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Organic Syntheses and Transformations Catalyzed by Sulfated Zirconia

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Contents

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1. Introduction

Solid acids and superacids are the topics of everlasting interest due to numerous applications in many areas of the chemical industry. The present understanding of acid-induced or catalyzed reactions cover an extremely broad field, ranging

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from large-scale industrial processes in hydrocarbon chemistry to enzyme-controlled reactions in the living cell. These are extremely useful catalysts in many large-volume applications, especially in the petroleum industry for alkylation, isomerization, and cracking reactions, as well as in the production of fine and specialty chemicals.[1−12]

In the last few decades, there has been a deep search for a catalyst that can meet the new requirements from both the legislation and the market. One class of catalysts that have received a lot of interest are the anion-modified metal oxides, which exhibit exceptional acidic properties. In particular, the focus has been on the sulfated zirconia (SZ), which was first prepared and explored as a hydrocarbon isomerization catalyst in 1962.[13] The SZ catalyst received renewed interest

in the late seventies when Hino and Arata[14] reported that butane could be transformed into isobutane over the SZ even at room temperature. They attributed the high activity of the catalyst to its super acidic properties, i.e., SZ is claimed to be a stronger acid than concentrated sulfuric acid.

Many efforts could be found in the literature to improve the activity and stability of SZ catalyst, including promotion of the catalyst with transition metals like Fe, Mn, and Cr and with the noble metal Pt.[15] Arata and Hino also reported that the solid superacids could be synthesized by incorporating W- or Mo-oxides into Zr- or Ti-hydroxides under certain preparation conditions and that the acidity of these catalysts is stronger than that of 100% sulfuric acid.[16,17] On the basis of Hammett acidity indicators, they suggested that the acidity of these catalysts is close to 14 ($H_o \leq -14$). However, Umansky et al.[18] reported that SZ sample did not demonstrate superacidity and its acidity was close to that of a mordenite or a Y-zeolite sample. They also argued that intensive factor of the acidity (acid strength) is more important than extensive factor (surface concentration of Brønsted sites) in controlling the acidity and, therefore, the catalytic properties of the solids. Other researchers also supported that the acidity of SZ is not as high as expected.[4,19−23] Since there is lack of satisfactory methods of determining the acidity of a solid, the superacidity of anion-modified zirconias is in question. Because of the complexity of the solid acid catalysts, all the experimental results should be interpreted with caution. In any case, it is important to note that the catalytic properties of solid acid catalysts strongly depend on method of preparation, precipitating agent, sulfating agent, calcination temperature, pretreatment, and storage. These diversities add to the disagreement of the acidity among various researchers. Even if the acidic properties of a solid acid could be accurately determined, it would still be difficult to relate the acidity to catalytic activity because of wide distribution of the type and strength of the surface acid sites and the uncertainty about which sites are catalytically active.

Apart from the differences added to the disagreement about the acidity among various researchers, very often, in connection with isomerization of alkanes, anion-modified zirconias, mainly sulfated zirconias, have been extensively used in organic chemistry. The main aim of this review is to focus on the utility of sulfated zirconia and its modified versions in organic syntheses and transformation reactions over the past few years. This will be the first review, to the best of our knowledge, to gather most of the results pertaining to organic syntheses and transformations catalyzed by sulfated zirconia on which the author's group has also contributed significantly.

2. Scope and Organization of the Review

Metal oxide comprised catalysts offer several advantages over zeolite and clay-based catalysts. These are active over a wide range of temperatures and more resistant to thermal excursions. Among several solid acid catalysts reported so far, SZ gained a great deal of attention because of its high activity to catalyze many reactions even at low temperatures.[3,9,12,24] However, the SZ catalyst deactivates rapidly at higher temperatures and in reducing atmosphere by forming H_2S and SO_x. Also, it forms sulfuric acid at high temperatures if there is water in the reaction medium, leading to the downstream contamination. Such problems in the liquid-phase organic synthesis are fewer, based on the fact that most of the reactions are conducted at lower temperatures and in

Table 1. Typical Preparation Procedure Adopted for Sulfated Zirconia Catalyst by Two-Step Precipitation Method

sr. no.	starting materials	precipitating agent	sulfating agent	calcination temperature (°C)	ref
1	$ZrOCl_2 \cdot 8H_2O$	NH_4OH	H_2SO_4	650	30
2	$ZrOCl_2 \cdot 8H_2O$	$N_2H_4 \cdot H_2O$	$(NH_4)_2SO_4$	600	31
3	$ZrCl_4$	$N_2H_4 \cdot H_2O$	$(NH_4)_2SO_4$	600	31
4	$ZrCl_4$	NH_4OH	$(NH_4)_2SO_4$	600	31
5	ZrO_2		$H_2S/SO_2/(NH_4)_2SO_4/Zr(SO_4)_2$	450	32
6	$ZrO(NO_3) \cdot xH_2O$	NH_4OH	H_2SO_4	500/600/700	33
7	ZrO_2		SO_3	400	34

inert atmosphere (N_2 or Ar), where the possibility for loss of sulfur, zirconia phase transformation, and sintering are negligible. This is strongly supported by recent literature reports on superior performance of SZ, and hence, it continues to generate great interest. Another anion-modified zirconia catalyst, the WO_x/ZrO_2, also exhibited promising activity, even better than that of SZ in the alkylation of phenols.[25,26] Nevertheless, zirconia-based solid acid catalysts are finding extensive applications in organic synthesis and transformations in the liquid phase.[1,3,4,12,27,28]

Though a number of studies have been reported about the SZ catalyst, the origin of superacidic properties of the SZ still remains controversial.[3,4,9] There has been a quantum jump in the number of papers that have appeared during the past few years describing the utility of these catalysts. Hence, we strongly felt the necessity of this review, which will be highly helpful to organic as well as catalysis chemists.

The present review focuses on the fine and specialty chemicals synthesis catalyzed by sulfated zirconia in the liquid phase. We will also comment briefly on the preparation of the SZ catalyst by various methods and its characterization by different techniques, as well as on the structure and the active sites. Also, the significance of W- or Mo-oxide prompted zirconia catalysts toward organic reactions is highlighted. It is out of the scope of this review to cover comprehensively all reactions that have ever been reported in the presence of zirconia-based solid acids.

3. Preparation of Sulfated Zirconia Catalyst

The catalytic properties of SZ significantly depend on category of precursor, type of sulfating agent used, method of impregnation, calcination temperature, etc. Though there are various ways for the preparation of SZ catalyst, these methods could be mainly classified into two types. The first one is precipitation followed by impregnation, and this process is carried out in two steps. Another one is sol−gel, which is a single-step method.

3.1. Two-Step Precipitation and Impregnation Method

This method includes the preparation of zirconium hydroxide in the first step followed by sulfate impregnation in the second step. Type of precursors used for the preparation of zirconium hydroxide play a vital role in the final texture and, hence, on the performance of the final catalyst (Table 1). Various zirconium compounds, such as zirconium nitrate, zirconium chloride, zirconium oxychloride, and zirconium isopropoxide are employed to prepare the zirconium hydroxide, and the precipitation is mostly carried out by using the agents, like ammonium hydroxide and urea. In the second step also the sulfate impregnation is carried out by using various sulfating agents; the most commonly used are H_2SO_4 and $(NH_4)_2SO_4$.[29] Some sulfur compounds, like H_2S and SO_2,

have also been used. It has been observed that higher sulfate concentrations and high specific surface areas are obtained with sulfuric acid. The schematic diagram shown in Figure 1 provides the details about this method.

3.2. One-Step Sol−Gel Method

Sol−gel techniques have become more popular in recent times because of their high chemical homogeneity, the low processing temperatures, and the possibility of controlling the size and morphology of the resulting particles. The sol−gel-derived materials provide excellent matrixes for a variety of organic and inorganic compounds. Concerning the preparation of SZ catalysts via sol−gel method, different procedures have been reported in the literature.[35−40] Ward and Ko[35] reported an efficient method to make SZ aerogels in a one-step process through the sol−gel technique. According to their method, sulfuric acid solution is added to the zirconium alkoxide precursor during the sol−gel formation of the alcogel in such a way that the sulfate is incorporated into the alcogel network, leading to a zirconium−sulfate cogel. After supercritical drying, the desired SZ aerogel was obtained. Tichit et al.[36,37] also investigated the influence of the preparation method and the activation treatment on the catalytic activity of SZ catalysts. They reported one-step sol−gel synthesis of SZ catalysts following two methods: one previously used by Ward and Ko[35] and a second one in which sulfuric acid was added to the solution of zirconium alkoxide in n-propanol and stirred for prehydrolysis, after which water was added dropwise to complete the hydrolysis.
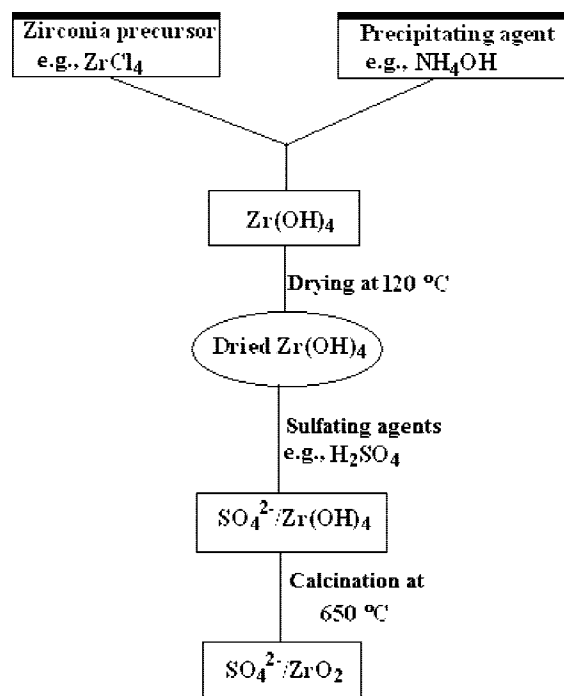
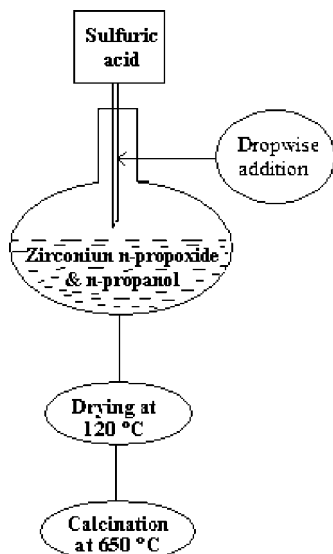**Figure 1.** Two-step preparation procedure of sulfated zirconia.

Figure 2. Single-step preparation of sulfated zirconia.

This typical procedure has been presented schematically in Figure 2. Morterra and co-workers[38,39] also reported a one-step preparation procedure of SZ catalysts. Catalysts synthesized via this route were found to exhibit higher surface areas and homogeneity. Recently, Hamouda and Ghorbel[40] reported a new process to control the hydrolysis step during sol−gel preparation. In this new route, the alcohol dehydration reaction, in the presence of a strong acid such as H_2SO_4, has been used to generate in situ hydrolysis water. They found an initial S/Zr molar ratio equal to 0.5, allowing optimal sulfur content and a high specific surface area. Most of the research groups preferentially used the sol−gel method for the synthesis of SZ or its modified versions.[41−44]

Also there is another interesting one-step method reported for the synthesis of SZ in which thermal decomposition of $Zr(SO_4)_2$ has been used where SO_3 is retained on the zirconia surface.[45,46] This method did not attract much attention because it does not allow control of the sulfate content.

Apart from the above-described methods, many groups working in this area also tried to incorporate modifications to these methods in order to get better surface area and mesoporous structure.[47−53] Sun et al.[47] prepared nanosized SZ with Brønsted acidic sites under solvent-free conditions, adopting a simple calcination procedure. Risch and Wolf[48,49] prepared SZ in which the pH-adjusted precipitated slurries were stirred under reflux at 90 °C during the 20 h digestion period. Morterra et al.[50] prepared the SZ catalyst using a hydrothermal precipitation route. Mesostructured SZ is reported by Sun et al.[51] and Yang et al.[52] by employing triblock copolymer and cetyl trimethyl ammonium bromide (CTAB), respectively, as structure-directing agents. Suh et al.[53] synthesized SZ catalyst having a large surface area by a different route using zirconium atrane derivate and CTAB surfactant.

4. Structural Characterization

Sulfated zirconia has been extensively characterized by various spectroscopic and nonspectroscopic techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FTIR), Raman spectroscopy (RS), differential thermal analysis/thermogravimetric analysis (DTA/TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM),
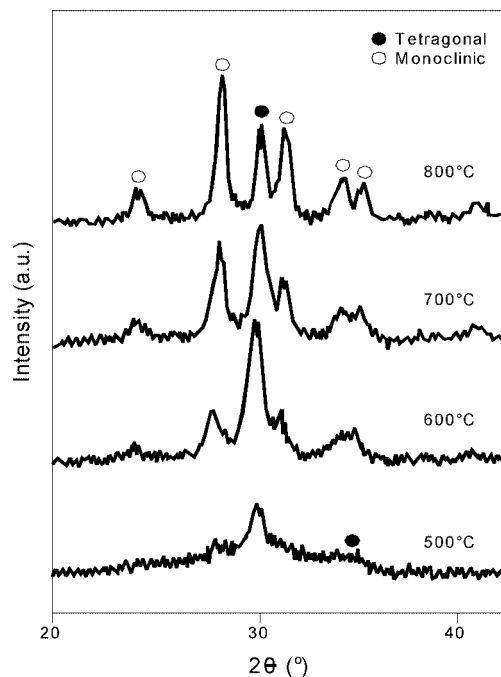

Figure 3. XRD patterns of sulfated zirconia calcined at 500, 600, 700, and 800 °C. Reproduced with permission from ref 57. Copyright 2002 Wiley InterScience.

ultraviolet−visible diffuse reflectance spectroscopy (UV−vis DRS), and other methods to understand the catalyst structure and the exact role of sulfate promoter on the catalytic activity. Some of these details are briefly discussed in the following paragraphs.

