

Modified zirconia solid acid catalysts for organic synthesis and transformations

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Abstract

A series of sulfate, molybdate and tungstate promoted ZrO_2 catalysts were prepared by wet impregnation method. To incorporate these promoters to $Zr(OH)_4$, sulfuric acid, ammonium heptamolybdate, and ammonium metatungstate were used as precursors, respectively. Further, a Pt promoted Mo- ZrO_2 catalyst was also prepared separately by impregnating with hexachloroplatinic acid. The surface and bulk properties of various promoted ZrO_2 catalysts were investigated by means of X-ray powder diffraction, BET surface area, ammonia-TPD, and Raman spectroscopy techniques. The unpromoted ZrO_2 when calcined at 873 K exists in the crystalline form with monoclinic phase dominating over the tetragonal phase. Incorporation of various promoters into $Zr(OH)_4$ shows a strong influence on the bulk and the surface properties. Addition of promoters enhanced the tetragonal zirconia phase and the surface acidity. In the case of Pt/Mo- ZrO_2 catalyst, a complete tetragonal ZrO_2 phase is observed. The ammonia-TPD results indicate that the impregnated sulfate ions show a strong influence on the acidity of ZrO_2 , which is followed by molybdate. The prepared catalysts were evaluated for various organic synthesis and transformation reactions in the liquid phase. All catalysts exhibit good catalytic activity for synthesis of diphenylureas, coumarines and 1,5-benzodiazepines, acylation of alcohols, phenols and amines, and protection of carbonyl compounds. In particular, the sulfate and molybdate promoted catalysts exhibited excellent catalytic activity.

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1. Introduction

Acid catalysts play a predominant role in organic synthesis and transformations. Many organic reactions such as alkylation, acylation, isomerization, nitration, esterification, and rearrangements like pinacol, Beckman, etc. are accomplished by acid catalysts. All these acid catalyzed reactions are mostly carried out by employing conventional mineral acids like H_2SO_4 , HNO_3 , and HF or Lewis acids such as $AlCl_3$ and BF_3 . In view of environmental and economical reasons, there is an ongoing effort to replace the conventional catalysts with newer solid acids. This is mainly due to the dis-

tinct advantage of solid acid catalysts such as non-toxicity, non-corrosiveness, ease of handling, less expensive, and easy to recover and reuse [1–6]. In this direction, various solid acid systems were introduced which include heteropolyacids, ion exchange resins (Amberlyst and Nafion-H), zeolites, and clays. The main disadvantage associated with heteropolyacids is that they are fairly soluble in polar solvents and lose their activity at higher temperatures by losing structural integrity. To prevent this there are some attempts to immobilize them in silica or activated carbon matrix, which however limits the accessibility and efficiency of the catalysts. Ion exchange resins pose various problems like poor thermal stability and low specific surface area. Styrene based resins like Amberlyst is stable up to 393–413 K and its acid strength and surface area are not very high ($H_0 = -2.2$, $SA = 0.4 \text{ m}^2 \text{ g}^{-1}$). Nafion-H exhibits better thermal stability (533–553 K) and acidity than

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Amberlyst but possesses less surface area ($H_0 = -12$ to -13 , $SA = 0.02 \text{ m}^2 \text{ g}^{-1}$) [5]. Although clays and zeolites are quite reliable, activities of these materials are much lower than the conventional homogeneous acids due to pore blocking and hydration. In view of these reasons there is an ongoing effort to develop stronger solid acid systems which are water tolerant, stable at high temperatures and suitable for both liquid and vapor phase conditions. Metal oxide based 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 the solid superacid catalysts reported, sulfated zirconia gained much attention due to its high activity to catalyze many reactions even at low temperatures [10–12]. However, it gets deactivated 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 down stream contamination. Arata and Hino reported that the solid superacids could be synthesized by incorporating WO_3 or MO_3 into Zr- or Ti-hydroxides under certain preparation conditions [13,14]. Activity of these oxides depends on various parameters such as nature of precursors, precipitation procedure, concentration of dopant, and calcination temperature [8]. In the case of sulfated catalysts, nature of sulfating agent and sulfation procedure also play a crucial role [15]. Variation in any of these parameters can drastically affect the resultant catalytic activity of these materials. Many research groups have studied these systems and explored them in petroleum industry, particularly for isomerization of light alkanes [16–18]. However, these catalysts are not exploited in the areas of fine chemicals synthesis. Therefore, a comprehensive investigation was undertaken on promoted zirconia catalysts for organic synthesis and transformation reactions in the liquid phase. In this study sulfate, molybdate and tungstate promoted zirconia catalysts were prepared and characterized by various physico-chemical techniques namely, X-ray diffraction, BET surface area, ammonia-TPD, and Raman spectroscopy. The prepared catalysts were evaluated for various commercially important organic reactions.

