Summary and Conclusions
Acid catalysis is an important area in organic synthesis and is of fundamental industrial importance. The acid catalyzed reactions are largely carried out by using homogeneous liquid acids like HF, H$_2$SO$_4$, AlCl$_3$ and FeCl$_3$ etc. These homogeneous catalysts, however, have some disadvantages such as they are required in more than stoichiometric amount to attain maximum conversion, corrosive to reaction system and a very careful handling is required, not recoverable from reaction mixture and thus not reusable. After reaction, either they form complex molecule with product or they are highly soluble in reaction mixture resulting into the hazardous waste influent. This also leads to the formation of hazardous inorganic acids as by-products. The disadvantages of homogeneous catalysts, environmental restrictions and requirement of non-polluting, atom-efficient and economic catalytic process inspired the need to find the alternative of the liquid acids.

Solid acids were found to be alternative to the homogeneous acids as they are non-corrosive, required in small catalytic amount, easy to separate, reuse and eco-friendly. Solid acid catalysts such as transition metal oxides when treated with sulfuric acid showed enhanced acidity than their pure oxides. Among the various transition metal oxides Sulfated Zirconia is a well-known solid super acid (-H$_0$ = 16.1) having both Bronsted as well as the Lewis acid sites (Figure 1) on its surface. The sulfate species are bonded with zirconium atom as bidentate chelating ligand and in presence of water molecule the sulfate group behaves like ionic sulfate and generates Bronsted acid sites on the surface. The desorption of water molecule converts the ionic sulfate to covalently bonded sulfate group, which generates Lewis acid sites on zirconium atom by reducing the electronic density at zirconium atom. The required site can be predominantly populated by changing the reaction conditions, so it is capable to conduct both Bronsted and Lewis acid catalyzed reactions.

![Figure 1. The Bronsted and Lewis sites on the surface of the sulfated-zirconia.](image-url)
Furthermore, nano-crystalline materials have improved catalytic activity because of large surface-to-volume ratio and also more corners and edges, which provides increased number of active sites available for a catalytic reaction.

Therefore, in view of above, the present thesis is focused on the synthesis and characterization of nano-crystalline sulfated-zirconia solid acid catalyst and its catalytic application for various organic transformations such as benzylation, acylation, isomerization and Pechmann reaction. The work done in the present thesis is summarized as below:

Nano-crystalline sulfated-zirconia solid acid catalyst was synthesized using one-step and two-step sol-gel techniques using zirconium propoxide as a precursor, water and/or aqueous ammonia as hydrolyzing agent and concentrated H$_2$SO$_4$ (1N) as sulfating agent. A number of samples have been synthesized with varying synthetic parameters such as concentration of precursor, mode of physical perturbation, drying temperature, the way of addition of sulfuric acid in alkoxide solution, water to alkoxide molar ratio, pH of the synthesis medium during hydrolysis and calcination temperature. The effect of various synthetic parameters was correlated with the structural, textural and catalytic properties of sulfated-zirconia catalysts.

The samples were characterized by X-ray Powder Diffraction study, FT-IR Spectroscopy, DRIFT study, FT-IR study of the samples adsorbed with pyridine, N$_2$ adsorption-desorption isotherm study, CHNS/O elemental analyzer and ICP (Inductive Couple Plasma) for Sulfur Analysis. The identification of crystalline phase and the measurement of the crystallite size of the phase in sulfated-zirconia samples were carried out by X-ray Powder Diffraction study using Scherrer formula. The nature of surface sulfates in the samples was studied by FT-IR spectroscopic study. The Lewis acidity in the samples was quantified by DRIFT study and the Bronsted and Lewis acidity were measured by FT-IR study of the samples adsorbed with pyridine at different temperatures from 150 to 450 ºC. The textural properties such as surface area, pore volume, pore size and pore size distribution of the sulfated-zirconia samples were characterized by N$_2$ adsorption-desorption isotherm study at liquid nitrogen temperature (77K). The Bronsted acidity of the samples was also assessed by dehydration of cyclohexanol to cyclohexene as a model test reaction. The catalytic evaluation of the sulfated-zirconia samples was
done for various acid catalyzed organic transformations such as benzylolation, acylation, isomerization and Pechmann reaction.