4.1. XRD Studies

Most of the XRD studies on SZ catalysts revealed formation of tetragonal ZrO_2 polymorph after sulfate ion incorporation. Reddy et al.[30,54] carried out systematic XRD studies on hydrous zirconia sample calcined at 650 °C and compared with SZ sample calcined at the same temperature. The hydrous zirconia sample exhibited poor crystallinity with a mixture of monoclinic and tetragonal phases. On the other hand, the sulfated sample exhibited prominent lines due to tetragonal phase, indicating that the impregnated sulfate ions show a strong influence on the phase modification of zirconia from thermodynamically more stable monoclinic to the metastable tetragonal phase. It was also observed that the SZ shows smaller crystallite sizes when compared to the unpromoted ZrO_2. It was confirmed from XRD results that the incorporated sulfate ions retard the formation of larger crystallites of zirconia and stabilize them in the metastable tetragonal phase.[55] Unpromoted ZrO_2 normally leads to the formation of thermodynamically more stable monoclinic form with larger crystallites.[56]

XRD patterns of SZ sample calcined at different temperatures were examined by Li and Li (Figure 3).[57] As shown in Figure 3, for the sample calcined at 500 °C, broad peaks of the tetragonal phase are detected, indicating that the sample is in an intermediate amorphous to tetragonal form. The peaks of tetragonal phase become stronger when the sample is calcined at 600 °C as that of the peaks of monoclinic phase. The peak intensities of the monoclinic phase grow steadily and those of the tetragonal phase decline with the increase in calcination temperature (700 and 800 °C). For the sample calcined at 800 °C, the monoclinic phase
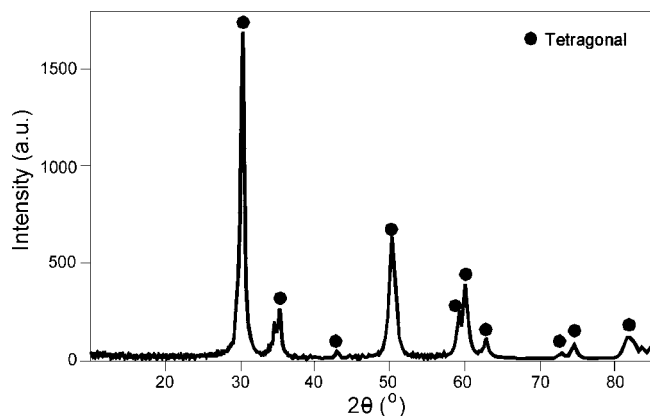
Figure 4. XRD patterns of sulfated zirconia calcined at 600 °C prepared by a sol−gel method.[58] Reproduced with permission from ref 58. Copyright 2005 Brazilian Chemical Society.

is predominant. On the other hand, a SZ sample prepared by a sol−gel method exhibited tetragonal as unique phase (ICSD collection code = 066787) represented by reflections at $2\theta = 30.18°$ (relative intensity in 100) as well as at 34.616, 35.283, 43.002, 50.214, 50.770, 59.291, 60.187, 62.724, 72.894, 74.617, and 81.768° (Figure 4).[58] Other studies also supported these observations, and the decrease in the crystallite size was mainly due to the doping of zirconia with sulfate ions, which retard crystallite growth, and the stabilization of zirconia tetragonal polymorph.[30,54]

4.2. FTIR Studies

Chen et al.[59] investigated FTIR spectra of pyridine adsorbed on SZ samples having different loadings of sulfate ions and recorded the characteristic bands in the range of 1400−1650 cm^{-1}. In general, the bands at 1545 and 1455 cm^{-1} could be assigned to Brønsted and Lewis acid sites, respectively, whereas the band at 1495 cm^{-1} is normally attributed to a combination band associated with both Brønsted and Lewis acid sites.[55] Generally, the IR spectrum of pure ZrO_2 exhibits vibrational bands associated only with Lewis acid sites (at 1455 and 1607 cm^{-1}), but the SZ sample shows existence of both Brønsted (at 1545 and 1640 cm^{-1}) and Lewis acid sites (at 1455 and 1607 cm^{-1}), as well as an additional band at 1495 cm^{-1} (combination band). These observations imply generation of Brønsted acid sites during the sulfation treatment of ZrO_2.

Babou et al.[60] carried out IR studies on SZ sample before and after calcination. The spectrum before calcination (after drying at 120 °C and rehydration in ambient air) showed bidentate SO_4^{2-} ion in C_{2v} symmetry with v_3 at 1207, 1136, and 1053 cm^{-1} and v_1 at 997 cm^{-1}. Similar results were also observed by Sohn and Kim.[29] Also, an additional broad and intense band at 3400 cm^{-1} corresponding to stretching vibrations (v_{OH}) of hydroxyl groups and absorbed water accompanied by the 1628 cm^{-1} (δ HOH) band were observed. After calcination at 550 °C, the spectrum exhibited a lightly upward shift of the first two bands and the appearance of shoulders at 1067 and 937 cm^{-1}. The 3400 cm^{-1} band intensity decreased strongly, while the band at 1626 cm^{-1} varied slightly, and better resolved bands appeared clearly at 746, 557, 500, and 514 cm^{-1}, characteristic of crystalline zirconia. From this they came to the conclusion that, because of the calcination, condensation of the hydroxyl groups of $Zr(OH)_4$ occurred, leading to a crystallized sample without any change of the sulfated species.
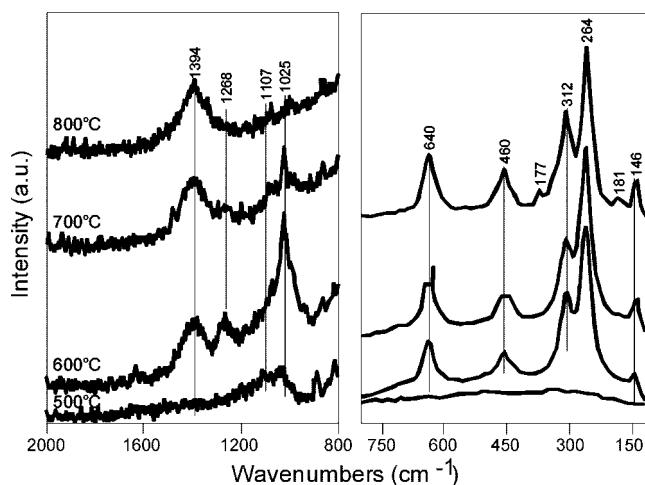

Figure 5. Raman spectra of sulfated zirconia calcined at 500, 600, 700, and 800 °C. Reproduced with permission from ref 57. Copyright 2002 Wiley InterScience.

4.3. Raman Studies

Raman spectroscopy is based on the inelastic scattering of photons, which lose energy by exciting sample vibration modes. Raman spectroscopy is adaptable for in situ studies, which make it an ideal tool for studying catalytic systems. UV−Raman spectroscopy is useful in distinguishing the monoclinic and tetragonal phases of zirconia.[61] This is important since the catalytic activity of SZ has been related to its crystal phases.[14,62] Highly active catalysts are tetragonal in nature, while monoclinic samples generally display low activity.[63]

Reddy et al.[64] carried out the Raman study of unpromoted and sulfate-ion promoted zirconia samples calcined at 650 °C. The spectra of unpromoted ZrO_2 revealed the Raman bands pertaining to a mixture of monoclinic (180, 188, 221, 331, 380, 476, and 637 cm^{-1}) and tetragonal (148, 290, 311, 454, and 647 cm^{-1}) phases, and the bands due to tetragonal phase were less intense than those of the monoclinic phase.[65,66] The spectra of sulfate-ion-promoted sample revealed relatively intense Raman bands pertaining to the tetragonal phase. Further, an additional weak band was observed at 1032 cm^{-1} that could be attributed to the hydrated sulfate groups.[50] Raman results thus supported the observations made from XRD studies, that sulfate ion increased the proportion of the tetragonal phase.

Kuba and Knözinger[67] examined the in situ Raman spectra of SZ between 720 and 1640 cm^{-1} prior to and during the *n*-pentane reaction at 50 °C. In this spectral region, bands of the surface sulfates are visible. The reference spectrum of the freshly activated SZ in a helium flow prior to the reaction exhibited bands in the Zr−O−S stretching region at 1015 and 1045 cm^{-1} and in the S=O stretching region at 1390 and 1409 cm^{-1}, suggesting the presence of two different surface sulfate species.

Li and Li[57] investigated the Raman spectra of SZ after calcination at 500, 600, 700, and 800 °C (Figure 5). The Raman bands pertaining to the sample calcined at 500 °C are not clearly visible, probably because the sample is still amorphous and also because of fluorescence interference. The Raman bands observed at 146, 264, 312, 460, and 640 cm^{-1} are due to tetragonal zirconia, and these bands were unchanged even after calcination at 800 °C. This suggests that the SZ retains its tetragonal phase up to relatively high temperatures. The bands at 1025, 1102, 1268, and 1394 cm^{-1},
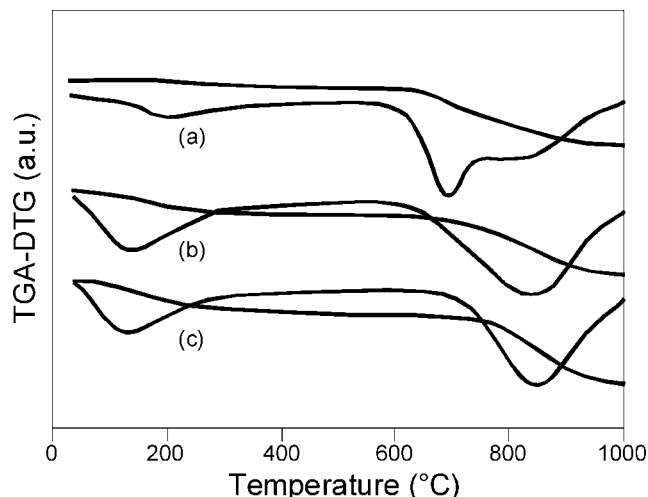
Figure 6. TGA and DTG profiles of sulfated zirconia calcined at (a) 575, (b) 600, and (c) 650 °C. Reproduced with permission from ref 68. Copyright 2006 Elsevier.
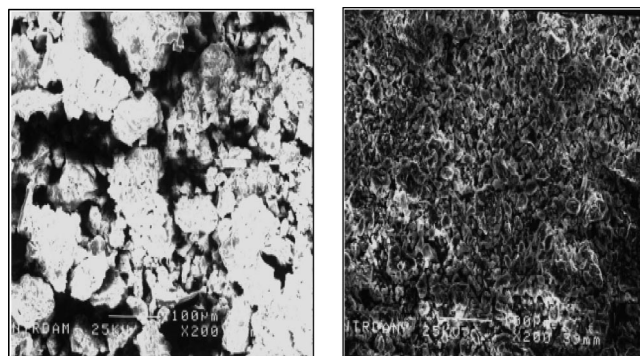

Figure 7. SEM micrographs of sulfated zirconia prepared at pH 10.0: (a) conventional preparation and (b) new preparation. Reproduced with permission from ref 48. Copyright 1998 Elsevier.

which are attributed to the symmetric and asymmetric vibrations of surface sulfated groups, changed in intensity with the increase in calcination temperature, but the band at 1394 cm^{-1} remained unchanged. Accordingly, the high stability of the tetragonal phase has been proposed partly because of the presence of the surface sulfate groups.

4.4. TG and DTG Analysis

Arata and co-workers[68] carried out thermogravimetric (TG) analyses of SZ samples calcined at 575, 600, and 650 °C (Figure 6). The first peak observed in all three samples at 200 °C is attributed to desorption of water adsorbed on the surface, and the broadness up to ~400 °C is an indication of heterogeneity of the strong acid sites. The second peak along with the third broad one at temperatures above 600 °C is ascribed to the decomposition of the sulfate species on the surface. It has been observed that the former peak close to 680 °C disappears when calcined at 600 °C, and vanishes almost completely with calcination at 650 °C. Also they observed that the materials obtained by calcination at 600−650 °C are still highly acidic and active for the butane conversion in comparison to the sample treated at 575 °C. Thus, it gave an indication that the third peak centered at 850 °C is associated with the active species.

Yi et al.[69] carried out the thermal analysis of SZ xerogel sample synthesized with a Zr/SO$_4^{2-}$ mole ratio of 4. The TG curve of the corresponding mesostructured SZ xerogel sample revealed at least three weight loss features over the whole range of temperatures studied. The first peak below 150 °C associated with endothermic response in DTA curve was attributed to desorption of the physisorbed species related to loss of water. The second weight loss processes between 200 and 500 °C are highly exothermic and are assigned to the combustion and continuous decomposition of the co-valently anchored ethoxy groups over the surface of the sample. Similar results were reported for the zirconia precipitates obtained by thermal decomposition of zirconium alkoxides in organic media,[70] where small amounts of alkyl groups covalently bonded to the surface oxygen atoms of the zirconia particles have been detected. The final weight loss feature centered at 680 °C is due to decomposition of SO$_4^{2-}$ species, which leads to the ultimate formation of SO$_3$ moieties.[71] Several inestigations could be found in the

literatre utilizing thermogravimetric techniques to analyze the synthesized samples.[72−75]

4.5. SEM and TEM

Most of the active supported catalysts, in general, consist of nanometer-sized particles dispersed on a high-surface-area support. Advances in characterization methods have led to a molecular-level understanding of the relationships between nanoparticle properties and the catalytic efficiency.[76−78] Scanning electron microscopy technique has been extensively used for physical characterization of catalyst particles, such as particle size, shape, surface structure, porosity, and dispersion of one phase on another. The magnification and resolution of SEM is relatively low compared to TEM.

Risch and Wolf[48,49] synthesized the SZ in which the pH-adjusted precipitated slurries were stirred under reflux at 90 °C during the 20 h digestion period and also by conventional precipitation method, and carried out particle size comparison by using SEM images. The pore volume was found to increase nearly by a factor of 3 for the catalyst prepared by a nonconventional method over the conventional-method catalyst. SEM micrographs of the catalysts at 200x magnification (Figure 7) show distinctly different morphologies: the conventional catalyst, Figure 7a, consists of large particles, whereas the newly prepared catalyst, Figure 7b, consists of much smaller particles. Yang et al.[52,79] prepared the SZ sample by using CTAB as a structure-directing agent. SEM images of the calcined sample are depicted in Figure 8. An examination of the images revealed that the sample consists of particles with identical morphology, especially spheres and aggregates of such spheres, and platelike aggregates were also observed.

Sun et al.[51] successfully synthesized a mesostructured SZ with large specific surface area (189 m^2/g) using a triblock copolymer as structure-directing agent. The TEM image (Figure 9) is spotted with wormlike pores. Selected-area electron diffraction patterns (Figure 9 inset) recorded for the same sample confirmed that the mesostructured walls are composed of tetragonal phase, displaying characteristic diffuse electron diffraction rings. Also, Sun et al.[47] synthesized nanosized SZ under solvent-free condition by a simple calcination method. The TEM image revealed that ZrO$_2$ particles in SZ have aggregated each other, forming meso-pores with the size of ~6 nm (Figure 10a). However, after ultrasonic dispersion for 10 min, it was observed clearly that ZrO$_2$ particles are in nanosize, with their size being 5−9 nm (Figure 10b). In Figure 10c, the magnified image of the
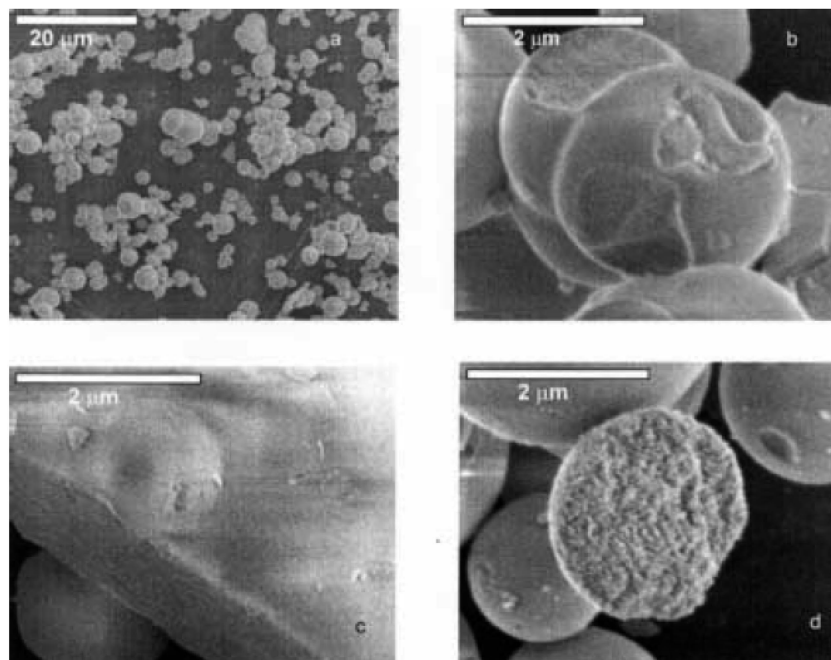
Figure 8. SEM images of sulfated zirconia synthesized by using CTAB: (a) an overview, (b) an enlargement of spherical particles, (c) a platelike aggregate, and (d) a broken sphere. Reproduced with permission from ref 52. Copyright 2002 Springer Science and Business Media.
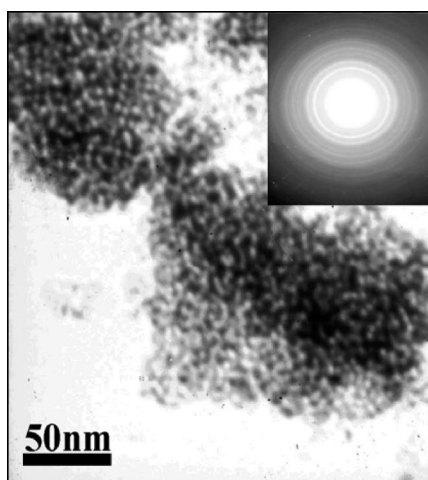

Figure 9. TEM images of mesoporous sulfated zirconia using triblock copolymer as structure-directing agent. Reproduced with permission from ref 51. Copyright 2003 Springer Science and Business Media.

selected area clearly shows that the SZ sample contains mesopores whose size is ∼6 nm aggregated by the nanocrystallites.