2. Experimental section

2.1. Catalyst preparation

Zirconium hydroxide was prepared from an aqueous solution of ZrOCl_2 (Aldrich, GR Grade) by adding dilute NH_4OH drop-wise from a burette up to pH 8. The obtained precipitate was washed several times until free from chloride ions and dried at 393 K for 48 h. To prepare sulfated ZrO_2 , a 0.5 M sulfuric acid solution (30 ml) was poured into the finely powdered $\text{Zr}(\text{OH})_4$, dried at 393 K for 12 h and calcined at 923 K for 4 h. To impregnate molybdate and tungstate promoters (6 mol%), the desired quantity of ammonium heptamolybdate and ammonium metatungstate were dissolved in excess water sepa-

rately and to which the powdered $\text{Zr}(\text{OH})_4$ was added. The excess water was evaporated on a water-bath with vigorous stirring, oven dried at 383 K for 12 h, and calcined at 923 K for 4 h in air atmosphere. To prepare Pt/Mo-ZrO₂ catalyst (0.5 wt.% Pt), the powdered Mo-ZrO₂ sample was added to the 5% solution of hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$). The excess water was evaporated on a water-bath and the resulting sample was oven dried at 393 K for 12 h and calcined at 973 K for 4 h.

2.2. Catalyst characterization

The powder X-ray diffraction patterns of various samples have been recorded on a Siemens D-5000 diffractometer by using $\text{Cu K}\alpha$ radiation source and scintillation counter detector. The XRD phases present in the samples were identified with the help of JCPDS data files. A conventional all glass volumetric high vacuum (up to 1×10^{-6} Torr) system was used for BET surface area measurements. The BET surface areas were measured by nitrogen physisorption at liquid nitrogen temperature by taking 0.162 nm^2 as the area of cross section of N_2 molecule. Raman spectra were recorded at ambient temperature on a DILOR XY spectrometer equipped with a CCD detector. The spectra were recorded in the range of $4000\text{--}100 \text{ cm}^{-1}$ and a spectral resolution of 2 cm^{-1} using the 514.5 nm exciting line from an argon ion laser (Spectra Physics, USA).

The temperature programmed desorption (TPD) measurements were carried on an AutoChem 2910 instrument (Micromeritics, USA). A thermal conductivity detector was used for continuous monitoring of desorbed ammonia and the areas under the peaks were integrated using GRAMS/32 software. Prior to TPD studies, the samples were pretreated at 473 K for 1 h in a flow of ultra pure helium gas (40 ml min^{-1}). After pretreatment, the sample was saturated with 10% ultra pure anhydrous ammonia gas (balance He, 75 ml min^{-1}) at 353 K for 2 h and subsequently flushed with He (60 ml min^{-1}) at 373 K for 2 h to remove the physisorbed ammonia. The heating rate for the TPD measurements, from ambient to 1023 K, was 10 K min^{-1} . All flow rates mentioned are at normal temperature and pressure (NTP).

2.3. Catalyst evaluation

All chemicals and solvents used in this study were commercially available and used without further purification. All the reactions were carried out in the liquid phase batch mode. These were carried out by taking a mixture of reactants, catalyst and a suitable solvent (some reactions were carried under solvent free conditions) in a round bottom flask provided with a condenser and stirred/refluxed for appropriate times. Completion of the reaction was monitored by TLC. After completion of the reaction, catalyst was recovered by simple filtration and reused. The products were recovered from the filtrate, concentrated on a rotatory evaporator and chromatographed on a silica gel column to offered pure

products. The isolated products were analyzed by ^1H NMR, mass spectroscopy methods and compared with authentic samples.

