii), ssz 4(iii), ssz 5a (iv, v), ssz 61(vi, vii).

TABLE 2 : Effect of Zr content on the crystallinity and crystallinte size of the zirconia in silica sulfated zirconia binary system.

Sample no. (ssz)	Zr (atom%) Product		Intensity of 111 Peak At 2θ = 30o (cps)	FWHM	Crystallite Size(Å)
	EDX	Chem. analysis			
3	0.45	0.19	21.7	0.945	97
4	0.94	0.23	121.2	0.315	385
5a	1.89	0.44	141.3	0.236	609
5b	2.15	0.57	163.1	0.472	222
61	5.08	0.59	239.3	0.315	384

Transmission electron microscopy (TEM) graphs were recorded on JEM-2100 electron microscope and atomic mapping of some of the samples were carried out. From TEM studies we have interpreted the following things; Figure 2 shows the TEM images of mesoporous sulphated zirconia silica with Zr loading ranging from 0.19 to 0.59 atom %. Notably these samples exhibit highly ordered hexagonal array of mesopores with uniform pore size. As observed in Figure 2 (i and ii) since there is no separated phase high dispersion of Zirconia on the mesoporous bed is indicated. However in Figure 2 (iii, vi and vii) the phase separation is very prominently visible. These results show that sample having ~ 0.2 atom % loading (ssz 3) has highly dispersed zirconia with very high ordered mesoporous structure. On the other hand, ssz 4 (Figure iii), ssz 5a (Figure iv), ssz 61 (Figure vi) where Zr loading are 0.23, 0.44, 0.57 atom % respectively the phase separation becomes prominent with increasing Zr loading. This reveals that these three samples possess sulphated bulk zirconia. Thus there is a maximum limit of loading of zirconia upto which there will be no phase separation; however beyond this phase separation occurs. In this case this is found to be ~ 0.2 atom % of Zr. These results are in agreement with our XRD report.

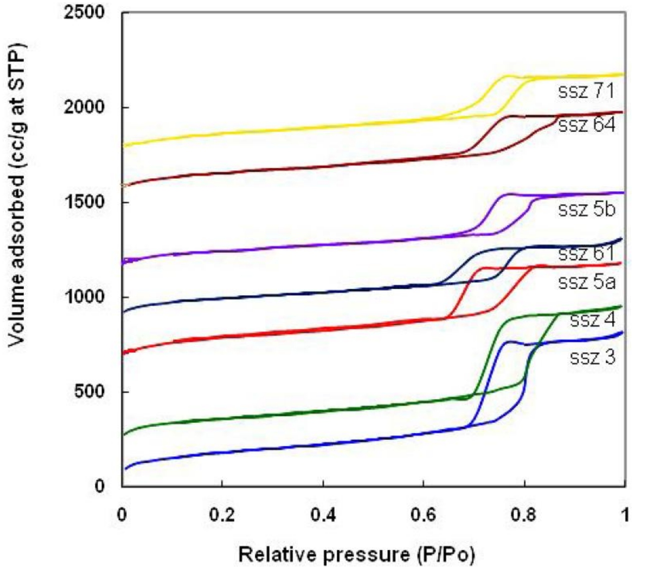


Figure 3 : Adsorption-desorption isotherms of different mesoporous sulphated zirconia silica catalyst.

Nitrogen adsorption-desorption isotherms of the selected samples were recorded at liquid nitrogen temperature (77 K) using ASAP 2010, Micromeritics, USA. From Nitrogen adsorption isotherms we have determined the surface area and porosity of the samples and also studied the effect of water on textual properties of the catalyst.

N_2 adsorption–desorption isotherms of sulphated zirconia silica samples synthesized by hydrothermal method, calcined at 600 °C shows the isotherm of type IV with H1 type hysteresis loop for all the samples as shown in Figure 4, which is characteristic of mesoporous adsorbents with narrow pore size distribution. In all the isotherms a sudden jump in the adsorption has been observed at about 0.75 relative pressure (p/p_0) indicating capillary condensation of the adsorbent in the pores of the samples[13].