In line with XRD and Raman results, the UV−vis study also showed the evidence for tetragonal zirconia. The spectrum of SZ displayed a broad signal centered at 210 nm that is assigned to the tetragonal phase of sulfated zirconia.[80]

5. Structure of Sulfated Zirconia

The surface structure of SZ has been studied extensively in order to elucidate the nature of active sites ever since the discovery of its catalytic property for isomerization of alkanes at low temperatures. Nevertheless, no consensus has been reached so far. A number of studies have attempted to determine the nature of acid sites in the catalyst.[4,9]

Using XPS and IR spectroscopy, Jin et al.[81] proposed a structure to be chelating bidentate complexes, in which the

sulfate species chelates to a single Zr atom as presented in Scheme 1, because sulfated zirconia shows IR bands at 1390, 1190, 1020, and 930 cm^{-1}, where the former two are due to stretching frequencies of the asymmetric and symmetric stretching frequencies of the O=S=O and O−S−O. Ward and Ko[35] studied SZ by using in situ and ex situ diffuse reflectance infrared Fourier transform (DRIFT) and XRD techniques and suggested a similar type of model as that in Scheme 1, but in this case a hydroxyl group is bonded to a Zr atom adjacent to the Zr chelated with a sulfate species. Thus, the proton is strengthened by the electron inductive effect of two S=O bonds in the sulfate group.[65]

Saur et al.[82] carried out an in situ experiment of ^{18}O exchange using H$_2$^{18}O in addition to IR analysis over sulfated alumina and titania and suggested a structural model (Scheme 2a) in which three oxygens of the sulfate group are bonded to Zr elements in a tridentate form, whereas, in the presence of H$_2$O, the sulfate species is converted to a bridged bidentate sulfate, accounting for the Brønsted acidity. They also pointed out the possibility of formation of a polysulfate structure (Schme 2b) with high sulfate loading.[32,83] This structure was supported by Morterra et al.[84] using IR data of adsorbed pyridine in the dehydration and rehydration investigation of SZ catalyst. Along similar lines, the generation of structure (Scheme 2c) by hydration of the structure (Scheme 2d) is suggested by Rosenberg and Anderson from the study of sulfated silica−zirconia metal oxide.[85]

Kustov et al.[86] investigated SZ using diffuse reflectance IR spectroscopy. It was found that sulfate modification enhanced the strength of both Brønsted and Lewis acid sites. They suggested separate models for Brønsted acidity (Scheme 3 parts a and b) and Lewis acidity (Scheme 3c). Another bisulfate structure was proposed by Riemer et al.[87] using Raman and ^{1}H MAS NMR spectroscopies; two oxygens are bonded to Zr atoms in a bridged bidentate state.

Models in which SO$_3$ species are coordinated with zirconia are also proposed. One of them is coordination of the SO$_3$ sulfur with lone pairs of the zirconia oxygen in addition to
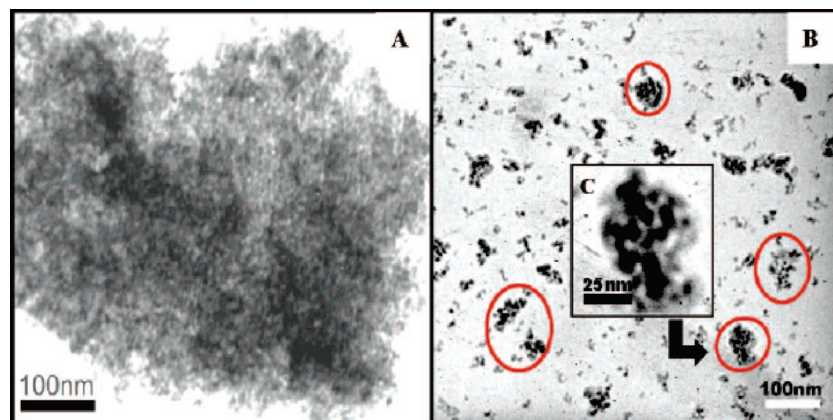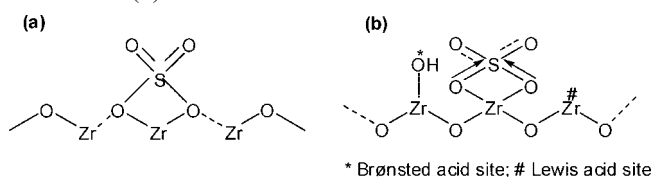
Figure 10. TEM images of sulfated zirconia: (A) image before ultrasonic dispersion, (B) image after ultrasonic dispersion, and (C) magnified image of selected area. Reproduced with permission from ref 47. Copyright 2006 American Chemical Society.
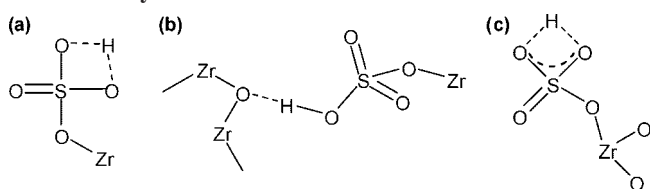
Scheme 1. Sulfated Zirconia Structure Proposed by (a) Jin et al.[81] and (b) Ward and Ko[35]

* Brønsted acid site; # Lewis acid site

Scheme 2. Structural Model Proposed by Saur et al.[82] (a and b) and Rosenberg and Anderson[85] (c and d)
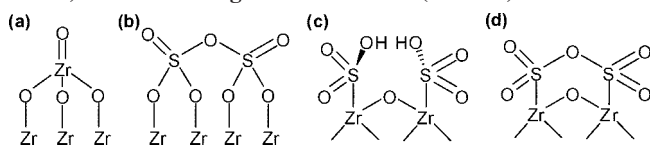
Scheme 3. Structure Suggested by Kustov et al.:[86] (a) and (b) Responsible for Brønsted Acidity and (c) Responsible for Lewis Acidity


one of the SO_3 oxygens with a Zr, suggested by Vedrine and co-workers[60,88] through IR study. The other one is depicted in such a way that two of the SO_3 oxygens are coordinated with surface zirconium atoms, leaving a single S=O moiety, proposed by White et al.[89] as shown in Scheme 4.

6. Superacidity and Measurement

6.1. Uncertainties about Superacidity

The classical Gillespie's definition of superacids relates to Brønsted acid systems.[90] While the Brønsted acid–base interaction involves a proton transfer reaction that allows consequential comparison, in the Lewis acid–base interaction there is no such common denominator.[7] The outcome is that the definition of acid strength has no real meaning with Lewis acids. Solid acids generally contain both Brønsted and Lewis acid sites. The application of H_o function to determine the "superacidity" of heterogeneous solid acid catalysts has many barriers. To examine the acidity, the basic indicator has to

Scheme 4. Sulfated Zirconia Structure Suggested by Vedrine et al.[88] and White et al.[89]
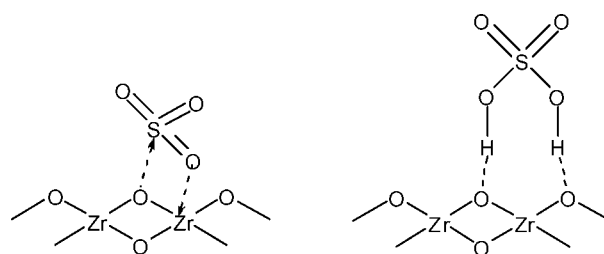
be weak enough not to affect the original acidity of the solid acid sample. As known regarding the surface of a solid sample, it is hard to achieve the equilibrium measurement using these indicators.[91,92] Further, the solid acid samples are often colored or dark and cause inaccuracy in visual observation of color changes. The acid sites on a solid surface are of different strengths, and the indicators may be adsorbed only to a part of the acid sites, not distinguishing how they are actually adsorbed. The surface area accessible for acidity determinations may have widely different acidic properties from the bulk material. It is possible that only a small part of the detected acidic sites are strong enough in catalysis of paraffin conversions. The generic term of acidity includes both acid strength and surface concentration of the acid sites. It is apparent from the literature that a single technique cannot provide adequate accurate information on solid acids.

The application of adsorption and desorption of base molecules facilitates other techniques to estimate the acidity of a solid acid. The adsorption heat[93] and activation energy from temperature-programmed desorption (TPD) measurements[94] have been correlated with the acid strength in terms of the Hammett acidity function. However, this method can also lead to inaccurate conclusions. For example, the TPD of adsorbate molecules may involve decomposition of the species, especially on strong acids, that can also be adsorbed on both acid and base sites. The base molecules could be adsorbed on the acid sites that are not catalytically active to participate in the reaction. The desorbed molecules could diffuse and readsorb on the acid sites.[95] Juskelis et al.[96] have even shown that a nonacidic solid, such as CaO, can also retain a base, NH_3, at high temperatures, which points out the uncertainty of the correlation of acid strength with the results of desorption tests.
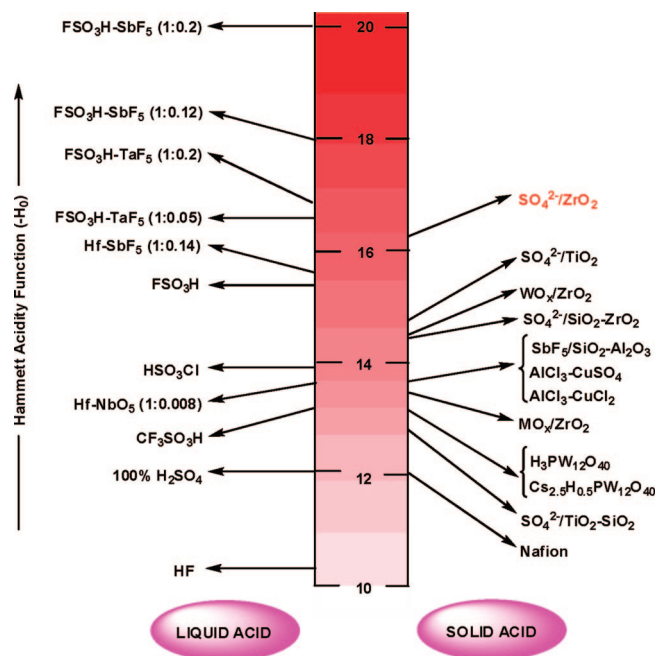
Figure 11. Acid strengths of various liquid and solid acids.

6.2. Acidity Measurement

The appearance of catalyst with sulfate treatment differs greatly from that without treatment. The former catalyst is finely powdered solid, which coats the wall of the glass ampule, obscuring vision, whereas the latter is not. This is an easy way to confirm whether superacidity has been generated or not.[97] There are various ways to establish the surface acidity such as Hammett-indicator method, TPD of base molecules, carrying out test reactions, and so on. However, no method is versatile for different types of solid acids. Arata et al.[9,97] compared the acid strength of various sulfated oxides determined by Hammett-indicator method and concluded that SZ is the strongest solid superacid. In this method, the acid strength of material is determined by its ability to change an organic solvent (adsorbed base) adsorbed on the solid into its conjugate acid form, which is associated with color change. The acid strength is measured in terms of H_o. The H_o values of various liquid and solid acids are summarized in Figure 11. Another equally important method used for acid strength is based on the test reactions, for example, an acid-catalyzed reaction such as skeletal isomerization of n-butane to isobutane at low temperatures. The skeletal isomerization of small alkanes has been investigated extensively in liquid superacid media and found to proceed via a protonated intermediate. Some NMR studies of SZ catalysts also indicated strong acidity,[87,98,99] and electron spin resonance spectroscopy studies also supported fairly strong acidity.[100] Recently, Yu et al.[101] inestigated the acidic properties of ZrO_2, SZ, SnO_2, and SO_4^{2-}/SnO_2 by employing solid-state NMR spectroscopy. Sommer and co-workers utilized another method where rate of H/D exchange for methane has been utilized to assess the relative acidity and reactivity of SZ catalyst.[102,103] The H/D exchange has been extensively explored to develop quantitative methods for Brønsted acid site titrations.[104,105] A study on the H/D exchange between methane and deuterated SZ, deuterated SZ supported on α-alumina, and deuterated Al-promoted SZ has shown that the apparent activation energy is the same for all the sulfated zirconia solids and smaller than that of HZSM-5.[102] Therefore, the acid strengths of all the sulfated

zirconia solids were proved to be identical and stronger than the acid strength of ZSM-5. Recently, Katada et al.[106] applied an interesting infrared−mass spectroscopy−TPD method for precise measurement of the acidic properties of SZ catalysts.

Sugunan et al.[107] investigated electron-donating properties of SZ from the adsorption of electron acceptors of different electron densities. It was observed that the electron-donating capacity of both zirconia and SZ decreased above 500 °C. In the case of SZ, there is a sharp decrease in the electron-donating power compared to unmodified sample. The decrease in the electron-donating capacity owing to sulfation may be due to the conversion of some of the basic sites into acidic sites.

## 7. Application of Sulfated Zirconia Catalysts

Many industrially important reactions have been investigated employing SZ catalyst because of its strong or superacidic character. Initially, the SZ catalyst was exploited for vapor-phase reactions such as isomerization of butane, pentane, and other hydrocarbons.[108−114] Recently, Ahmed et al.[115] have explored the SZ catalyst for dehydration of ethanol. Interestingly, the SZ catalyst has been found to be very active for various organic reactions facilitating synthesis of fine and specialty chemicals in the liquid phase, and it attracted very much attention due to its reusability and easy handling. Some of these interesting methodologies envisaged include synthesis of aromatic *gem*-dihalides,[116] stereocontrolled glycosidation,[117−119] regioselective ring-opening of aziridines,[120] production of diaryl sulfoxides,[121] and so on. The application of SZ catalyst for some of these reactions not only is industrially important but also has academic merit because very little is known about the exact functioning of these catalysts. Some of the reactions envisaged in the literature by utilizing SZ catalyst are outlined below. Comparison is also made with other known acid catalysts.

7.1. Biginelli Reaction

The three-component condensation reaction between aldehyde, β-keto ester, and urea under strong acidic conditions to furnish 3,4-dihydropyrimidin-2(1H)ones is known as the Biginelli reaction. This reaction was first reported by Biginelli in 1893 but suffers from low product yields, especially with substituted aromatic aldehydes.[122] The Biginelli reaction was carried out employing many reagents such as lanthanum chloride,[123] montmorillonite KSF,[124] heteropolyacid,[125] silica-supported sulfuric acid,[126] metal triflates,[127] and so on. Of course, most of these reported catalysts suffer from various drawbacks.

Reddy et al.[121] reported a facile method for the synthesis of 3,4-dihydropyrimidone-2(1H)-ones by a one-pot condensation reaction between an aldehyde, β-keto ester, and urea or thiourea under solvent-free conditions employing SZ catalyst at 100 °C. The reaction proceeds efficiently under these conditions, and the dihydropyrimidinones were produced in excellent yields in short reaction times (40−60 min). The mechanism of this typical reaction is shown in Scheme 5. Also Gopalakrishnan et al.[128] and Kumar et al.[129] carried out the Biginelli reaction by using SZ catalyst under microwave irradiation. The phosphotungstic acid-impregnated SZ was also found to be more active for this reaction, as reported by Kumar and co-workers.[130]

Angeles-Beltrán et al.[131] carried out a competitive study of multicomponent Biginelli versus Hantzsch reactions

Scheme 5. Mechanism of Biginelli Reaction
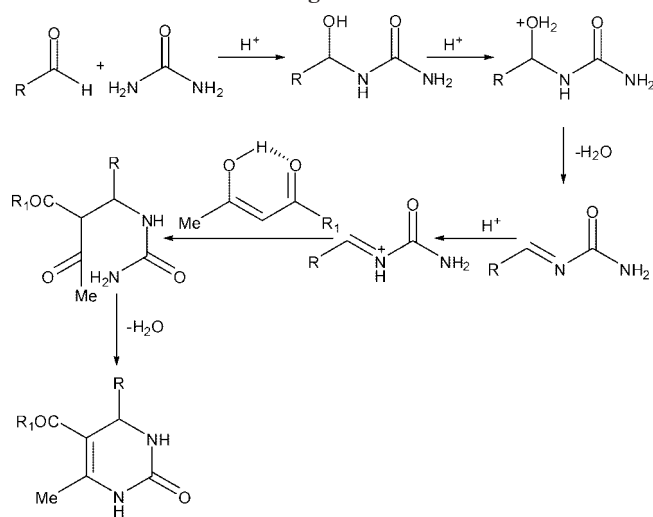
(Scheme 6) using SZ catalyst and urea as an amine. The reaction was conducted at various temperatures under solvent-free condition. At 60 °C, no Hantzsch reaction products were observed. However, at 80 °C, traces of Hantzsch products were noted. A further temperature increase, however, favored the decomposition of urea into ammonia, thus promoting the Hantzsch reaction and allowing a competitive reaction leading to Biginelli and Hantzsch condensation products to take place. Thus, formation of Hantzsch product increased and Biginelli product decreased with the increase in temperature from 60 to 150 °C.