3. Results and discussion

3.1. Influence of promoters

The XRD patterns of zirconia and promoted zirconia catalysts are shown in Fig. 1. The corresponding phase composition and crystallite size measurements are presented in Table 1. The hydrous zirconia sample calcined at 923 K is in a poorly crystalline form with a mixture of monoclinic and tetragonal phases. A strong influence on the phase modification from thermodynamically more stable monoclinic to the metastable tetragonal phase can be observed when various dopants are incorporated into the $\text{Zr}(\text{OH})_4$ structure. It is well known from the literature that the tetragonal phase of zirconia is more active in catalysis [9]. Generally, the tetragonal phase of zirconia can be stabilized by incorporating the promoters like lanthanum, cerium, and yttrium into the zirconia lattice [19]. The present investigation reveals that all the incorporated promoters stabilize the tetragonal phase at ambient conditions. The incorporation of various promoters into the zirconia system may limit the formation of large ZrO_2 crystallites with the consequent stabilization of tetragonal phase [19,20]. It can be observed from XRD results (Fig. 1 and Table 1) that the sulfated zirconia shows smaller crystallite size and more tetragonal phase when compared to molybdated and tungstated catalysts. A complete tetragonal phase can be observed in the case of Pt/Mo-ZrO₂ catalyst, whereas in the case of Mo-ZrO₂, and W-ZrO₂ catalysts the tetragonal phase dominates over the monoclinic phase. A through examination of the XRD lines further indicates that the molybdate shows relatively strong influence than tungstate on the monoclinic to tetragonal phase transformation of ZrO_2 . Specific surface areas of all the promoted catalysts are higher than that of ZrO_2 (Table 1). Among all these catalysts, sulfated zirconia shows higher specific surface area followed by Pt/Mo-ZrO₂, Mo-ZrO₂, and W-ZrO₂, respectively. The loss in the surface area of W-ZrO₂ sample may be due to penetration of the doped W-oxide into the pores of the zirconia. Where as in the case of Mo-ZrO₂ and Pt/Mo-ZrO₂ samples the observed large specific surface areas could

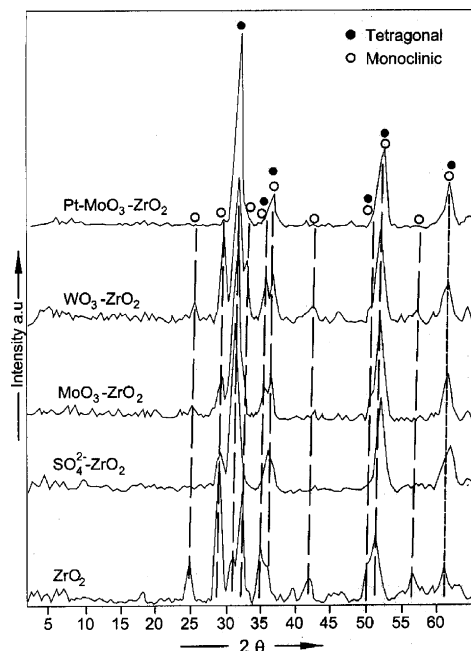


Fig. 1. X-ray powder diffraction patterns of pure and promoted zirconia samples calcined at 923 K. (●) Characteristic lines due to tetragonal zirconia; (○) characteristic lines due to monoclinic zirconia.

be explained as due to the formation of Mo–O–Zr linkages resulting in the formation of porous materials [21]. These results are in agreement with the earlier published reports where sulfation inhibited the crystal growth and increased the surface area and stabilized the tetragonal phase of zirconia [7,8,12,22].

The ammonia-TPD results (Table 1) revealed that there are at least two types of different acid sites on all the investigated samples. The total amount of ammonia desorbed in the case of sulfate and Pt/Mo-, Mo-promoted samples was observed to be higher than that of W-promoted sample. It appears from the NH_3 -TPD results that sulfate and molybdate promoters exhibit a strong influence on the surface acidity of the zirconia.