Both one step as well as two-step sol-gel techniques were found to be an appropriate route to synthesize nano-crystalline zirconia and sulfated-zirconia having crystallite size in range of 10-17 nm having predominantly tetragonal crystalline phase.

During the two-step sol-gel technique the zirconium hydroxide gel formed after the hydrolysis and condensation of zirconium propoxide precursor and dried at 110 ºC was found to be amorphous in nature. The crystallinity was developed on thermal treatment at higher temperatures. The zirconia gel, after calcination at 400 ºC, was observed to be crystalline having purely tetragonal phase and crystallite size of 13 nm. Calcination at higher temperatures results into the transformation of tetragonal to monoclinic crystalline phase and also increase in the crystallite size of tetragonal phase. The crystallite size of tetragonal phase of pure zirconia samples (ZrO₂) increases progressively from 13 to 23 nm with an increase in calcination temperature (400-600 ºC), which shows the sintering of zirconia crystallites with temperature forming larger crystallites. The monoclinic phase gradually increased from 4 to 29% with an increase in the calcination temperature from 450 to 600 ºC. The transformation of tetragonal to monoclinic phase occurs due to the loss of hydroxyl groups by the dehydroxylation.

The sulfated zirconium hydroxide sample, calcined at 450 ºC, was amorphous. The samples, calcined at 500 ºC, were crystalline and had predominantly the tetragonal phase. With increase of calcination temperature, the monoclinic phase started to increase. In sulfated-zirconia, crystallization of an amorphous sample to a crystalline phase occurs at higher temperature (450 ºC) than that of pure sample (400 ºC). The reason of increase in crystallization temperature in sulfated-zirconia samples is the presence of SO₄⁻ ions, which requires higher thermal energy for the removal of hydroxyl groups for dehydroxylation during crystallization. Dehydroxylation of the amorphous phase at 500 ºC generated mainly tetragonal zirconia. The transformation of tetragonal to monoclinic phase in sulfated-zirconia samples has been found at higher temperature, which is attributed to the presence of sulfate groups resisting the dehydroxylation of the sample.

The effect of synthetic parameters such as physical perturbation during the hydrolysis and condensation of the precursor and drying temperature for the gel showed
remarkable effect on the formation of crystalline phase and crystallinity of the phase. The sulfated-zirconia samples, prepared using sonication, shows the presence of predominantly tetragonal phase even after calcination at 600 °C. While, at same calcination temperature (600 °C), the samples prepared using magnetic stirring, shows monoclinic phase also (22 %) along with tetragonal phase. The higher thermal stability of the tetragonal phase in samples prepared using ultrasonication as compared to conventional stirring probably is due to higher loading and proper dispersion of sulfate ions on zirconium oxide surface during ultrasonication, which is also confirmed by a higher sulfur content retained (0.78- 1.91 wt.%) in these samples. The duration of ultrasonication was also found to be affecting the sulfur loading. In the samples, prepared by ultrasonication, the retained sulfur after calcination increased from 0.78 to 1.77 wt.% with increasing the ultrasonication time from 30 to 120 min keeping other conditions same.

Effect of drying temperature of gel, before calcination, was also found to be affecting the calcination temperature and formation of phase. The samples initially dried, before calcination, at 80 or 110 °C have only tetragonal phase after calcination at 600 °C, whereas the sample initially dried at room temperature, showed predominantly a monoclinic phase (89 %) after calcination at 600 °C. The drying of gel at room temperature could not remove the solvent (n-propanol) completely, which is present with precursor and also formed during the hydrolysis of the alkoxide. The presence of n-propanol filled inside the gel pores affected sulfate loading, as sulfate ions could not go inside the pores during the sulfation process and therefore, forms the monoclinic phase at lower calcination temperature.