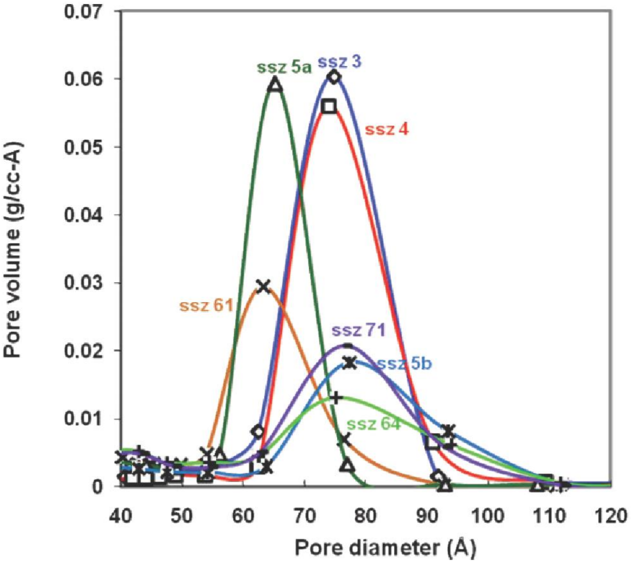


Figure 4 : BJH desorption pore size distribution of sulphated zirconia silica samples.

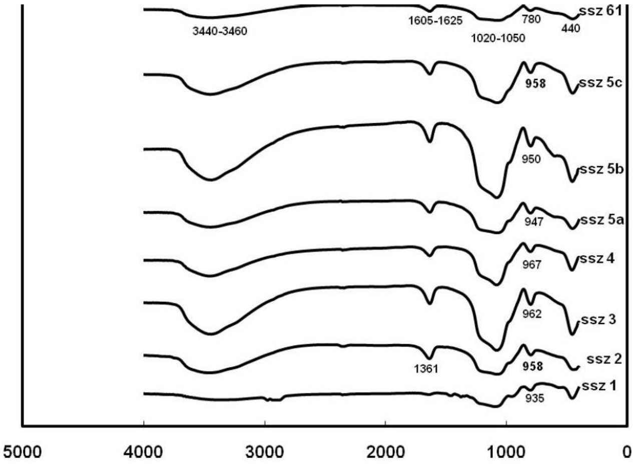


Figure 5 : FTIR spectra of sulphated zirconia silica samples.

On increasing the Zr/Si mole ratio above 0.16, decrease in the surface area of the product was observed. However, unusual results have been obtained for the surface area of the sample ssz 4. Except samples 1, 2 and 3 all the other samples were prepared using H_2SO_4 (TABLE 1). Figure 5 shows the desorption/adsorption pore size distribution of various catalysts prepared. The narrow pore size distribution of ssz 3 indicates its highly ordered mesostructure. As the zirconia content increases, the pore size distribution also gets broadened. This is again in agreement with the XRD pattern and TEM images from which we concluded that the increase in zirconia content reduces the uniformity of the structure. In TABLE 4 effect of the addition of water on the textual properties of the catalyst i.e. its surface area has been demonstrated.

TABLE 3 : Textural properties of silica sulfated zirconia samples.

Sample no. (ssz)	Zr/Si (M/M)	Surface Area (m$_2$/g)	Pore volume (cc/g)	BJH Pore Diameter (Å) Desorption branch
3	0.05	650	1.26	75
4	0.07	578	1.16	74
5a	0.16	649	0.88	65
5b	0.28	512	0.69	63
61	0.24	509	0.71	77
64	0.23	553.89	0.73	75
71	0.21	577.68	0.72	77

TABLE 4 : Effect of water on the textural property of catalyst.

Sample no. (ssz)	Amount of water added (mmol)	Surface area m$_2$/g
4	7860	578.09
61	9500	512.18
71	11167	577.67

TABLE 5 : The observed and reported IR peaks of silica sulfated zirconia samples.

Reported peak (cm -1)	Observed peak (cm -1)	Nature of the bond/ species present
460	440	O-Si-O bending
815	780	Symmetric Si-O-Si stretching
960	935-967	Silanol bond (which is a measure of the homogeneity of ZrO2 -SiO2)
1000-1024	1020-1050	Antisymmetric Si-O-Si stretching
1380	1361	Presence of sulphate species
1631-1635	1605-1625	-OH bending mode of H2O
3400	3440-3460	-OH stretching mode of H2O

FTIR spectra were recorded on Perkin Elmer GX (USA), spectrophotometer. Figure 6 shows the IR spectra of different mesoporous sulphated zirconia silica samples with varying Zr/Si ratio. TABLE 5 illustrates the peaks corresponding to the bonds present in the sample. The peak ranging between 935-967 cm^{-1} corresponds to the silanol bond, which is a key signal in measuring the homogeneity of SiO_2-ZrO_2 mixed-oxides[31]. The interaction between silica and zirconia would lead to the decrease in the band intensity at the given wave number range of the silica zirconia material[32]. A band is observed ~ 935-967 cm^{-1} and the intensity of this band is significantly reduced for the series of sulphated zirconia silica. These results provide additional evidence for the interaction between silica & zirconia.