7.2. Knoevenagel Condensation

The Knoevenagel condensation of aldehydes with active methylene compounds has been commonly employed in the synthesis of numerous specialty chemicals and chemical intermediates[132,133] such as carbocyclic as well as heterocyclic compounds of biological significance,[134] calcium antagonists,[135] polymers,[136,137] coumarin derivatives, cosmetics, perfumes, and pharmaceuticals.[138–140] This reaction was thoroughly investigated employing SZ catalyst.[64] This condensation was performed using various aliphatic, aromatic, and heterocyclic aldehydes with malononitrile under solvent-free conditions in a one-step process (Scheme 7). Most of the reactions investigated with SZ catalysts were almost complete in 0.5–6.0 h duration to produce the corresponding electrophilic alkenes in 78–98% yield.

7.3. Synthesis of Formamidine

Lin et al.[141] investigated the reaction between aniline and trimethyl orthoformate to produce formamidine by employing various sulfated metal oxide catalysts, namely, SO_4^{2-}/ZrO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/Al_2O_3, SO_4^{2-}/Fe_2O_3, SO_4^{2-}/HfO_2, SO_4^{2-}/SnO_2, and other catalysts such as hydrogen form of mordenite, ammonium form of mordenite, sodium form of mordenite, and β-zeolite. In a typical reaction protocol, 45.1 mmol of aniline was mixed with an excess of trimethyl orthoformate (130.2 mmol) and to this 0.3 g of catalyst was added and stirred at 40 °C for a specific period of time. A comparison of the activities and selectivities of different catalysts after 1 h of reaction revealed that SZ is the most productive catalyst among all the solid acids tested with an aniline conversion of 35% and a formamidine selectivity of 98%. It was also found that, under aniline-deficient condi-

tions, the most reactive SZ produced almost quantitative yield (97%) of formamidine as the major reaction product with methyl N-phenylformimidate in <3% yield, and no formation of N-methylformanilide was observed even after an overnight reaction at 40 °C (Scheme 8).

7.4. Acylation of Aromatic Compounds

Aromatic ketones are valuable intermediates in the production of various fine chemicals, which are synthesized mainly by acylation of aromatics with acid chlorides or carboxylic anhydrides.[142,143] Traditionally, these reactions have been carried out using stoichiometric amounts of liquid Brønsted acids or Lewis acids. Also aromatic ketones are the valuable intermediates or final compounds used in the production of pharmaceuticals, cosmetics, agrochemicals, dyes, and specialty chemicals. 4-Chlorobenzophenone could be synthesized by acylation of benzene with 4-chlorobenzoyl chloride. 4-Chlorobenzophenone is useful as an organic and pharmaceutical intermediate, for instance, in the manufacture of a well-known drug, Cytrazin-a. Nowadays, the restrictions imposed by the waste-minimization laws and economic considerations driven to the development of new catalytic technologies. Modern processes are, in fact, based on solid acids. Several authors have employed SZ catalyst for acylation of aromatic compounds, which are outlined below.
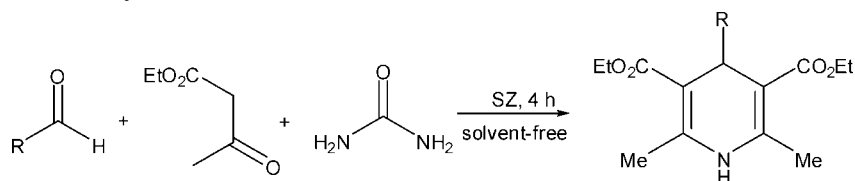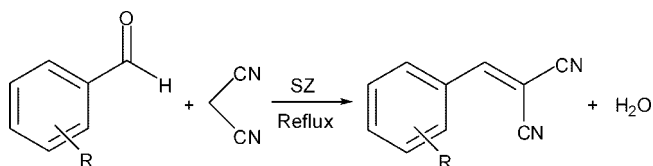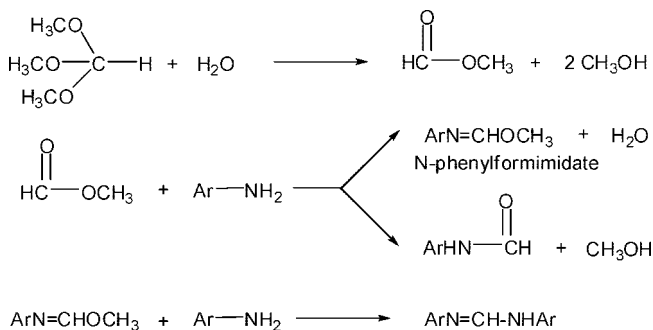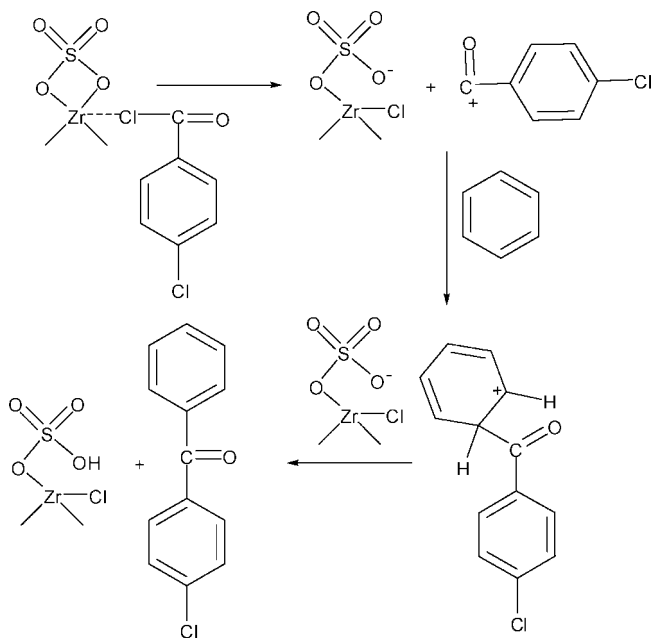
7.4.1. Acylation of Benzene

Yadav and Pujari[144] reported that SZ exhibits the best performance in the acylation of benzene with 4-chlorobenzoyl chloride. They compared the activities of several solid acid catalysts, namely, dodecatungstophosphoric acid (DTPA), DTPA/K-10 clay, K-10, Amberlite, Amberlyst-15, Indion-130, Filtrol-24 clay, and SZ. Their study revealed that SZ is the most effective, leading to 100% selective formation of 4-chlorobenzophenone. They also investigated the kinetics of the reaction and established that the reaction obeys the Langmuir–Hinshelwood–Hougen–Watson mechanism with very weak adsorption of the reactants and the reaction is intrinsically kinetically controlled. The mechanism of this reaction suggested by these authors is shown in Scheme 9.

Koyande et al.[145] also investigated the kinetics of this reaction on sulfate ion-promoted metal oxide catalysts. The synergistic effect of the dopant metal oxide in the matrix of the parent sulfated oxide, SO_4^{2-}/ZrO_2, has also been studied for the alkylation of benzene with benzyl chloride. An attempt has also been made to decrease the polyalkylation observed on the highly reactive catalyst, SO_4^{2-}/Fe_2O_3. In conclusion, it was stated that sulfate ion-promoted mixed oxide, $ZrO_2–Fe_2O_3$, prepared by a coprecipitation method exhibits better reusability in comparison to SO_4^{2-}/ZrO_2 and SO_4^{2-}/Fe_2O_3 catalysts.

7.4.2. Acylation of Substituted Benzenes

Deutsch et al.[146] investigated the benzoylation of anisole, 2-chloroanisole, 3-chloroanisole, mesitylene, and m-xylene with benzoylating agents, benzoic anhydride, and benzoyl chloride, and the acetylation of aromatics, except 3-chloroanisole, with acetic anhydride. These authors also compared the activity of several solid acid catalysts, namely, SZ, Nafion-H, Amberlyst-15, K-10, H-BEA, and H-mordenite, in the benzoylation of anisole with benzoic anhydride. Their study revealed that SZ exhibits a dramatically higher activity

Scheme 6. Sulfated Zirconia-Catalyzed Hantzsch Reaction

Scheme 7. Sulfated Zirconia-Catalyzed Knoevenagel Condensation

Scheme 8. Sequence of Reactions for the Formation of Formamidine

Scheme 9. Reaction Mechanism of Acylation of Benzene with 4-Chlorobenzoyl Chloride over Sulfated Zirconia Catalyst

Deutsch and co-workers[147] also investigated various aliphatic carboxylic anhydrides and acid chlorides for acylation of anisole employing SZ catalyst and concluded that acetic anhydride and benzoic anhydride acylate the aromatic substrates significantly faster than benzoyl chloride. The reaction between anisole and carboxylic anhydrides could be performed at 55 °C, whereas the use of benzoyl chloride demands a higher temperature.
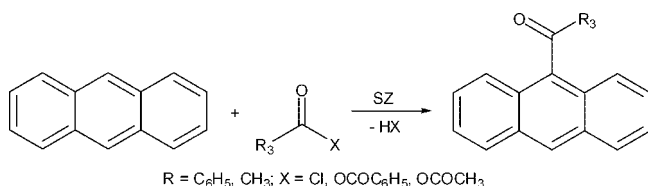
In another study, acylation of anisole, *o*-, *m*-, and *p*-xylene with benzoic anhydride, acetic anhydride, and propionic anhydride were performed employing SZ and other catalysts.[148] These experiments were carried out using an excess of aromatic substrates as solvents. It was found that SZ is better than H β-zeolite. Further, the SZ catalyst prepared by sol−gel method exhibited better performance than the conventional precipitated sample. The same group also described benzoylation of anisole with benzoic anhydride over SZ, especially with respect to catalyst reactivation and regeneration. Calcined and spent SZ catalysts were characterized by Brunauer−Emmett−Teller (BET) surface area, C−H elemental analysis, DRIFTS, NH_3−TPD, ^{13}C NMR, and UV−vis spectroscopy techniques.[149]

Also, Zane et al.[150] carried out the acylation of anisole with benzoic anhydride using SZ catalyst. They have carried out the catalytic tests at different temperatures (30−50 °C). They also investigated the effect of preparation conditions, e.g., precipitation pH, calcination temperature, and activation temperature on the catalytic performance. Quaschning et al.[151] proposed that strong Brønsted acid sites are responsible for the production of acyl or benzyl cation by activating the acylating agent as shown in Figure 12, although the Friedel−Crafts acylation with acyl chlorides is generally known to be catalyzed by Lewis acids.

7.4.3. Acylation of Naphthalenes and Anthracenes

The SZ catalyst has also been utilized in the acylation of methoxynaphthalenes, methylnaphthalenes, naphthalene, and anthracene with benzoic anhydride, benzoyl chloride, and acetic anhydride to synthesize aromatic ketones.[152] The influence of solvents for the acetylation of 2-methoxynaphthalene has also been examined and it was noted that the use of solvents with low donor numbers is advantageous. The SZ exhibited a high catalytic performance in the benzoylation of 1-methoxynaphthalene. Naphthalene was the least reactive of the bicyclic aromatics investigated. Therefore, its acylation with benzoic anhydride and benzoyl chloride proceeded slowly to provide <10% of the target product. Also 1- and 2-methylnaphthalene and naphthalene were not acylated in the reaction with acetic anhydride. The acetylation and benzoylation of 1-methoxynaphthalene and 2-methoxynaphthalene, and benzoylation of 1,3-dimethyl-naphthalene and anthracene, could be carried out with high ketone yields and with low quantities of SZ catalyst (Scheme 10). The sulfuric and sulfonic acid groups of the catalysts such as SZ were able to react with acylating agents to furnish acylsulfates and acylsulfonates, respectively.[153] Thus, acyl-

in comparison to H-BEA and H-mordenite. In addition, the performance of SZ in the reaction of sterically demanding benzoic anhydride was less dependent on the acidity level and more dependent on the pore size. Comparative experiments surprisingly confirmed that benzoyl chloride (yield 52%) was less active than benzoic anhydride (yield ≈ 100%). Also, reactivity of aromatics for benzoylation on SZ decreased in the following order: anisole > mesitylene > 3-chloroanisole ≈ *m*-xylene ≈ 2-chloroanisole > toluene.

Scheme 10. Sulfated Zirconia-Catalyzed Acylation of Anthracenes

R = C₆H₅, CH₃; X = Cl, OCOC₆H₅, OCOCH₃

sulfonates were synthesized and isolated by Effenberger et al.;[153] the acylsulfonates are very active toward aromatics. The probable mechanism for aromatic acylations on SZ-type heterogeneous catalysts containing sulfate or sulfonate groups is shown in Scheme 11.

7.4.4. Acylation of Phenols, Alcohols, and Amines

Acylation of alcohols is an important method for the preparation of organic esters, which are valuable intermediates in the production of fine chemicals. Also the acylation of alcohols, phenols, and amines is one the most frequently used transformations in organic synthesis. The SZ-catalyzed acylation of alcohols, phenols, and amines with acetic anhydride proceeded smoothly at ambient temperature to afford corresponding acylated products (Scheme 12) in good-to-high yields (85−95%) in short reaction times (10−15 min).[154] Major advantages associated with this protocol include short reaction times, mild reaction conditions, easy workup procedure, and reusability of the catalyst.

7.5. Stereocontrolled α- and β-Glycosidation

Glycosidation is one of the most important and basic synthetic methodologies to prepare several types of glycosides and oligosaccharides. Therefore, highly efficient chemical glycosidation reactions have attracted considerable attention in the carbohydrate chemistry related to certain biomolecules and functional materials. From a synthetic standpoint, the efficiency of the glycosidation generally demands a high chemical yield, regioselectivity, and stereoselectivity.

7.5.1. Syntheses of α- and β-Mannopyranosides

Nagai et al.[117] employed SZ catalyst for glycosidation of totally benzylated mannopyranosyl fluoride and alcohols to

Scheme 11. Possible Mechanism of Aromatic Acylations on Heterogeneous Catalysts Containing Sulfate or Sulfonate Groups Such As Sulfated Zirconia
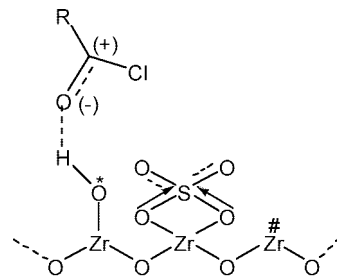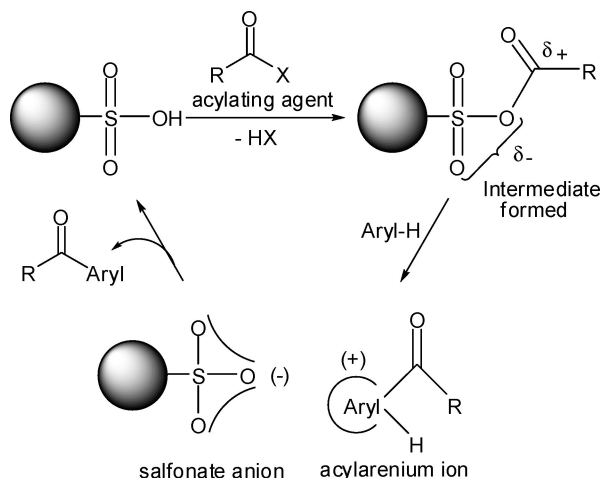
* Brønsted acid site; # Lewis acid site

Figure 12. Hydrogen bond activation of acyl chloride by Brønsted sites of sulfated zirconia.

synthesize α- and β-mannopyranosides directly. They also compared the activity of several solid acid catalysts, namely, montmorillonite K-10, Nafion-H, and SZ, for glycosidation of totally benzylated α-mannopyranosyl fluoride and cyclohexylmethanol in CH₃CN solvent at 25 °C for 15 h. They found that SZ exhibits better activity and α-selectivity in comparison to Nafion-H and montmorillonite K-10 catalysts. Also, they have investigated the effect of various solvents on this novel glycosidation reaction. Interestingly, the stereoselectivity of glycosidation was found to change dramatically with the nature of the solvent employed. β-Mannopyranosides were predominately produced when Et₂O was used as the solvent. Further, the use of molecular sieve 5Å as an additive in the glycosidation with Et₂O solvent lead to high chemical yield and stereoselectivity for β-mannopyranosides.