The surface sulfates species in the prepared sulfated-zirconia samples were found to be present as inorganic chelating bidentate sulfate groups on the surface of zirconia. The presence of water molecules adsorbed...
Chapter 6

with surface sulfates by hydrogen bonding gives the ionic form (I). The desorption of
water molecule converts the ionic sulfate to covalently bonded sulfate having S=O double
bonds, which is evident from the presence of a weak to medium band at around 1401 cm
\(^{-1}\), attributed to asymmetric stretching (\(\nu_{S=O}\)) of S=O double bond. This structure (II) is
responsible for the formation of the Lewis acid sites on the surface by attracting the
electron density from the zirconium atom (Scheme 1). The peak area of the \(\nu_{S=O}\) band
(-1400 cm\(^{-1}\)) was used to quantify the amount of Lewis acidity of the sample, which
gradually increases on in-situ heating from 150 °C to 450 °C and shows the sensitivity of
sulfated-zirconia samples towards moisture.

The total sulfur content was correlated with covalently bonded sulfur, which
represents Lewis acid sites and quantified by peak area of the \(\nu_{S=O}\) band, which shows
that the samples having < 1.0 wt.% sulfur content (< 0.8 S atoms/ \(\text{nm}^2\)) have higher
Lewis acid sites, whereas the samples with 1.0- 2.0 wt.% or > 2.0 wt.% sulfur content (> 0.8 S atoms/ \(\text{nm}^2\)) have less Lewis acid sites and higher Bronsted acid sites.

The catalytic activity of the sulfated zirconia samples was tested by carrying out
the benzylation of toluene with benzyl chloride in liquid phase batch reactor taking
toluene and benzyl chloride in 1:1 molar ratio, substrate to catalyst weight ratio of 10 at
450 °C for 2 h. The sample, synthesized by ultrasonication method showed higher
catalytic activity giving maximum conversion of toluene (68 %) after 4 h with 100 %
selectivity of the \(p\)-benzyl toluene. The higher catalytic activity of the sample is attributed
to higher sulfur content (1.91 wt.% or 1.4 S atoms/ \(\text{nm}^2\)) in the sample, which results to
higher Bronsted acid sites. However, the concentration of the precursor used for the
synthesis of sulfated-zirconia, was also observed to be affecting the activity of the
samples. The samples, synthesized by using higher concentration (70 wt.%) of the
precursor showed higher activity (61- 68 %) in comparison to samples prepared by using
a lower (10 wt.%) concentration of the precursor (17- 53 % conversion). The catalytic
activity of the sulfated zirconia samples increases with increasing total sulfur content of
the sample, which is attributed to the increase in Bronsted acidity.

During the one-step sol-gel technique the synthetic parameters such as the way
of addition of sulfuric acid in alkoxide, water to alkoxide molar ratio, and calcination
temperature were observed to influence the physicochemical and catalytic properties of the sulfated-zirconia catalysts.

By one-step sol-gel method, three samples were synthesized. One sample (SZO1) was synthesized by adding sulfuric acid and water mixture (water to alkoxide molar ratio = 4) to zirconium propoxide precursor to hydrolyze the zirconium propoxide to zirconium hydroxide. The gel was dried and calcined at 600 ºC for 2 h in static air atmosphere. The second sample (SZO2) was synthesized by adding concentrated sulfuric acid in zirconium propoxide followed by addition of distilled water (water to alkoxide molar ratio = 4) to hydrolyze the zirconium propoxide to zirconium hydroxide. The gel was dried and calcined at 600 ºC for 2 h in static air atmosphere. The third sample (SZO2-600) was synthesized by following the similar procedure as used for the synthesis of second sample, however, by using lesser quantity of water (water to alkoxide molar ratio = 2.7) just sufficient to form the gel. The sample was further calcined at higher temperatures of 700 and 800 ºC for 2 h in static air atmosphere to study the effect of calcination temperature on the structural, textural and catalytic properties of the sample.

The X-Ray Diffraction study of sulfated-zirconia samples calcined at 600 ºC show the presence of purely tetragonal crystalline phase in all samples. The sample (SZO2-600) was observed to be less crystalline after calcination at 600 ºC and the crystallinity of the sample increases with increasing the calcination temperature from 600 to 800 ºC. However, only tetragonal crystalline phase was observed even after calcination at 800 ºC. The less crystalline nature of this sample was observed to be related to higher sulfur content (3 wt.%). The sulfate ions attached with hydroxyl groups resist the crystallization process. The higher thermal energy is required for the removal of hydroxyl groups for crystallization. It results into increase in calcination temperature required for crystallization. The crystallite size of this sample increases from 9 to 14 nm with increase of calcination temperature from 600 to 800 ºC.