Raman spectra of unpromoted and promoted zirconia samples are shown in Fig. 2. Normally, crystalline zirconia shows characteristic Raman bands in the range 150–700 cm^{-1} [23]. The spectrum of the ZrO_2 calcined at 873 K exhibit the Raman bands pertaining to a mixture of monoclinic (180, 188, 221, 331, 380, 476, and 637 cm^{-1}) and tetragonal (148, 290,

Table 1

BET surface area, total acidity, and amount of monoclinic and tetragonal phases of ZrO_2 and their crystallite size in various catalysts

Entry	Catalyst	BET SA ($\text{m}^2 \text{g}^{-1}$)	NH_3 desorbed (ml g^{-1})	Monoclinic ZrO_2		Tetragonal ZrO_2	
				Amount (%)	Size (nm)	Amount (%)	Size (nm)
1	ZrO_2	42	5	76	11.2	24	13.0
2	$\text{SO}_4^{2-}/\text{ZrO}_2$	100	16	20	07.3	80	12.3
3	Mo-ZrO ₂	94	11	16	08.5	84	14.3
4	W-ZrO ₂	35	9	32	11.9	68	16.2
5	Pt/Mo-ZrO ₂	98	11	–	–	100	12.8

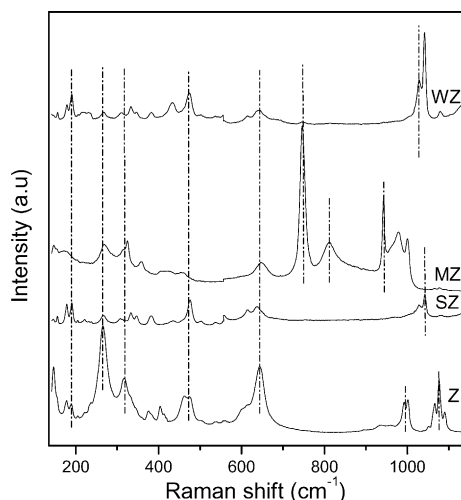


Fig. 2. Raman spectra of pure and promoted zirconia samples in the range of 140–1060 cm^{-1} : (Z) ZrO_2 ; (SZ) $\text{SO}_4^{2-}/\text{ZrO}_2$; (MZ) Mo-ZrO_2 ; (WZ) W-ZrO_2 .

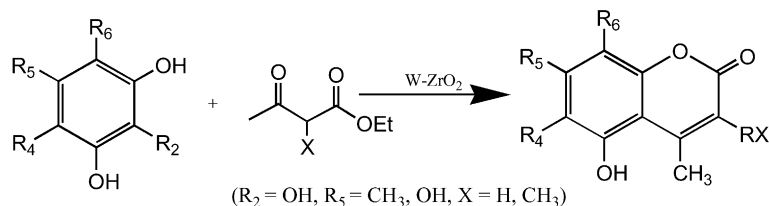
311, 454, and 647 cm^{-1}) phases and the lines due to tetragonal phase are less intense than the lines due to monoclinic phase [16,24]. Whereas in the spectra of sulfate, molybdate and tungstate promoted catalysts bands representing the tetragonal phase are intense. The Pt/Mo- ZrO_2 and Mo- ZrO_2 catalysts exhibited a similar spectrum. In the case of sulfated zirconia catalyst the band at 1032 cm^{-1} with a shoulder can be attributed to the hydrated sulfated groups [25]. Crystalline WO_3 shows characteristic Raman bands at 807, 715, and 274 cm^{-1} [16]. Absences of these bands indicate that microcrystalline WO_3 is not formed on the surface of W- ZrO_2 catalyst. These results agree well with the XRD results where no independent peaks due to crystalline WO_3 are observed. The band at 1020 cm^{-1} assigned to $\text{W}=\text{O}$ stretching mode is normally observed for mono- and polytungstate species. The presence of shoulder peaks at high frequency region indicates the presence of geometrically different WO_x species on the surface [24]. These may be octahedrally and tetrahedrally coordinated WO_x species. The well-crystallized MoO_3 shows characteristic Raman bands at 998 cm^{-1} ($\text{Mo}=\text{O}$), 821 and 668 cm^{-1} ($\text{Mo}-\text{O}-\text{Mo}$) [25]. The Mo- ZrO_2 sample treated 923 K exhibits two additional bands at 746 and 943 cm^{-1} which suggest the formation $\text{Zr}(\text{MoO}_4)_2$ compound between zirconia and molybdenum [21,26]. However, the XRD peaks

corresponding to $\text{Zr}(\text{MoO}_4)_2$ are not observed. Here too the absence of all characteristic bands due to crystalline MoO_3 suggests that the impregnated molybdenum oxide strongly interacted with the zirconia.