They have also carried out the glycosidation of totally benzylated α- mannopyranosyl fluoride with primary and secondary alcohols using 5 wt % SO₄²⁻/ZrO₂ catalyst in CH₃CN solvent at 40 °C for 15 h, which effectively proceeded to provide the corresponding α-mannopyranosides in high yields with high stereoselectivity.[117] Further, employing 100 wt % SO₄²⁻/ZrO₂ and molecular sieves 5Å as an additive in Et₂O solvent at 25 °C, β-mannopyranosides were obtained in high yield with good stereoselectivity (Scheme 13).

Toshima et al.[118] have utilized the SZ catalyst for glycosidation of totally benzylated α- and β-mannopyranosyl sulfoxides and alcohols for direct synthesis of α- and β-mannopyranosides. They examined the glycosidation of the totally benzylated α- and β-mannopyranosyl sulfoxides (Scheme 14) with cyclohexylmethanol using several heterogeneous solid acid catalysts such as montmorillonite K-10, Nafion-H, and SZ. They showed that SZ (300 wt %) exhibits better activity and β-selectivity in comparison to Nafion-H and montmorillonite K-10.

7.5.2. Syntheses of 2-Deoxy-α- and β-Glucopyranosides

The SZ has also been profitably employed for glycosidation of 2-deoxyglucopyranosyl α-fluorides with several alcohols in MeCN, which smoothly proceeded resulting in α-stereoselectivity, while those with the same activator in the presence of molecular sieve 5Å in Et₂O proceeded with

Scheme 12. Acylation of Phenols, Alcohols, and Amines Employing Sulfated Zirconia Catalyst

X= O, NH
R= 2-naphthyl, p-acylphenyl, benzyl, cyclopentane etc.
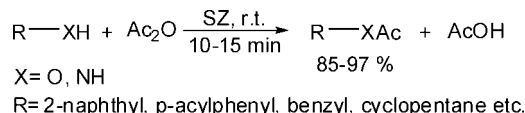
Scheme 13. Stereocontrolled Glycosidation of Totally Benzylated Mannopyranosyl Fluoride Using Sulfated Zirconia Catalyst
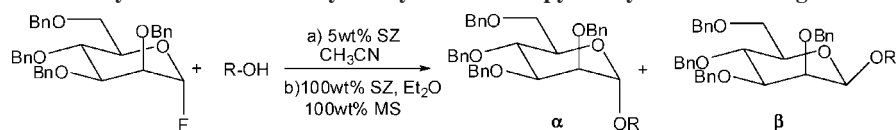
Scheme 14. Stereocontrolled Glycosidations of Totally Benzylated Mannopyranosyl Sulfoxides Using Sulfated Zirconia Catalyst
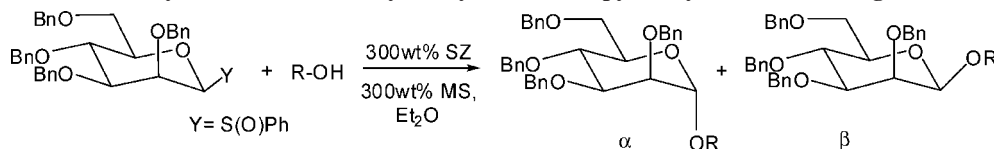
Scheme 15. Synthesis of 2-Deoxyglucopyranosides Employing Sulfated Zirconia Catalyst
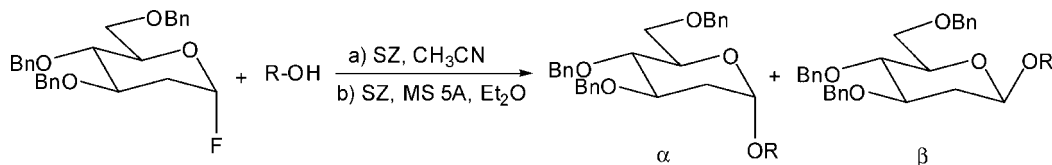
Scheme 16. Probable Mechanism for Glycosidation Reaction Involving Sulfated Zirconia Catalyst
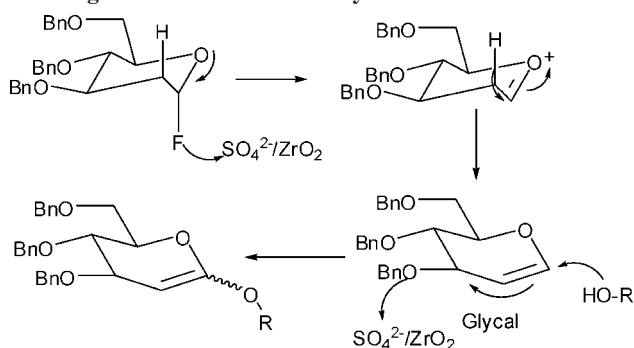
β-stereoselectivity (Scheme 15).[119] A plausible mechanism for glycosidation of 2-deoxyglucopyranosyl α-fluorides with alcohol using SZ has also been proposed.[155] According to it, the 2,3-unsaturated glycoside has been produced by Ferrier reaction of the glycal, as shown in Scheme 16.

7.6. Regioselective Ring-Opening Reactions

Regioselective ring-opening of N-tosyl aziridines with amines, thiols, and potassium thiocyanate has been efficiently performed using SZ catalyst.[120] Also, SZ exhibited good catalytic activity in comparison to other solid acids for regioselective ring-opening of epoxides with amines and N-heterocycles.[156−159]

### 7.6.1. Ring-Opening of Aziridines

Aziridines, apart from being important precursors for the synthesis of many nitrogen-containing biologically active molecules, are attracting lot of attention as versatile intermediates in organic synthesis. Also, there is growing interest in the ring-opening reactions of aziridines with various nucleophiles because of their high reactivity and ease of preparation. As a result, several procedures have been developed for the ring-opening of aziridines with nucleophiles such as hydroxy compounds, organometallics, Wittig reagents, silyl nucleophiles, and amines. The regioselective ring-opening of aziridines with KSCN and thiols provides β-aminothiocyanates and β-aminosulfides, respectively. β-Aminothiocyanates are the precursors of thiazoles or benzothia-

Scheme 17. Ring-Opening of Bicyclic Aziridines with KSCN Involving Sulfated Zirconia Catalyst
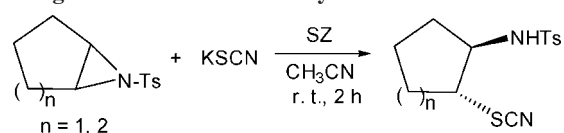
Scheme 18. Ring-Opening of N-Tosyl-2-arylaziridines with KSCN Involving Sulfated Zirconia Catalyst

R = C₆H₅, p-Me-C₆H₄, n-C₄H₉ etc.
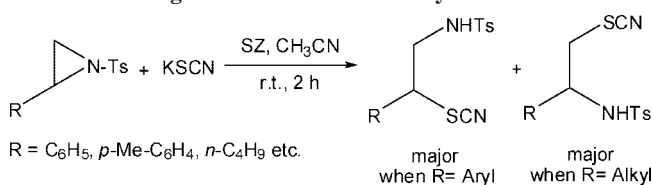
Scheme 19. Ring-Opening of Bicyclic Aziridines with Thiols Involving Sulfated Zirconia Catalyst
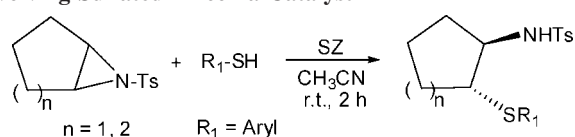
Scheme 20. Ring-Opening of N-Tosyl-2-arylaziridines with Thiol Involving Sulfated Zirconia Catalyst
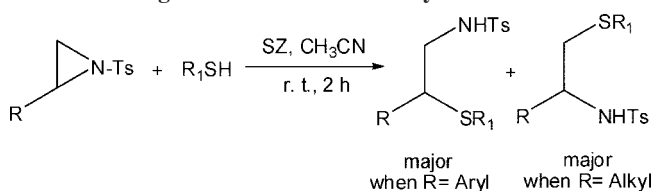
zoles having pesticidal properties,[160] and the β-aminosulfides are the precursors of various bioactive compounds.[161] Das et al.[120] carried out the aziridine ring-opening with KSCN involving SZ catalyst to provide the corresponding β-aminothiocyanates (Schemes 17 and 18), and with thiols to form β-aminosulfides (Schemes 19 and 20).

7.6.2. Ring-Opening of Epoxides

β-Amino alcohols are the key intermediates to many organic compounds, including biologically active natural and synthetic products, and are chiral auxiliaries for asymmetric

Scheme 21. Epoxides Ring-Opening with Anilines Employing Sulfated Zirconia Catalyst
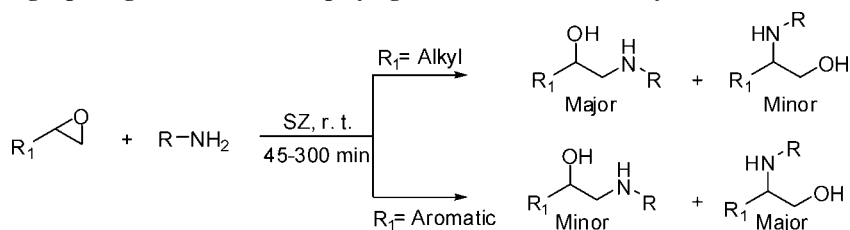
Scheme 22. Epoxides Ring-Opening with Nitrogen Heterocycles Catalyzed by Sulfated Zirconia
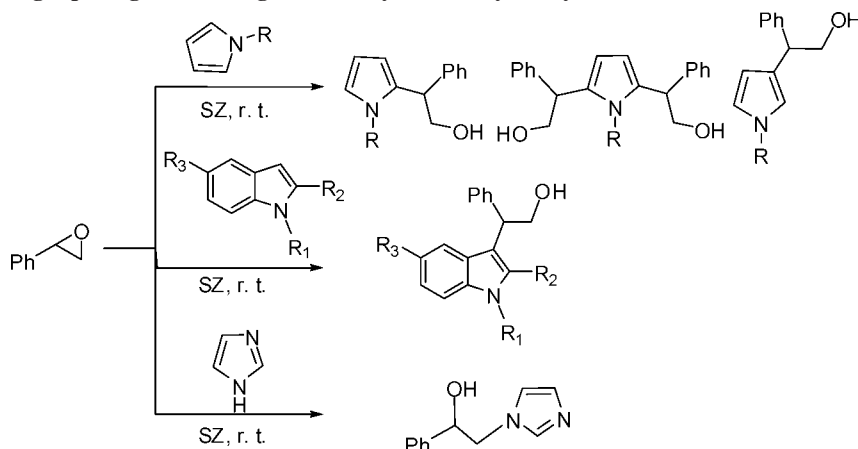
synthesis. β-Amino alcohols are synthesized by acid-catalyzed ring-opening of epoxides. Reddy et al.[157] carried out the ring-opening of cyclohexene oxide, propylene oxide, and styrene oxide with various aromatic amines toward the synthesis of β-amino alcohols catalyzed by SZ, affording high yields of products under solvent-free conditions (Scheme 21); the reaction is regioselective. Also, Negron-Silva et al.[158] employed SZ and SZ/MCM-41 catalysts for the synthesis of β-amino alcohols using various epoxides with aniline or benzyl amine at 60 °C under solventless condition. Both catalysts exhibited good activity, and the used catalysts were recovered and reused without any appreciable loss of their activity.

The SZ catalyst has also been found to be active for the synthesis of alkylated nitrogen heterocycles at room temperature from various epoxides and nitrogen heterocycles such as indoles, pyrroles, and imidazoles in CH_2Cl_2 (Scheme 22).[159]

7.7. Friedel−Craft Alkylations

Friedel−Craft alkylations are ubiquitous reactions in fine chemical, intermediate, and petrochemical industries. The SZ catalyst has been successfully utilized for various Friedel−Craft alkylation reactions.

7.7.1. Alkylation of Diphenyl Oxide with Benzyl Chloride

Yadav and Sengupta[162] investigated the alkylation of diphenyl oxide with benzyl chloride to produce the corresponding benzyldiphenyl oxide products in excellent yields, employing SZ catalyst at 90 °C (Scheme 23). They have also studied the kinetics of the reaction. A Langmuir−Hinshelwood−Hougen−Watson model was found to fit well, which revealed that the reaction is intrinsically kinetically controlled. The in situ generated HCl was desorbed from the reaction mixture, and it did not catalyze the reaction.

Scheme 23. Alkylation of Diphenyl Oxide with Benzyl Chloride Using Sulfated Zirconia Catalyst
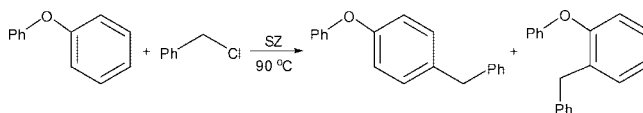
Scheme 24. Sulfated Zirconia Catalyzed Alkylation of Guaiacol
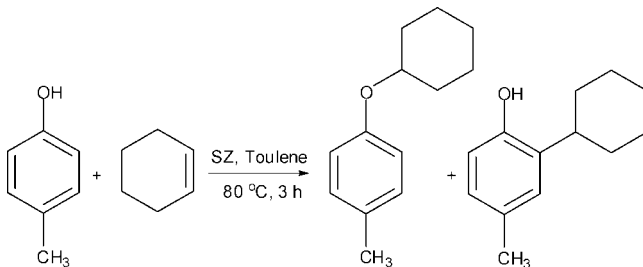
7.7.2. Alkylation of Guaiacol and p-Cresol with Cyclohexene

Yadav et al.[163,164] investigated systematically the O- versus C-alkylation of p-cresol and guaiacol (2-methoxyphenol) with cyclohexene by employing SZ catalyst. They also compared the activity of several solid acid catalysts for this reaction. It was observed that SZ exhibits moderate activity and highest selectivity for O-alkylated product. For the reaction with p-cresol, the conversion was 47% and the selectivity to O-alkylated product (1-cyclohexyloxy-4-methyl benzene) was 82%, which is commercially important as a perfume (Scheme 24). On the other hand, with guaiacol, the conversion was 74% and selectivity to O-alkylated product (cyclohexyl-2-methoxyphenyl ether) was 68%, which is also a promising perfume. Hence, it is desirable to produce these products selectively.