The sulfated-zirconia samples, calcined at 500- 600 ºC, are mesoporous in nature as they show isotherms of type IV with hysteresis of H2 or H3 type. The crystalline sulfated-zirconia samples show higher surface area (71- 116 m²/g) than amorphous sulfated-zirconia (25- 41 m²/g) and pure zirconia (6- 9 m²/g). The surface area increases with increasing calcination temperature but after certain calcination temperature
it decreases, which may be due to sintering of pores at higher temperature. The pore size
distribution in all the samples was found to be broad, ranging from 20 to 100 Å.

Among the one-step and two-step sol-gel method, sulfated zirconia samples
prepared by one-step method were observed to have better structural and textural
properties in terms of lower crystallite size, higher sulfur loading, higher surface area,
pore volume and pore size as compared to the samples synthesized by two-step sol-gel
method. Further, among the samples prepared by one-step method, the sulfated zirconia
sample (SZO2-600) showed maximum surface area (150 m²/g), pore volume (0.33 cm³/g)
and pore size (89 Å). The surface area of the sample decreases with increasing
calcination temperature (600 to 800 ºC) due to increase of crystallite size and sintering
but the pore volume increased due to formation of larger pores due to collapse of
micropores.

The sulfated-zirconia catalysts are having higher Bronsted acidity as they were
found highly active for dehydration of cyclohexanol to cyclohexene giving conversion of
cyclohexanol from 78- 100 % with ~100 % selectivity of cyclohexene, however, the
method of activation (in air or nitrogen atmosphere) plays an important role in order to
attain maximum activity.

The nano-crystalline sulfated-zirconia samples, synthesized by one-step and
two-step sol-gel methods, were found active for acylation reaction showing the
conversion of anisole and veratrole in the range of 25- 36 % and 29- 42 % respectively at
110 ºC after 3 h, with substrate to catalyst weight ratio of 10. The sample, synthesized by
two-step sol-gel method in alkaline medium, showed higher conversion of anisole (36 %)
and veratrole (42 %).

The conversion of anisole and veratrole was found to be significantly increased
from 19 to 35 % and 22 to 60 % respectively at 110 ºC after 3 h with increase of
calcination temperature from 600- 700 ºC, which was observed to be dependent of the
sulfur content. However, the sample, calcined at higher temperature (800 ºC) showed the
decrease in the conversion of both anisole and veratrole due to very less sulfur content
(0.6 wt.%) in the sample, which generates less and very weak Bronsted and Lewis acid
sites. The optimum amount of sulfur (~1 wt.%) is required to generate reasonable amount
of stronger Bronsted and Lewis sites and thus higher catalytic activity of the sulfated-zirconia.

The conversion of anisole as well as veratrole was also found to be gradually increased with increase in reaction temperature and showed maximum conversion of anisole (46 %) and veratrole (60 %) at 150 ºC after 3 h, while selectivity remained constant.

The time study of the reaction showed that the acylation reaction is very fast with sulfated-zirconia catalyst. The maximum conversion of anisole was achieved within 30 min. with 46 % conversion and 98 % selectivity of 4-methoxy acetophenone while veratrole showed maximum conversion (60 %) within 10 min. with 100 % selectivity of 3, 4-dimethoxy acetophenone.

With decreasing the substrate to catalyst weight ratio from 10 to 5, the conversion of anisole and veratrole was increased from 32 to 52 % after 1 h and 48 to 66% after 30 minutes respectively at 150 ºC, while the selectivity of the acylated products remains steady.

The spent catalyst can be easily regenerated by simple thermal treatment showing similar activity and selectivity for the desired product of acylation of anisole and veratrole as fresh catalyst.

The nano-crystalline sulfated-zirconia catalysts, synthesized by one-step and two-step sol-gel methods, were studied for solvent free single step isomerization of longifolene to isolongifolene. The isomerization of longifolene to isolongifolene is an important reaction finding applications as perfumery agent and intermediate compound for the synthesis of other perfumery chemicals. The sulfated-zirconia catalysts were found potential for selective isomerization of longifolene to isolongifolene with higher catalytic conversion in range of 90- 93 % with ~100 % selectivity of isolongifolene, within 15 min at 180 ºC by using small catalytic amount (0.1 g catalyst/ 10 g longifolene) of the catalyst. Kinetic study shows that the maximum conversion and selectivity for isolongifolene was achieved within 15 min of the reaction after that it remains steady till 360 min.