Scanning electron microscopy (LEO 1430 VP) of the samples was conducted to study the particle morphology of the samples. Figure 6 describes the SEM morphologies of various sulphated zirconia silica samples. It was noticed that the SEM morphologies were highly dependent on the different synthetic parameters used. In all the SEM images the hexagonal pattern was quite visible. Although in ssz 1 a circular morphology was obtained, as soon as the source of zirconia was changed from zirconium propoxide in ssz 1 to Zirconium oxychloride in ssz 2, ssz 3 and ssz 4, the hexagonal morphology along with capsule type rapid clustering was observed.

ACIDITY MEASUREMENT BY TPD & CATALYTIC ACTIVITY

Samples ssz 3, ssz 4, ssz 5a and ssz 61 were used as catalyst in the synthesis of coumarone via Pechmann reaction. TABLE 6 highlights the conversion and selectivity of the various catalysts. In ssz 4 and ssz 6 the conversion is found to be comparatively lower than ssz 3 and ssz 5a. But selectivity of ssz 5a is poor in comparison to the rest of the three. Thus ssz 3 appears to be a better catalyst than others in terms of catalytic activity as its selectivity and conversion capability are very high. This difference is due to the phase separation that has occurred in ssz 4, ssz 5a and ssz 61 as seen from XRD. Due to the phase separation, number of effective active sites might have been reduced for catalytic reaction. But in ssz 3 as evident from TEM & XRD there is an even distribution of zirconia which results in greater number of active sites on the surface for catalytic reaction.

The TPD measurement of both the ssz 3 and ssz 61 samples produce three peaks each as shown in TABLE 7. These correspond to weak acidity in the low temperature range, strong acidity in the medium temperature range and very strong acidity in the higher temperature range. The sample ssz 3 is found to have the first two peaks very remarkably compared to the third region. The quantity of ammonia desorbed in the low and medium temperature range in the sample ssz 3