Scheme 25. Sulfated Zirconia Catalyzed *tert*-Butylation of 4-Methoxyphenol
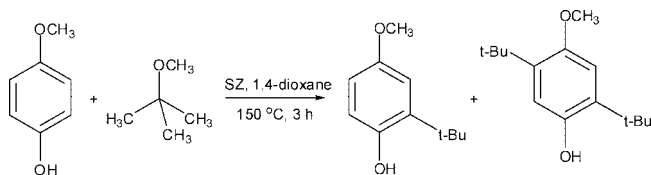
Scheme 26. Sulfated Zirconia-Catalyzed Alkylation of Benzene
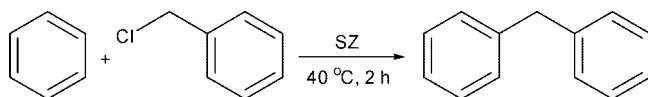
7.7.3. Alkylation of 4-Methoxyphenol with MTBE

The antioxidants most commonly used to stabilize food against auto-oxidation are butylated hydroxytoluene (BHT), butylated hydroxy anisole (BHA), and *n*-propyl gallate. BHA is more in demand, and both mono- and dialkylated products are used as antioxidants. BHA is produced by alkylation of 4-methoxyphenol with methyl *tert*-butyl ether (MTBE). Yadav and Rahuman[165] investigated the alkylation of 4-methoxyphenol with MTBE employing several solid acid catalysts, namely, Filtrol-24, DTP/K-10, Deloxane ASP resin, K-10 montmorillonite clay, and sulfated zirconia. Their study revealed that only two products, 2-*tert*-butyl-4-methoxyphenol and 2,5-di-*tert*-butyl-4-methoxyphenol, are formed with maximum selectivity; both of them are useful as antioxidants either as a mixture or alone (Scheme 25). Filtrol-24 was found to be more active (conversion = 75%) as compared to other solid acid catalysts tested, and SZ was found to be the least active (conversion = 22%) but its selectivity to 2-*tert*-butyl-4-methoxyphenol was maximum (selectivity = 85%). Alkylation of 4-methoxyphenol with MTBE involves two distinct steps. The first one involves the in situ cracking of MTBE, giving methanol and isobutylene, and the other involves the addition of the isobutylene formed with 4-methoxyphenol providing 2-*tert*-butyl-4-methoxyphenol and 2,5-di-*tert*-butyl-4-methoxyphenol via consecutive reactions.

Also, Yadav and Thorat[166] studied the alkylation of *p*-cresol with isobutylene employing SZ catalyst. The SZ was found to be a better catalyst than ion-exchange resins for this reaction.

7.7.4. Alkylation of Benzene with Benzyl Chloride

Katada et al.[167] investigated the alkylation of benzene with benzyl chloride to synthesize diphenylmethane in the liquid phase using 5−30 wt % SZ catalysts. The reaction of benzene with benzyl chloride yielded diphenylmethane with almost 100% selectivity (Scheme 26). The material balance was >90%, whereas the color of the catalyst became light-brown after the reaction, revealing the formation of a small amount of polymerized species. The activity for the alkylation of benzene showed a maximum for 5−15 wt % SO_4^{2-}/ZrO_2 catalysts. Excess sulfate loading suppressed the activity.

7.8. Koach Carbonylation Reaction

Direct transformation of alcohols with carbon monoxide to carboxylic acid is a very attractive process in both industrial and synthetic organic chemistry. Although numerous attempts related to this transformation in strong liquid acid media have been reported by many groups, many of

Scheme 27. Sulfated Zirconia-Catalyzed Conversion of Primary Alcohol to Ethers

n = 1, 2, 3
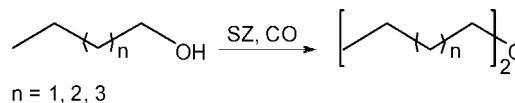
Scheme 28. Koach Carbonylation of Tertiary Alcohol Catalyzed by Sulfated Zirconia

$$ROH \xrightarrow{SZ, CO} \textit{tert}\text{-}RCO_2H$$
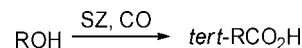
Scheme 29. Sulfated Zirconia-Catalyzed Tetrahydropyranylation of Alcohol and Phenols

R = Alkyl, Aryl
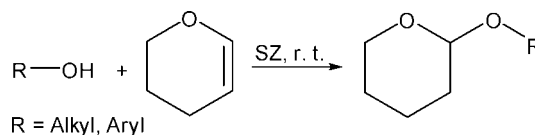
them have been carried out under extremely severe conditions such as high CO pressure and high temperature. Mori et al.[168] investigated the catalytic activity of SZ for Koach carbonylation. In their systematic study, catalytic optimization was carried out by using different sulfated metal oxides (Zr, Ti, Sn, Al, and Fe) and hexane as the solvent for carbonylation of *tert*-butyl alcohol. The SZ catalyst was observed to be the best among various catalysts tested. Commercially available SZ catalyst was found to be less reactive than freshly prepared catalyst. They also studied the effect of temperature and pressure and found that the reaction at 150 °C under 5 MPa pressure is most favorable for high yield of *tert*-carboxylic acid. Interestingly, primary alcohols selectively provided the corresponding ethers in good yields with no carboxylic acids (Scheme 27). On the other hand, reaction with *tert*-butyl alcohol, 1-adamantanol, 3-methyl-3-pentanol, and 2-methyl-2-butanol provided corresponding carboxylic acids in >60% yields (Scheme 28).

7.9. Protection of Alcohols, Phenols, and Aromatic Aldehydes

The use of protecting groups is very important in organic synthesis, often being the key for the success of many synthetic enterprises. The tetrahydropyranylation is one of the most frequently used processes to protect hydroxyl groups in organic synthesis since the resulting ethers have remarkable stability under a variety of reaction conditions, such as strongly basic media, oxidation, oxidative alkylation, reduction, reactions involving Grignard reagents and lithium alkyls, acylation, and so on. *Geminal* or 1,1-diacetates are synthetically useful as aldehyde-protecting groups, as alternatives to acetals. These diacetates are stable toward aqueous acids and mild bases.

Reddy and Sreekanth[169] carried out the tetrahydropyranylation reaction of alcohols and phenols under solvent-free condition employing SZ catalyst (Scheme 29). Reaction of 3,7-dimethyl-octa-2,6-dien-1-ol completed on slight heating, and all other reactions were completed on just addition of the reactants and the catalyst. This is an exothermic reaction, and a slight increase in the temperature indicates that the reaction is taking place.

There is another approach in which methoxymethyl ethers formed due to methoxymethylation of alcohols and phenols are commonly utilized in protecting alcohols and phenols in natural product synthesis. The reagent employed for methoxymethylation is chloromethyl methyl ether, which is no

Scheme 30. Sulfated Zirconia-Catalyzed Protection of Aromatic Aldehydes
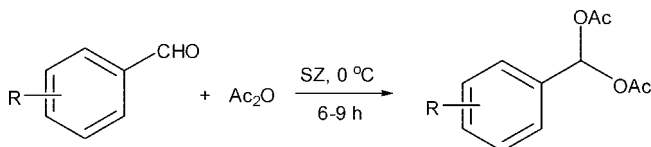
R = H, o-CH₃, p-CH₃, o-OCH₃, p-OCH₃, o-NO₂, p-NO₂ etc.

Scheme 31. Sulfated Zirconia-Catalyzed Condensation of o-Phenylendiamine with Ketones

Scheme 32. Sulfated Zirconia-Catalyzed Dypnone Synthesis from Acetophenone

Scheme 33. Transesterification of Triacetin by Acid or Base Catalysts
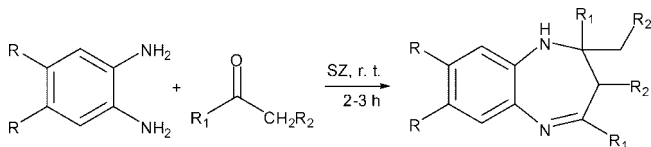
longer appropriate due to its extreme carcinogenicity. For this reason, the condensation of dimethoxymethane with alcohols has been adopted as a safe and sound method. Lin et al.[170] carried out methoxymethylation of cyclohexylmethanol with an excess of dimethoxymethane over various sulfated metal oxides and Nafion NR-50 at ambient temperature. They found that SZ is the best among various catalysts tested, which provided excellent yield (93%) within a short period of time (3 h).

The SZ catalysts were also profitably employed for the protection and deprotection of aldehydes. Thus, a variety of aldehydes and ketones were reacted with acetic anhydride at 110 °C in the presence of commercial SZ catalyst with a specific surface area of 10 m^2 g^{-1} to afford the corresponding 1,1-diacetates.[171] Negrón et al.[58] prepared the SZ catalyst by sol−gel process possessing a surface area of 93 m^2 g^{-1}. They used this SZ catalyst to convert aromatic aldehydes including heteroaromatics to acylals at 0 °C with acetic anhydride in acetonitrile solvent or solvent-free condition, and obtained excellent yields of the corresponding products (Scheme 30). Further, deprotection is carried out by using acylals to aldehyde at 60 °C in acetonitrile solvent employing SZ catalyst.

7.10. Synthesis of 1,5-Benzodiazepine Derivatives

Benzodiazepines are important and interesting compounds, widely used in the past few decades as anticonvulsant, antianxiety, hypnotic, antidepressive, and anti-inflammatory agents.[172] These compounds are also used as dyes for acrylic fibers in photography. In addition, 1,5-benzodiazepines are valuable synthons for the preparation of other fused ring systems such as triazole, oxazino- or furanobenzodiazepines. Reddy and Sreekanth[173] synthesized 2,3-dihydro-1H-1,5-benzodiazepines by the condensation of o-phenylendiamine and various ketones in the presence of SZ catalyst under solvent-free conditions (Scheme 31). Most of the reactions were found to complete within 2−3 h with excellent product yields.

7.11. Synthesis of Dypnone from Acetophenone

Dypnone is a useful intermediate for the production of a large range of compounds. It has been used as a softening agent, plasticizer, and perfumery base. Venkatesan and Singh[174] investigated the synthesis of dypnone from acetophenone by utilizing SZ catalyst. These authors compared the activity of several acid catalysts, namely, SO₄$^{2-}$/TiO₂,
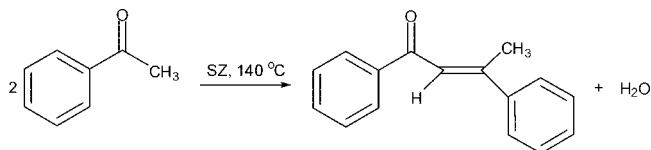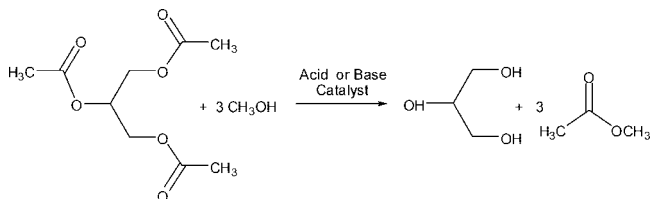
H-β, AlCl₃, and SO₄$^{2-}$/ZrO₂ for dypnone synthesis. They found that SZ exhibits highest acetophenone conversion (40 wt.%) and highest selectivity for dypnone (86%) among various catalysts inestigated (Scheme 32). They also studied the effect of SZ concentration and reaction temperature. The conversion of acetophenone was found to increase markedly up to 2 h of reaction time with an increase of SZ/acetophenone ratio from 0.05 to 0.15. However, for longer reaction times (5 h), the conversion of acetophenone was the same at all catalyst concentrations. Also, increasing the reaction temperature (140, 150, 160, and 170 °C) increased the catalytic activity sharply up to 3 h of reaction time, and the conversion of acetophenone leveled off with further reaction time at all reaction temperatures studied.

7.12. Transesterification

Transesterification is a process where one ester is transformed into another through interchange of the alkoxy moiety. Different groups investigated the transesterification of triacetin with methanol and methyl salicylate with phenol, respectively, by employing SZ catalyst.

Biodiesel is a particularly attractive renewable and environmental friendly fuel because it can be used in existing engines and is readily synthesized from animal fats and vegetable oils. Lopez et al.[175] investigated transesterification of triacetin with methanol (Scheme 33). Triacetin was taken as a model compound for larger triglycerides as found in vegetable oils and fats. They carried out the reaction at 60 °C in a batch reactor with a variety of solid and liquid acid and base catalysts, namely, NaOH, H₂SO₄, Amberlyst-15, Nafion NR50, SZ, tungstated zirconia (13.4 wt % W), silica-supported phosphoric acid (SPA), zeolite H-β, and ETS-10 (Na and K). Among various acid catalysts tested, H₂SO₄ was found to be the most reactive, and only H₂SO₄ and Amberlyst-15 are more active than SZ. In the case of SZ catalyst, triacetin conversion is 57%, and for tungstated zirconia there is 10% conversion.

Salol has got a pleasant taste and odor and is used in suntan lotions and as an antiseptic, anodyne, and pain-relieving agent. Shamsuddin and Nagaraju[176] carried out salol synthesis via transesterification of methyl salicylate with phenol over various solid acid catalysts, namely, ZrO₂, MoO₃, SO₄$^{2-}$/ZrO₂, MoO₃/ZrO₂, poisoned MoO₃/ZrO₂, and poisoned SO₄$^{2-}$/ZrO₂ in the liquid phase with molecular sieves and without molecular sieves. The MoO₃/ZrO₂ and SO₄$^{2-}$/ZrO₂ catalysts were poisoned by exposing them to NH₃ vapors

Scheme 34. Sulfated Zirconia-Catalyzed Synthesis of Diaryl Sulfoxides

R$_1$ = H, OMe, Me etc.; R$_2$ = OMe, Br, Ph
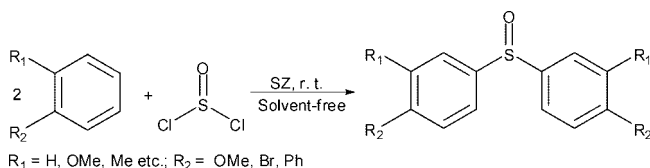
for 15 min and heating to 120 °C for 2 h in an air oven. They found that SZ exhibits the best phenol conversion with moderate selectivity to salol. The SZ with molecular sieves provided more phenol conversion and selectivity for salol than without molecular sieves.

Lopez et al.[177] carried out transesterification of triglycerides with ethanol using modified zirconias, namely, sulfated zirconia, tungstated zirconia, and titania−zirconia. Among these catalysts, titania−zirconia exhibited better activity than the tungstated zirconia for transesterification. Sulfated zirconia was found to be the most active catalyst (on weight basis) for transesterification; however, it exhibited significant sulfur loss, which greatly reduced its long-term activity.

7.13. Synthesis of Diaryl Sulfoxides

Sulfoxides and sulfones have fascinated organic chemists for a long time because of their varied reactivity as functional groups for transformation into a variety of organosulfur compounds. These transformations are highly useful for the synthesis of drugs and sulfur-substituted natural products. Optically active sulfoxides continue to receive tremendous attention as important chiral auxiliaries in asymmetric synthesis and in C−C bond-forming reactions. Synthesis of diaryl sulfoxides also provide a convenient route to triaryl-sulfonium salts, which are employed as photoactive cationic initiators and for the photogeneration of protonic acids in the lithographic resist field. Reddy et al.[121] carried out synthesis of diaryl sulfoxides by taking arene and thionyl chloride (2:1 mol ratio) with a catalytic amount of SZ in a round-bottom flask and stirring for an appropriate time under solvent-free conditions. Diaryl sulfoxides were formed in good-to-excellent yields with various activated and nonactivated arenes (Scheme 34).

7.14. Synthesis of Aromatic *Gem*-Dihalides

The chlorination of aldehydes to the corresponding *gem*-dichlorides is a useful transformation in organic synthesis since the product dichloroarylmethanes are of immense value in the pharmaceutical and agricultural industries. They can be used as starting materials for several C−C coupling reactions and synthesis of imines as well as parent raw materials for synthesis of their corresponding amines, acids, and alcohols.