The effect of substrate to catalyst weight ratio on isomerization of longifolene to isolongifolene was carried out at different substrate to catalyst ratio ranging from 10 to
100 at 180 °C for 1 h. The conversion of longifolene to isolongifolene is in similar range (93- 95 %) with ~ 100 % selectivity of isolongifolene till substrate to catalyst weight ratio of 100 after 1 h. It shows that sulfated-zirconia catalyst is highly active catalyst for isomerization of longifolene and the minimal catalytic amount is sufficient to obtain maximum conversion.

Isomerization of longifolene was also carried out at large scale of 100, 500 and 1000 gm in large volume liquid phase reactor taking substrate to catalyst ratio of 100 at 180 °C for 6 h. The conversion of longifolene in all three batches was found to be 95 % with ~100 % selectivity of isolongifolene.

The catalyst was easily regenerated by simple thermal regeneration and reused for several reaction cycles (10th) with similar activity as fresh catalyst. Isomerisation of longifolene was found a Bronsted acid catalyzed reaction.

The sulfated-zirconia catalysts having optimum sulfur content (1.3- 1.6 wt.%, after calcination at 600 °C) showed selectivity (~100 %) isolongifolene from the isomerization of longifolene, however, one of the catalyst (SZO2-600) having higher sulfur content (3 wt.%) resulted further isomerization of isolongifolene to tetraline derivative (7-isopropyl 1, 1-dimethyl tetr aline) and other products. The further isomerization of isolongifolene is an acid catalyzed reaction, reported to be carried out under excess acidic condition. The catalyst SZO2-600 showed 92 % conversion of longifolene with ~3 % selectivity of isolongifolene, 56 % selectivity of tetraline derivative and 41 % of other products at 180 °C for 1 h. The catalyst SZO2-700, calcined at 700 °C, showed the increase in the selectivity of isolongifolene to 37 % and the selectivity of tetraline derivative and other products decreased to 25 % and 38 % respectively. The catalyst SZO2-800, calcined at 800 °C, showed further increase in the selectivity of isolongifolene ~100 % and tetraline derivative and other products were not observed to be formed. Calcination at higher temperature (700 °C) decreased the sulfur content (1.1 wt.%) reducing the number and strength of Bronsted acid sites and therefore, the formation of tetraline derivative was decreased. The calcination at further higher temperature (800 °C) significantly reduced the sulfur content (0.6 wt.%) generating less number of acid sites that are not sufficient for further isomerization of isolongifolene.
The kinetic study of the isomerization of longifolene to isolongifolene and further to tetraline derivative (taking substrate to catalyst ratio of 10 at 180 °C) showed that the maximum conversion of longifolene (96 %) and selectivity of isolongifolene (~100 %) were obtained within 2 minutes of the reaction time. After 2 minutes, the selectivity of isolongifolene was observed to be successively decreasing with time and the selectivity of tetraline derivative and other products gradually increased giving ~56 % tetraline derivative and ~41 % other products with small amount (~3 %) of isolongifolene after 1 h. The selectivity of tetraline derivative, other products and isolongifolene remains constant up to 4 h. The kinetic study clearly shows that longifolene initially isomerizes to isolongifolene and then further to tetraline derivative along with other products, which was also confirmed by recording ¹H NMR spectra of the reaction mixture after 1 minute, 10 minutes and 1 h.

The regenerated catalyst has similar activity for isomerization of longifolene to isolongifolene; however, the selectivity of the products varies showing the decrease in the selectivity of tetraline derivative.