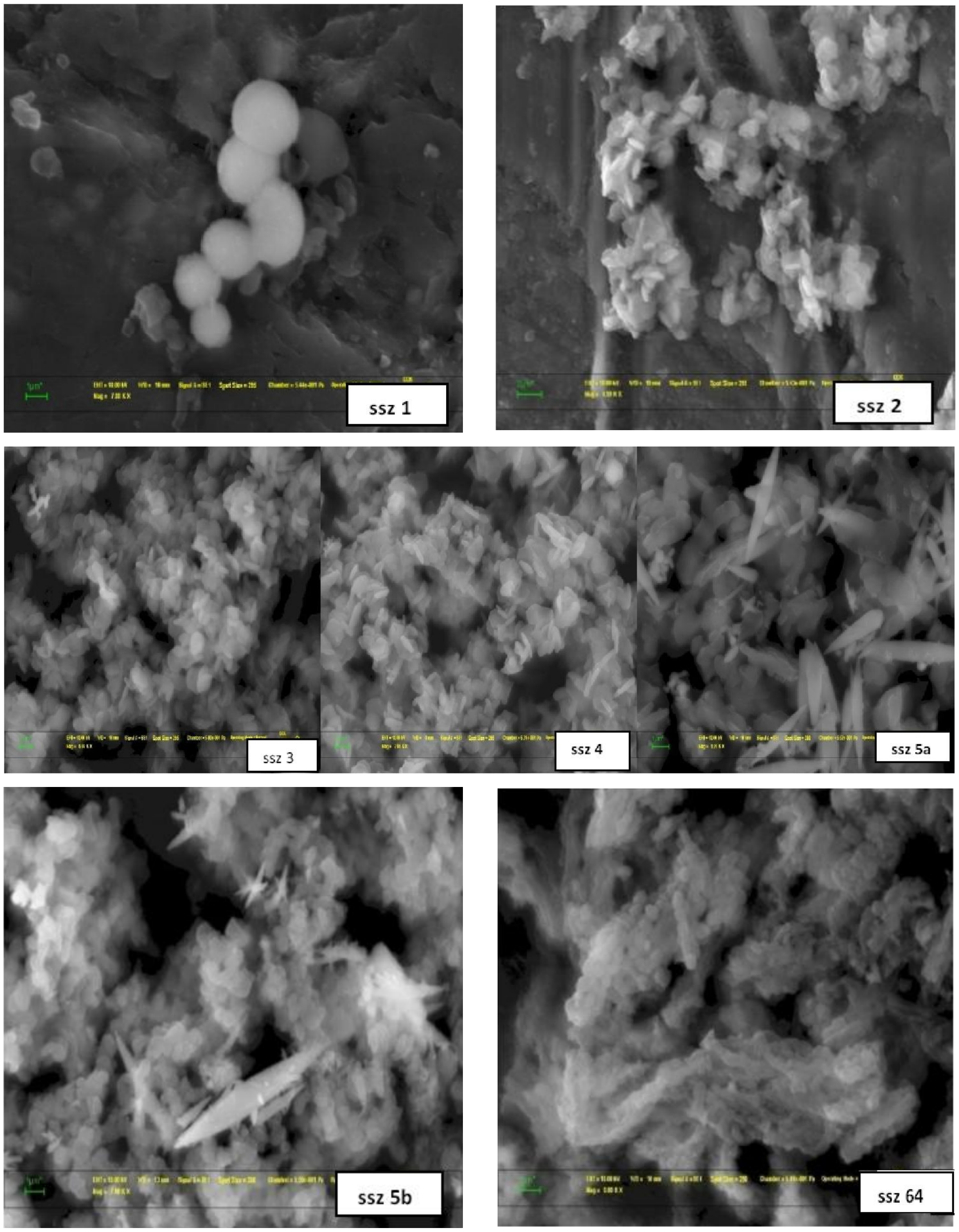


Figure 6 : Morphologies of sulphated silica zirconia synthesized in solutions with different precursors, different ageing time and different Zr/Si ratio.

TABLE 6 : Physical parameters and catalytic activities in Pechmann reaction for different silica sulfated zirconia catalyst.

Sample no.(ssz)	% conversion	%selectivity	Zr/Si	S/Zr
3	94.31	98.6	0.05	0
4	88.59	94.56	0.07	0
5a	98.25	88.46	0.16	0.06
61	85.55	96.21	0.28	0.04

TABLE 7 : TPD results of SSZ samples.

Sample No. (ssz)	Peak No.	Max at Temp. (°C)	Quantity of NH3 desorbed (mmol/g)	Peak concentration (%)
3	1	187.7	0.43943	0.24
	2	630.1	0.40061	0.15
	3	997.4	0.00353	0.02
61	1	196.5	0.68016	0.50
	2	628.2	0.11459	0.14
	3	816.9	0.23328	0.29

is almost same due to the very uniform distribution of zirconia in this sample. In the higher temperature range ammonia is almost negligibly desorbed. This signifies that it exhibits poor acidity at the higher temperature due to presence of negligible amount of sulphate. But ssz 61 demonstrates handsomely high acidity in the high temperature range due to the presence of appreciable amount of sulphate in it.

When the Zr/Si ratio was changed from 0.25 (in ssz 1 to ssz 4) to 0.67 and 1.0 in ssz 5a & ssz 5b respectively, needle shaped clusters along with hexagonal clusters were observed. Further with the increased ageing time in ssz 64 (48 hours) as compared to all the other samples (24 hours), hexagonal/circular pattern arranged in a chain like form resulted.

CONCLUSION

In the present work non-ionic surfactant templated, ordered mesoporous silica sulphated zirconia binary oxide with improved acidic and textural properties has been synthesized. Mesoporous SSZ materials were prepared using tri-block co-polymers as template by changing various parameters like the precursors used, different Si:Zr ratio, pH of the gel and the effect of ageing time. The prepared materials show successful catalytic activity which is utilized for the synthesis of coumarone by Pechmann Reaction. The results of X-ray diffraction analysis and atomic mapping of Zr during TEM analysis revealed that homogeneous distribution of zirconia in SSZ SBA-15 mesoporous material was obtained when ZrO_2 content was less than 10 wt %. When ZrO_2 content was made higher than 10 % in SSZ catalyst, phase separation of zirconia was observed. The TEM images showed the presence of ordered hexagonal mesostructure. Results of N_2 adsorption exhibited typical type IV isotherm and uniform pore distribution. The Si/Zr ratio was found to be almost similar in the precursor gel and in the final product when pH of the solution was increased. The ageing time and Si/Zr ratio in the gel had a profound influence on the morphology of the catalyst as manifested by the SEM images. Ammonia TPD results showed desorption peaks at 628 ºC, 817 ºC and 997 ºC indicating the presence of very strong acidic sites. The catalytic activity of the prepared SSZ catalysts was evaluated through the synthesis of coumarone by Pechmann Reaction.

ACKNOWLEDGEMENT

The financial support from CSIR, India is gratefully acknowledged. Authors are sincerely thankful to Indian School of Mines, Dhanbad and CSMCRI, Bhavnagar for instrumental facility and guidance.

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