Wolfson et al.[116] investigated the synthesis of aromatic *gem*-dihalides. They compared the reactivity of various solid acids for the synthesis of benzal chloride from benzaldehyde (23.6 mmol) and benzoyl chloride (47 mmol) at 110 °C for 1 h in dichlorobenzene solvent. Among various solid acids employed, SZ exhibited the best performance (22%) (Scheme 35). Benzoyl chloride was more reactive than acetyl and propionyl chloride. Replacing the chloride with bromide also resulted in increased activity. Performance of the reaction in polar solvent and in benzaldehyde as self-solvent resulted in higher product yields. They also carried out the oxidative regeneration of spent SZ catalyst in air at 550 °C and fully

Scheme 35. Sulfated Zirconia-Catalyzed Condensation of Benzaldehyde and Benzoyl Chloride
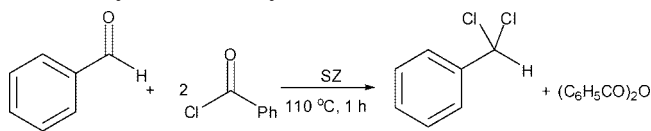
Scheme 36. Sulfated Zirconia-Catalyzed Bis(indolyl)methanes Synthesis

R = H, Me   R$_1$ = Aromatic, heteroaromatic
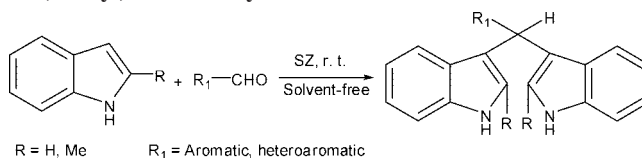
recovered its catalytic activity, which allowed multiple catalyst recycling.

7.15. Synthesis of bis(Indolyl)methane Derivatives

Development of bis(indolyl)alkane synthesis routes has been of considerable interest in organic synthesis because of their wide occurrence in various natural products possessing biological activity and usefulness for drug design. Bis(indolyl)methanes are the most active and highly recommended cruciferous substances for promoting beneficial estrogen metabolism and inducing apoptosis in human cancer cells. The acid-catalyzed electrophilic substitution reaction of indoles with aldehydes is one of the most simple and straightforward approaches for the synthesis of bis(indolyl)methanes. Reddy et al.[121] successfully synthesized bis(indolyl)methanes by the reaction of indole with various aldehydes in the presence of SZ catalyst (Scheme 36). It was observed from this study that SZ is an efficient catalyst for the synthesis of bis(indolyl)methanes in terms of product yields, reaction temperature, and reaction times.

7.16. Isomerization of Longifolene and α-Pinene

Sulfated zirconia is a well-investigated catalyst for various isomerization reactions in the vapor phase such as isomerization of butane,[108−110] pentane,[112] and so on as described earlier. Apart from those, it has also been used as a catalyst for isomerization of longifolene and α-pinene in the liquid phase.

Isomerization of α-pinene produces bicyclic and monocyclic compounds, and various other products. Monocyclic compounds are limonene, terpinolene, and α- and γ-terpinene obtained by means of the rupture of one of the rings, and bicyclic compounds are camphene, tricyclene, and bornylene obtained through a cycle rearrangement (Scheme 37). Grzona et al.,[178] Comelli et al.,[179] and others employed SZ catalyst for isomerization reaction of α-pinene.

Grzona et al.[178] systematically investigated the isomerization of α-pinene in the liquid phase by using 5, 10, and 20 wt % SO$_4^{2-}$/ZrO$_2$ catalysts. An increase of conversion was observed as the amount of sulfuric acid concentration increased and selectivity for camphene was around 0.7 per unit area of catalyst. As the temperature increased from 100 to 153 °C, the conversion also increased from 17 to 99% and selectivity decreased from 84 to 14%.

Comelli et al.[179] also investigated the isomerization reaction of α-pinene employing SZ catalyst and reported similar results. Various catalysts containing 15% SO$_4^{2-}$ over ZrO$_2$ and calcined at different temperatures were investigated

Scheme 37. Isomerization of α-Pinene Utilizing Sulfated Zirconia Catalyst

Camphene   Tricyclene   α-Frenchene   Bomylene

α-Pinene

γ-Terpinene   Limonene   α-Terpinene   Terpinolene   p-Cynene
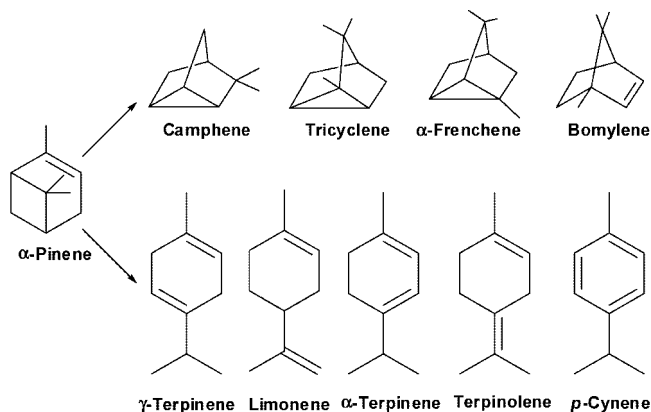
Scheme 38. Isomerization of α-Pinene Oxide Utilizing Sulfated Metal Oxide Catalyst

I   II
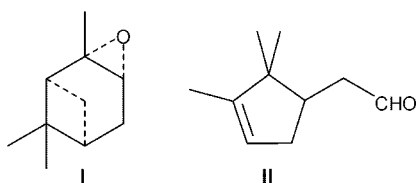
Scheme 39. Mechanism of Sulfated Zirconia-Catalyzed Isomerization of Longifone to Isolongifone

I
Longifolene

II
Iso-longifolene
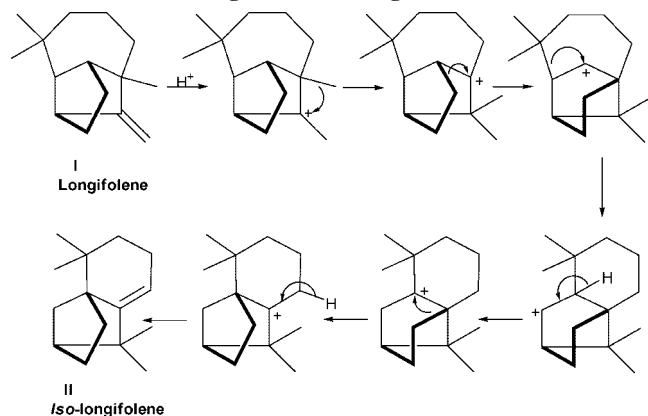
systematically and compared with H_2SO_4 after 2 h of reaction. Almost all catalysts exhibited excellent product yields at 120 °C reaction temperature. They also studied the α-pinene isomerization using Fe−Mn-promoted SZ catalyst and reported excellent product yields.[180]

Flores-Moreno et al.[181] carried out the isomerization of α-pinene oxide (I) to campholenic aldehyde (II) using sulfated metal oxides (Scheme 38). They found that SZ produces 37% campholenic aldehyde at full conversion of the reactant.

Tyagi et al.[182] synthesized nanocrystalline SZ catalyst using sol−gel technique in acidic, basic, and neutral medium. These catalysts were employed for solvent-free isomerization of longifolene to isolongifolene at 180 °C. All catalysts exhibited excellent selectivity (90−93%) with 100% conversion of the substrates. The mechanism of longifolene to isolongifolene is shown in Scheme 39.

7.17. Nitration of Chlorobenzene

Nitration of aromatic compounds is a ubiquitous reaction to produce organic intermediates required in large tonnages

Scheme 40. Sulfated Zirconia Catalyzed Nitration of Chlorobenzene
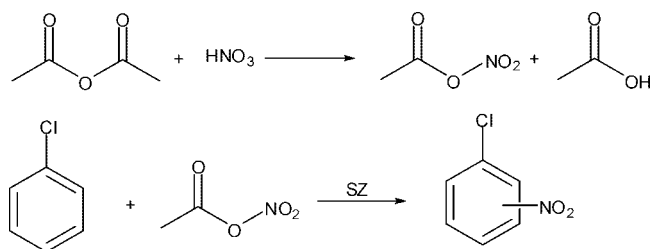

for the fine chemicals industry. Mononitrohalo benzenes, especially *para*-nitrochloro benzene, are versatile intermediates for dyes, pharmaceuticals, and perfumes. Because of the commercial importance of *para*-chloronitro benzene, several studies were carried out to increase the *para*-selectivity. Yadav and Nair[183] investigated the nitration of chlorobenzene using various catalysts including SZ (Scheme 40). Among various catalysts investigated, the SZ provided maximum conversion (47%) with 91% *para*-selectivity in 30 min of reaction. Also, *meta*-products as well as dinitrated byproducts were not formed. After 1.5 h of reaction time, the conversion reached 100% and the *para*-selectivity dropped to 77%.[3]

7.18. Cyclization of 1,4-Dicarbonyl Compounds to Tetrahydroindolones

The general procedure to prepare pyrrole derivatives involves the reaction of an enolizable 1,4-dicarbonyl compound with a dehydrating agent (H_2SO_4, P_2O_5, $ZnCl_2$, etc.) and ammonia or a primary amine, or an inorganic sulfide (Paal−Knorr reaction).[184,185] However, this method suffers from various disadvantages such as severe reaction conditions, use of excess and dangerous reagents, and tedious workup procedure. Negron et al.[186] studied cyclization of 1,4-dicarbonyl compounds and substituted anilines to tetrahydroindolones employing SZ catalyst (Scheme 41). The SZ catalyst was found to exhibit excellent catalytic activity for this cyclization reaction.

7.19. Condensation of Hydroquinone with Aniline and Substituted Anilines

N,N′-Diphenylenediamines are extensively used as antioxidants in rubber manufacturing. These are prepared commercially by acid-catalyzed reaction of hydroquinone with aniline and substituted anilines. The condensation of hydroquinone with aniline and substituted anilines was investigated utilizing SZ catalyst, and it was realized that SZ is comparable to that of PTSA (*p*-toluene sulfonic acid) (Scheme 42).[187] Since SZ is a reusable catalyst, it proved more advantageous. The reactivity order for substituted anilines was found to follow this order: *p*-toluidine > aniline > *o*-toluidine.

Scheme 41. Sulfated Zirconia-Catalyzed Synthesis of Tetrahydroindolones

R = H, 4-CH₃, 4-OCH₃, 4-F, 4-Cl, 4-Br etc
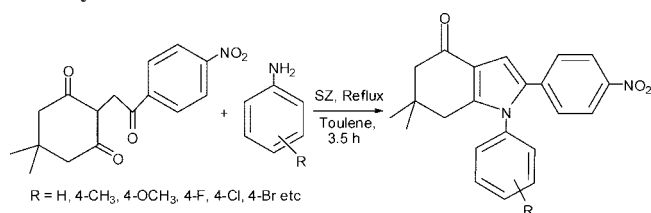
Scheme 42. Sulfated Zirconia-Catalyzed Synthesis of N,N′-Diphenylenediamines
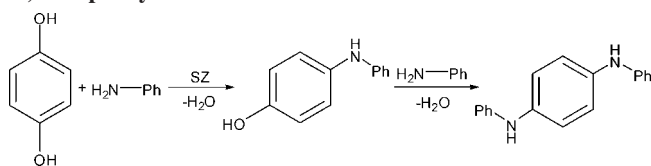
Scheme 43. Sulfated Zirconia-Catalyzed Synthesis of Hydroxyl Coumarines

Scheme 44. Sulfated Zirconia-Catalyzed Synthesis of β-Amino-α,β-Unsaturated Esters and Ketones

Scheme 45. Solid Acid-Catalyzed Esterification of Phthalic Anhydride
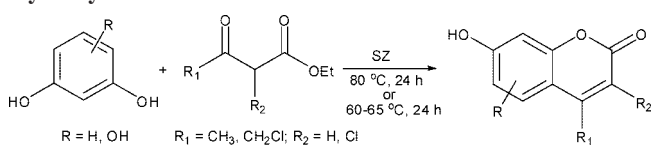
7.20. Cyclodehydration of Diols

Cyclodehydration of diols is a useful method to obtain oxygen heterocycles. Conversion of 1,4-butanediol into tetrahydrofuran is used for the production of solvents and other chemicals on the industrial scale.[188] 2,5-Dihydrofuran is useful as an intermediate in the production of drugs and pesticides.[189] Wali and Pillai[190] investigated cyclodehydration of some 1,n-diols. They also compared the reactivity of various catalysts for cyclodehydration of diethylene glycol. They found that SZ is highly active with respect to time and yield of 1,4-dioxane (mol/g catalyst). They also carried out the cyclodehydration of butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, diethylene glycol (DEG), and triethylene glycol (TEG) employing SZ catalyst (catalyst/diol = 1:25 w/w). Butane-1,4-diol and pentane-1,5-diol furnished the respective cyclic ethers, namely, tetrahydrofuran and tetrahydropyran, in respectable conversion and high selectivity. Hexane-1,6-diol yielded a mixture of oxepine, tetrahydro-2-methyl-2H-pyran, 4-methyl-1-penten-3-ol, hexenols, and dienes. Cyclohexane-1,4-diol also reacted similarly to provide a mixture of products that include oxabicylo[2.2.1]heptane and cyclohexadiene. Both DEG and TEG produced 1,4-dioxane with 89 and 73% selectivity and 83 and 47% conversion, respectively.

7.21. Synthesis of Coumarines

Coumarins are structural units of several natural products and feature widely in pharmacologically and biologically active compounds; many exhibit a high level of biological activity. Besides functionalized coumarins, polycyclic coumarins such as calanolides, isolated from *Calophyllum* genus, and others have shown potent anti-HIV (NNRTI) activity.[191,192]

Rodrı́guez-Domı́nguez and Kirsch[193] carried out the synthesis of hydroxycoumarines using SZ catalyst under solvent-free condition from phenols and acetoacetyl esters (Scheme 43). Coumarines were obtained in moderate-to-good yields. Tyagi et al.[194,195] also investigated the usefulness of SZ catalyst for the synthesis of 7-substituted 4-methylcoumarines. Reaction was conducted employing microwave energy and under solvent-free conditions. The SZ catalyst exhibited good activity for activated *m*-hydroxyphenol substrates, providing the product yields ranging from 78 to 85% within 5−20 min of reaction time at 130 °C. However, under the same experimental conditions, the less activated phenol and *m*-methylphenol were observed to be inactive for the synthesis of coumarins.
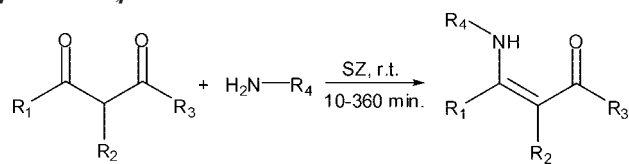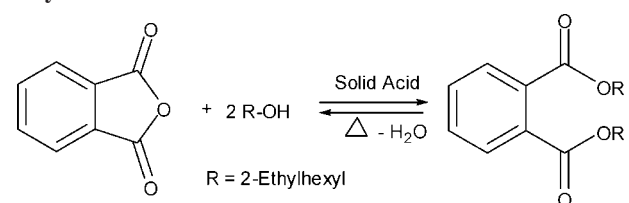
7.22. Synthesis of β-Amino-α,β-Unsaturated Ketones and Esters

β-Amino-α,β-unsaturated esters and ketones are useful synthetic intermediates, particularly in the construction of heterocyclic compounds such as dihydropyridines, pyridines, pyrimidines, indoles, and isothiazoles. Recently, β-amino-α,β-unsaturated acids have also been widely used in the synthesis of β-amino acids and peptidyl mimetics. For the synthesis of β-amino-α,β-unsaturated ketones and esters, condensation of 1,3-dicarbonyl compounds with amines is one of the most simple and straightforward routes. Zhang and Song[196] reported the synthesis of β-amino-α,β-unsaturated esters and ketones from 1,3-dicarbonyl compounds and amine under solvent-free conditions at room temperature (Scheme 44) by using SZ catalyst. Interestingly, the SZ catalyst exhibited a high catalytic efficiency and a high yield of products in short reaction times.

7.23. Esterification Reaction

Dibutylphthalate, dioctylphthalate, dioctyladipate, and diisopentylphthalate are some of the commercially available plasticizers that are usually prepared via esterification reaction between corresponding acids/anhydrides and alcohols in the presence of acidic catalysts. Sejidov et al.[197] carried out the esterification reaction of phthalic anhydride with 2-ethylhexanol in the presence of several solid acid catalysts such as zeolites, heteropolyacids, and SZ under solvent-less conditions (Scheme 45). They observed that SZ exhibits better activity and efficiency among various catalysts investigated. They also carried out the synthesis of important plasticizers and ester base oils through esterification reaction of anhydrides and acids by alcohols in the presence of SZ catalyst. All the esterification reactions studied proceeded smoothly with excellent conversion (>90%) within a short period of time (90−150 min) at 110−190 °C.