Incorporation of platinum has often been reported to induce significant changes in the nature and acidity of promoted ZrO_2 catalysts [7]. In particular, Pt addition makes the catalyst bifunctional with acidic and noble metal properties together. In the case of platinum promoted Mo- ZrO_2 catalyst only tetragonal phase is observed. In the presence of hydrogen, platinum prevents rapid deactivation of the catalyst by supplying hydrogen to acid sites in isomerization reactions [27]. There are some reports, which predict that the impregnated platinum creates Brønsted acid sites by hydrogen spillover from metallic platinum particles [28]. Hattori et al. reported that heating the platinum promoted tungstated zirconia in the presence of hydrogen creates Brønsted acid sites at the expense of Lewis acid sites [29]. In view of its significance, a Pt promoted Mo- ZrO_2 catalyst was prepared in this investigation. Indeed, this catalyst exhibits excellent catalytic property in line with other promoted ZrO_2 catalysts.

3.2. Catalytic activity for synthesis of coumarins

Coumarins belong to the benzopyrone class of compounds that are present in many natural products. These compounds have great biological importance. Many coumarin derivatives act as antibiotics. Generally, coumarins are prepared by the Pechmann reaction, that is, condensation of phenols with malic acid or with β -keto ester in which sulfuric acid is used as the catalyst [30]. Recently many alternatives to sulfuric acid were reported which include zeolites, clays, and sulfonic acid resins [31,32]. However, most of the reported catalysts suffer from various drawbacks such as rapid catalyst deactivation and long reaction times, and some of the reagents used are expensive. To overcome these difficulties, we employed the promoted ZrO_2 catalysts for the synthesis of substituted coumarins from resorcinol and substituted resorcinols with ethyl acetoacetate and ethyl- α -methylacetoacetate (Scheme 1) [33]. All catalysts exhibited good to excellent yields for this reaction. The results obtained with W- ZrO_2 catalyst are summarized in Table 2. From entries 1–4 the reaction was carried out with ethyl acetoacetate, and from entries 5–8 the reaction was carried out with ethyl- α -methylacetoacetate.

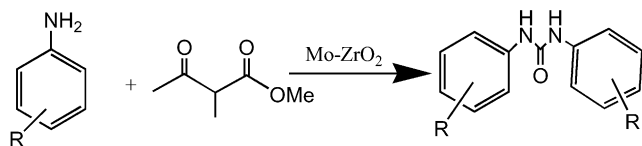


Scheme 1.

Table 2
W-ZrO₂ solid acid catalyzed synthesis of coumarins

Entry	Substrate	Product yield
1	Resorcinol	80
2	5-Methyl resorcinol	70
3	2-Hydroxy resorcinol	65
4	5-Hydroxy resorcinol	56
5	Resorcinol	67
6	5-Methyl resorcinol	65
7	2-Hydroxy resorcinol	60
8	5-Hydroxy resorcinol	50

Note: From entries 1–4 the reaction is carried out with ethyl acetoacetate; from entries 5–8 the reaction is carried out with ethyl- α -methylacetoacetate.



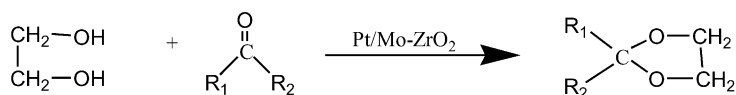
Scheme 2.

Table 3
Synthesis of diphenylureas catalyzed by Mo-ZrO₂ solid acid catalyst

Entry	Substrate	Product yield
1	Aniline	70
2	Methylaniline	75
3	Methoxyaniline	58
4	Hydroxyaniline	72
5	Chloroaniline	70
6	Fluoroaniline	65

3.3. Synthesis of diphenylureas

In recent years diphenylureas gained tremendous interest towards their synthesis due to their diverse applications in various domains like tranquilizing and antidiabetic drugs, antioxidants in gasoline, and corrosion inhibitors. The conventional method for the synthesis of diphenylureas is based on phosgene, carbonates, carbamates or carboxylic acid derivatives [34,35]. However, phosgene and isocyanates are highly toxic and expensive to handle. Therefore, there is an ongoing interest in the catalytic synthesis of ureas via phosgene free routes. The promoted ZrO₂ catalysts were employed to perform this reaction with non-toxic methyl acetoacetate as carboxylating agent (Scheme 2) [36]. This reaction was carried out at 453 K with substituted anilines and β -keto ester by using 1,2-dichlorobenzene as the solvent. All promoted catalysts exhibited good catalytic activity. The results of the experiments carried out with Mo-ZrO₂ catalyst and with various substituted diphenylamines are summarized in Table 3.