The nano-crystalline sulfated-zirconia catalysts, synthesized by one-step and two-step sol-gel methods, were found highly active solid acid catalyst for the synthesis of 7-amino 4-methyl coumarin and 7-hydroxy 4-methyl coumarin by acid catalyzed Pechmann reaction replacing the use of the conventional homogenous acids. 7-substituted 4-methyl coumarins such as 7-hydroxy 4-methyl coumarin (β-methylumbelliferone) and 7-amino–4-methyl coumarin are important coumarins finding applications as fluorescent brightener, efficient laser dye, standard for fluorometric determination of enzymatic activity, synthesis of insecticides, as precursor for furano coumarins and many other derivatives of substituted coumarins.

The sulfated-zirconia catalysts showed excellent conversion or yield for the synthesis of 7-substituted 4-methyl coumarins in solvent and solvent free conditions. The m-amino phenol is more reactive towards Pechmann reaction. The catalysts, synthesized by one-step and two-step sol-gel methods, were found highly active for synthesis of 7-amino 4-methyl coumarin and similar in activity showing 100 % conversion with ~100 % selectivity of 7-amino 4-methyl coumarin at 150 °C after 1 h in presence of solvent as well as in solvent free condition. Solvent free synthesis of 7-amino 4-methyl coumarin...
gives 100 % conversion with 100 % selectivity of 7-amino 4-methyl coumarin at comparatively low temperature, i.e., 110 ºC within 2 minutes. The presence of solvent was observed to be slowing the kinetics and lowering the selectivity in presence of polar solvent.

The yield of 7-hydroxy 4-methyl coumarin was found higher (40- 43 %) in solvent free synthesis than with solvent (21- 24 %) at 150 ºC after 1 h. The synthesis of 7-hydroxy 4-methyl coumarin in presence of solvent gives low yield (43 %) at higher temperature (170 ºC) after 24 h. Solvent free synthesis of 7-hydroxy 4-methyl coumarin gives higher yield (78 %) at 170 ºC within 3 h. The lower yield in presence of solvent is attributed to inhibitory effect of the solvent molecule, resisting the approach of reactant molecules with acid sites. The nature of solvent i.e., polarity, does not affect the reaction but makes the reaction slower due to the resisting effect of solvent molecules. In presence of solvent, the yield of 7-hydroxy 4-methyl coumarin was observed to be decreasing with increasing the substrate to catalyst weight ratio, but in solvent free synthesis, the yield of 7-hydroxy 4-methyl coumarin successively increases from 57 to 94 on increasing the substrate to catalyst ratio from 2 to 80. The maximum yield of 7- hydroxy 4-methyl coumarin under solvent free condition is 94 % at optimized reaction conditions (at 170 ºC for 3 h) using substrate to catalyst weight ratio of 80. The use of very small catalytic amount of sulfated-zirconia catalyst for the synthesis of coumarins and the reusability of the sulfated-zirconia catalyst after simple activation for several times with similar activity are advantageous properties of the catalyst. The solvent free microwave assisted synthesis of 7-hydroxy 4-methyl coumarin was found more effective way of coumarin synthesis giving excellent yield (99 %) decreasing the reaction time (15 minutes) compare to thermal heating.

- The present study shows that the sulfated-zirconia is highly active solid acid catalyst for acid catalyzed organic transformations such as benzylolation of toluene, acylation of anisole and veratrole, isomerization of longifolene and for synthesis of 7-hydroxy 4-methyl coumarins by Pechmann reaction.

- The use in small catalytic amount, fast reaction kinetics, easy separation from reaction mixture and simple regeneration method with retention of...
catalytic activity after several reaction cycles makes the sulfated-zirconia an efficient heterogeneous catalyst of industrial application. However, the catalytic activity of sulfated-zirconia was observed to be affected by the method of synthesis and synthetic parameters. The different synthetic parameters of sol-gel technique were observed to be affecting the structural, textural and acidic properties and therefore, the catalytic activity of the catalyst.

- The presence of both type of acidity, i.e., Bronsted and Lewis, in the sulfated-zirconia provides a wide scope of application in Bronsted and Lewis acid catalyzed organic transformations.
- The higher Bronsted acidity of the sulfated-zirconia catalyst shows higher activity for Bronsted acid catalyzed reactions.
- The sulfated-zirconia can also be applied for several other acid catalyzed reactions such as electrophilic addition reactions, cycloaddition reactions, cyclization reactions, etc. giving valuable products to replace the conventional homogeneous acid catalysts.