Ardizzone et al.[198] synthesized the SZ catalysts by sol−gel method by modulating the conditions of alkoxide hydrolysis and polycondensation steps employing sulfuric acid or $(NH_4)_2SO_4$ as the sulfating agents. They carried out esterification of benzoic acid to methyl benzoate with methanol using SZ catalyst and found that SZ exhibits excellent catalytic activity.

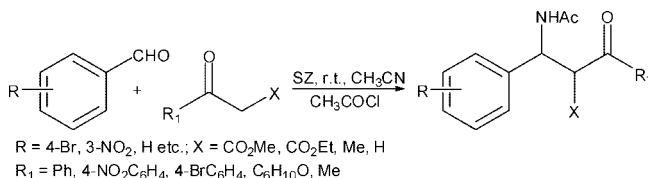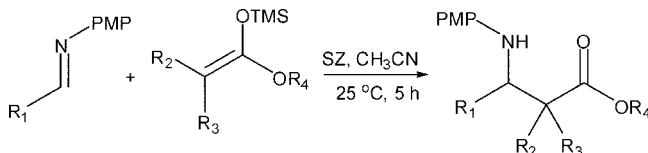**Scheme 46. Mechanism for Sulfated Zirconia-Catalyzed Synthesis of Triazenes from Cyclic Amines**
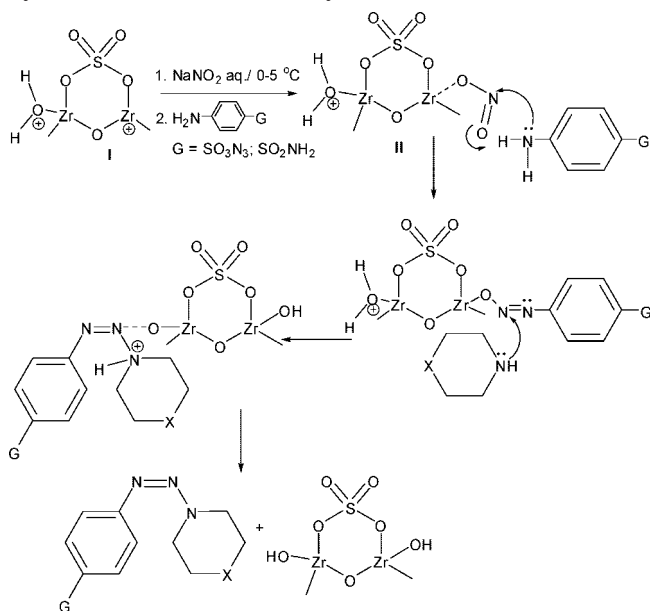
7.24. Synthesis of Triazenes from Cyclic Amines

Dabbagh et al.[199] carried out diazotization and diazocoupling reactions of *para*-aminobenzene-1-sulfonyl azide and *para*-aminobenzene-1-sulfonyl amide with cyclic amines of various ring sizes using different solid acid catalysts, namely, K10, bentonite, kaolin, HZSM-5, and SZ. *para*-Aminobenzene-1-sulfonyl azide or *para*-aminobenzene-1-sulfonyl amide, dilute $NaNO_2$ solution, and solid acid catalyst were mixed to a paste and then cooled down to 0−5 °C. The diazonium−solid acid complex formed was subsequently coupled with cyclic amines. Control reactions were also carried out with the same reagents in the presence of mineral acids like HCl and bases by following the conventional procedure for the purpose of comparison. The product yields observed, *para*-aminobenzene-1-sulfonyl azide in the range of 50−75% and *para*-aminobenzene-1-sulfonyl amide in the range of 40−60%, are found to be slightly lower than the values obtained by employing mineral acids. Structure of SZ before and after the adsorption of sodium nitrite is depicted as I and II in Scheme 46, respectively. They also also proposed the mechanism that is depicted in Scheme 46.

7.25. Synthesis of β-Acetamido Carbonyl Compounds

Multicomponent reactions are becoming a more and more important class of reactions since they allow combining several starting materials in a single compound and in a one-flask operation. β-Acetamido carbonyl compounds are useful building blocks for a number of biologically and pharmaceutically important compounds. β-Acetamido ketones or esters are synthesized by multicomponent reaction of an aromatic aldehyde, acetonitrile, an enolizable ketone or β-ketoester, and acetyl chloride by using SZ catalyst.[200] Different aromatic aldehydes investigated underwent the transformation smoothly (Scheme 47). The conversion was complete at room temperature within 1−3 h, providing excellent isolated product yields (72−94%). Major advantages associated with this protocol include short reaction times, mild reaction conditions, easy workup procedure, and reusability of the catalyst.

Scheme 47. Sulfated Zirconia-Catalyzed Synthesis of β-Acetamido Carbonyl Compounds via Multicomponent Reaction

R = 4-Br, 3-NO$_2$, H etc.; X = CO$_2$Me, CO$_2$Et, Me, H
R$_1$ = Ph, 4-NO$_2$C$_6$H$_4$, 4-BrC$_6$H$_4$, C$_6$H$_{10}$O, Me

Scheme 48. Coordination of H$_2$O with Sulfated Zirconia Catalyst

Scheme 49. Sulfated Zirconia-Catalyzed Mannich-Type Reaction of Ketene Silyl Acetals and Aldimines
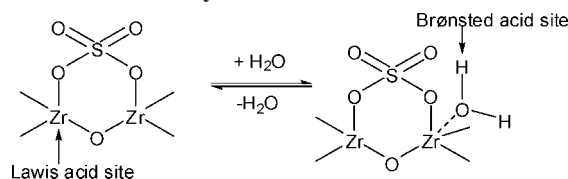
7.26. Mannich-type Reaction

Mannich-type reaction of ketene silyl acetals and aldimines giving β-amino esters in a single step is of considerable importance for synthesizing biologically attractive molecules containing nitrogen atom. The SZ-catalyzed Mannich-type reactions of ketene silyl acetals and aldimines proceeded smoothly at room temperature to afford β-amino esters (Scheme 48) in good-to-excellent yields (65−100%).[201] On the basis of the mechanism of generation of the Brønsted acidic sites by coordination water with the Zr in SZ (Scheme 49), recycling of the catalyst has been easily achieved. Toshima et al.[201] further synthesized the SZ catalyst containing differing water contents by drying the wet catalyst under 2 mmHg at room temperature. It was found that SZ containing more water provides β-amino esters in high yield, while the yield was significantly decreased when the SZ containing less water was used. These results clearly indicated that the reactivity of SZ for the Mannich-type reaction is highly dependent on its water content, and satisfactory results were obtained when SZ containing ∼30 000 ppm water was employed. In addition, it was reported that a mixture of MeCN and H$_2$O (10:1) could be used as an effective solvent.

7.27. Aza-Michael Reaction

The aza-Michael addition is one of the most important reactions in organic chemistry especially for the synthesis of C−N heterocycles containing β-amino carbonyl functionality. Because of the intrinsic importance of β-amino carbonyl compounds, this reaction attracted continued attention in organic synthesis, and the methods of construction of the functionality have undergone a metamorphosis from the classic Mannich-type reaction to the more widely used conjugated addition of nitrogen nucleophiles to α,β-unsaturated carbonyl compounds, which is commonly known as the aza-Michael reaction. The SZ-catalyzed aza-Michael reactions of amines and α,β-unsaturated carbonyl compounds

Scheme 50. Sulfated Zirconia-Catalyzed Michael Addition Reaction
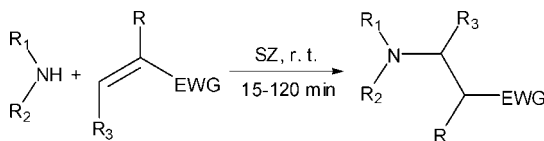
Scheme 51. Chemoselectivity of Sulfated Zirconia-Catalyzed Michael Reaction
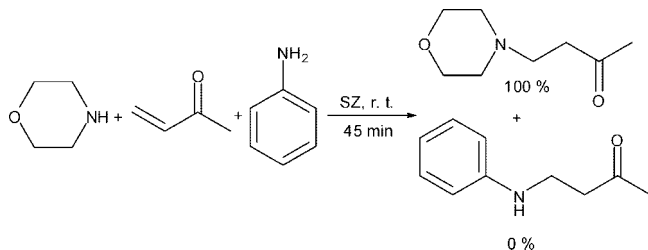
Scheme 52. Sulfated Zirconia-Catalyzed MCR of Aldehyde, Amine, and TMSCN
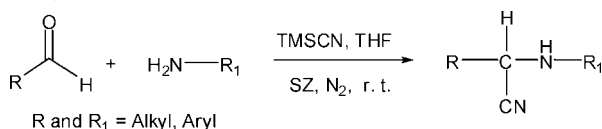
proceeded smoothly at room temperature to afford β-amino carbonyl compounds (Scheme 50) in good-to-excellent yields (70−95%).[30] To check the chemoselectivity aspect, a mixture (1:1) of morpholine and aniline was treated with an excess methyl vinyl ketone in the presence of SZ catalyst, and it was observed that only morpholine adduct was formed as the sole product (Scheme 51).

7.28. Strecker Synthesis

The Strecker reaction, discovered in 1850,[202] has been recognized as the first multicomponent reaction published ever and has a central importance to the life sciences.[203−205] Reddy et al.[206] performed this synthetic methodology by employing various solid acid catalysts. Among sulfate-, molybdate-, and tungstate-promoted zirconia catalysts, SZ was found to be the most efficient catalyst for this reaction (Scheme 52). Also, to evaluate the possibility of 1,3-asymmetric induction, this multicomponent reaction was extended to the preparation of optically active α-aminonitriles derived from (R)-(+)-methylbenzylamine, aldehydes, and trimethylsilyl cyanide (TMSCN). The reaction with both aryl and alkyl aldehydes in each case produced mixtures of diastereoisomers, with one diastereoisomer predominating. From the mechanistic study, it was proposed that the reaction proceeds via the formation of an iminium from the starting amine and aldehyde. This iminium is then trapped by a cyanide ion in situ generated from TMSCN in the presence of solid acid catalyst. However, the iminium formation is equilibrated, and this equilibrium is again influenced by the solid acid catalyst.

Apart from these described above, there are some more examples of liquid-phase reactions in which SZ has been used as a catalyst to provide moderate-to-good activity for synthesis of conjugated nitroalkenes under microwave irradiation,[207] thioacetalization of carbonyl compounds,[208] tetrahydro pyranylation and acetalization reaction,[209] formation of 6-allyl-2,4-di-*tert*-butylphenol from allyl-2,4-di-*tert*-butylphenyl ether,[210] acetylation of benzo-crown ethers,[211]

synthesis of 7-isopropyl-1,1-dimethyltetralin,[212] synthesis of 2,5-di-*t*-butyl-4-fluorophenol,[213] and so on. Arata and co-workers[214,215] investigated Friedel−Crafts benzoylation of alkylbenzenes with benzoic anhydride, and Mukaiyama aldol reaction of 1-trimethylsilyloxy-1-cyclohexene with benzaldehyde catalyzed by solid superacids including SZ catalyst. Very recently, isomerization and arylation of oleic acid was also inestigated using modified zirconia catalysts including SZ and tungstated zirconia.[216]

8. Alternatives to Sulfated Zirconia

Arata and co-workers showed that sulfate-free ZrO₂-based solid superacids could be synthesized by incorporating molybdate or tungstate promoters under certain preparation conditions.[9,97,217,218] The typical H_o values reported for WO$_x$/ZrO₂ and MoO$_x$/ZrO₂ catalysts calcined at 800 °C are −14.6 and −13.3, respectively, which reveal the superacidic character.[111,219]

WO$_x$/ZrO₂ solid acid catalyst is mostly used for vapor-phase reactions.[220−222] Also, it exhibited good catalytic activity in some liquid-phase reactions.[25,223−226] Like tungstated zirconia, molybdated zirconia also exhibited good catalytic activity for certain liquid-phase reactions.[227−229] Though both WO$_x$/ZrO₂ and MoO$_x$/ZrO₂ are considered as solid superacids and free from deactivation disadvantages unlike sulfated zirconia, they are less exploited for organic synthesis and transformation reactions as compared to that of sulfated zirconia.

Many efforts could be found in the literature to improve the activity and stability of the sulfated zirconia catalysts, including promotion of the catalyst with transition metals like Fe, Mn, and Cr and with noble metal Pt.[15,230] Mixed metal oxides often show different forms of acidity from the individual component oxides due to charge imbalance imposed upon the minor component oxide by the imposition of the bond matrix of the major component oxide.[231,232] or charge imbalance resulting from heteroatom linkages and subsequent creation of acid centers.[233,234] The acidity exhibited by supported oxides is incompatible with models that rely on the extent of component mixing and the formation of heterolinkages. It is also reported in the literature that sulfated zirconia-based mixed oxides show more stability and enhanced acidity than the transition/noble metal-promoted sulfated zirconia catalysts alone.[235−238] Three types of mixed oxides, namely, silica−zirconia,[236] alumina−zirconia,[237] and titania−zirconia,[238] were mainly investigated for the sulfation and subsequent catalytic applications. Also, molybdate and tungstate ion-promoted Al₂O₃−ZrO₂ and TiO₂−ZrO₂ and sulfate ion-promoted CeO₂−ZrO₂ were found to exhibit strong solid acidity.[239−242] Also SO₄²⁻, MoO$_x$, and WO$_x$ promoted Al₂O₃−ZrO₂ catalysts exhibited good catalytic activity for acetylation of alcohols and amines with acetic anhydride in the liquid phase, with SO₄²⁻/Al₂O₃−ZrO₂ being the best among them.[232] Mo/TiO₂−ZrO₂ catalyst showed excellent catalytic activity for diacetalization of aldehydes under solvent-free conditions.[240] Most important reactions such as Mannich reaction at room temperature[241] and coumarins synthesis from phenols at 120 °C under solvent-free condition were efficiently catalyzed by SO₄²⁻/Ce$_x$Zr$_{1−x}$O₂ in the liquid phase.[242] These investigations reveal that there is lot of scope to exploit the sulfated as well as sulfate-free solid acid catalysts for numerous organic reactions in the liquid phase.

9. Concluding Remarks

The surface and bulk properties of the solid superacid sulfated zirconia were examined by various spectroscopic and nonspectroscopic techniques, which revealed that the incorporated sulfate ions show a strong influence on the surface and bulk properties of the zirconia. In particular, characterization results suggested that impregnated sulfate ions stabilize the metastable tetragonal phase of ZrO_2 at ambient conditions. Ammonia–TPD and BET surface area results indicated that sulfated catalyst exhibits enhanced acid strength and specific surface area versus that of unprompted ZrO_2. Superacidic character of sulfated zirconia depends on the preparation conditions as well as on the source of protons. The butane isomerization reaction under mild conditions has been taken as a proof of the superacidic nature of sulfated zirconia catalyst. Sulfated zirconia has been found to catalyze efficiently a wide variety of organic syntheses and transformation reactions, facilitating the formation of various biologically and pharmacologically important molecules such as 1,5-benzodiazepines, bis(indolyl)methane derivatives, β-aminothiocyanates, β-aminosulfides, β-aminoalcohols, α- and β-mannopyranosides, 2-deoxy-α- and β-glucopyranosides, dihydropyrimidinones, and so on. MO_x and WO_x modified zirconia also exhibit comparable activity for certain organic reactions. Sulfated zirconia catalysts could be modified with various transition and noble metals such as Pt, Pd, Ir, Fe, Mn, etc., which were found to exhibit better catalytic activity. Among these modifying agents, Pt, Fe, and Mn tend to exhibit better catalytic activity. Also, some sulfated binary oxides showed strong acidic properties and excellent catalytic activity. Sulfated zirconia and its promoted versions are much more promising for various organic reactions of practical significance and are expected to gain great interest in the coming years.

10. Acknowledgments

11. References

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