Scheme 3.

Table 4
Pt/Mo-ZrO₂ solid acid catalyzed protection of carbonyl compounds

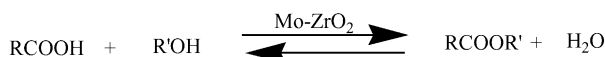
Entry	Substrate	Product yield
1	Cyclopentanone	98
2	Cyclohexanone	93
3	Cycloheptanone	84
4	Acetophenone	87
5	Cinnamaldehyde	40
6	4-Methoxy benzaldehyde	80
7	4-Nitro benzaldehyde	65
8	4-Chloro benzaldehyde	95

3.4. Protection of carbonyl compounds

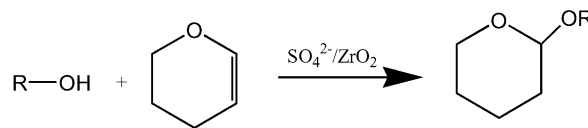
The carbonyl group protection is a commonly used reaction in organic chemistry. In most of the multistep organic synthesis processes carbonyl group should be protected from the nucleophilic attack until its electrophilic property is utilized. The frequently used processes for the carbonyl group protection are acetalization or thio-acetalization [37]. We have carried out the selective protection of various aldehydes and ketones with ethane-1,2-diol as protecting group by using various promoted ZrO₂ catalysts (Scheme 3). In all the experiments 1,3-dioxolane was obtained exclusively in good yields and in short reaction times. All catalysts exhibited excellent product yields. In particular, the Pt/Mo-ZrO₂ catalyst exhibited remarkable activity for the carbonyl group protection as presented in Table 4. It also converted the α,β -unsaturated carbonyl compounds into oxolanes without effecting the double bond [38].

3.5. Catalytic activity for esterification reactions

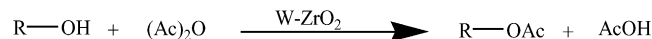
Esters are the compounds of considerable interest due to their diverse applications in many areas of chemical industry. Esters are useful as solvents, artificial flavors, plasticizers, essences, and in perfumery industry. General methods available for the preparation of esters include reaction between acid and alcohol, anhydride and alcohol, acid chloride and alcohol, and transesterification [37,39]. The conventional catalyst used in esterification reactions is sulfuric acid, which presents many drawbacks. Importantly it is toxic, corrosive and causes environmental problems by producing large amounts of byproducts. It is also difficult to recover from the reaction mixture. Many alternatives were reported in the literature for the preparation of esters including zeolites, heteropolyacids, silica-supported sulfuric acid, and Ti-loaded montmorillonite [40–42]. We have employed various promoted ZrO₂ catalysts for this reaction. As in the previous cases, all catalysts exhibited excellent catalytic activity. In



Scheme 4.



Scheme 5.



Scheme 6.

Table 5

Esterification of alcohols catalyzed by Mo-ZrO₂ solid acid catalyst

Entry	Carboxylic acid	Alcohol	Yield
1	Acetic acid	Butanol	95
2	Acetic acid	Isobutanol	85
3	Benzoic acid	Butanol	57
4	Acetic acid	Ethylene glycol	63
5	Acetic acid	Benzyl alcohol	71
6	Oxalic acid	Methanol	77
7	Malonic acid	Methanol	95

this process various esters were synthesized in good yields from both aliphatic, aromatic alcohols and acids [43]. Since esterification is a reversible reaction, an excess of alcohol was taken in the reaction to shift the equilibrium to right-hand side (Scheme 4). The results obtained with Mo-ZrO₂ catalyst are presented in Table 5.

3.6. Tetrahydropyranylation of alcohols and phenols

Protection of hydroxyl group is an important and frequently used process in organic synthesis mainly in carbohydrate, peptide, and steroid chemistry [37]. Under acidic conditions alcohols and phenols react with 3,4-dihydro-2H-pyran (DHP) to give tetrahydropyranyl ethers. These THP ethers are stable under a variety of reaction conditions including reduction, oxidation, strongly acidic and basic media [44]. Many reagents were employed for this reaction in the literature, which include hydrochloric acid, Al-ZnCl₂, HY-zeolite, Nafion-H, montmorillonite clay, boron trifluoride-diethyl ether complex, *p*-toluenesulfonate, supported heteropolyacids, and metal triflates [45–47]. Most of the reagents employed are expensive and require stringent reaction conditions. We have carried out these transformations with less expensive, environmentally benign, and reusable promoted ZrO₂ catalysts under solvent free conditions at room temperature [48]. Under these conditions tetrahydropyranyl ethers were produced in excellent yields at less reaction times. The catalytic results obtained with sulfated zirconia are summarized in Table 6 (Scheme 5).

Table 6

Sulfated ZrO₂ catalyzed tetrahydropyranylation of alcohols and phenols

Entry	Substrate	Product yield
1	Benzyl alcohol	94
2	3-Methoxybenzyl alcohol	96
3	Phenol	82
4	2-Nitrophenol	90
5	Geraneol	91
6	2-Butanol	94
7	4-Benzyloxyphenol	86
8	Cinnamyl alcohol	92

3.7. Acetylation of alcohols, phenols and amines

Acylation of alcohols is an important method for preparing organic esters, which are valuable intermediates for the production of fine chemicals (Scheme 6). Acylation is frequently used for the derivatization and characterization of alcohols and also for further transformations in organic chemistry [37]. Generally, acylation of alcohols can be effected with compounds having activated acyl groups like acid anhydrides and acylchlorides. Traditionally the acylation reactions are carried out in the presence of basic catalysts such as 4-dimethylaminopyridine (DMAP), 4-pyrrolidinopyridine, tributyl phosphene, Lewis acids like AlCl₃, FeCl₃, BF₃, indium(III) chloride and with conventional Brønsted acids like sulfuric acid, polyphosphoric acid, and with metal triflates [49–51]. The conventional acylation reactions require Lewis acid catalysts or amine base catalysts in stoichiometric quantities. These catalysts form complexes with both the acylating agents and the products thus restricting their reuse. The use of strong mineral acids leads to several disadvantages as outlined earlier. Therefore, there is an ongoing effort to look for efficient catalysts. We have employed promoted ZrO₂ solid acid catalysts for the direct acylation of various alcohols and phenols with acetic anhydride into their acetates under mild reaction conditions [52]. All catalysts effected the transformations smoothly at ambient conditions and the acetates were produced in high purity and in excellent yields. Table 7 shows the catalytic results with W-ZrO₂ for the acylation of alcohols and phenols.

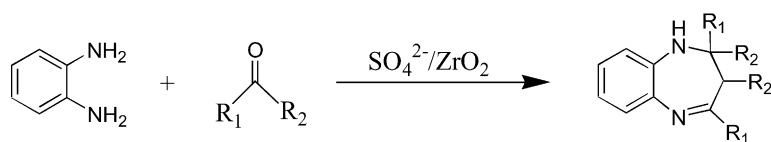
3.8. Synthesis of 1,5-benzodiazepines

Benzodiazepines and their polycyclic derivatives are important class of bioactive compounds. They are known to

Table 7

W-ZrO₂ solid acid catalyzed acetylation of alcohols phenols and amines

Entry	Substrate	Product yield	Time (h)
1	Methanol	95	4
2	Geraneol	97	2
3	4-Nitrobenzyl alcohol	92	4
4	4-Methyl phenol	90	3
5	Resorcinol	92	3
6	Cinnamyl alcohol	89	3
7	Benzylamine	95	1
8	Cyclohexylamine	98	1



Scheme 7.

Table 8
Sulfated zirconia catalyzed synthesis of 1,5-benzodiazepines

Entry	Diamine	Ketone	Product yield
1	<i>o</i> -Phenylenediamine	CH ₃ COCH ₃	94
2	<i>o</i> -Phenylenediamine	CH ₃ COPh	96
3	<i>o</i> -Phenylenediamine	CH ₃ COCH ₂ CH ₃	91
4	<i>o</i> -Phenylenediamine	CH ₃ CH ₂ COCH ₂ CH ₃	84
5	4,5-Dimethyl- <i>o</i> -phenylenediamine	CH ₃ COCH ₃	94
6	4,5-Dimethyl- <i>o</i> -phenylenediamine	CH ₃ COPh	93

act as anti-convulsant, anti-inflammatory, analgesic, hypnotic, sedative, and anti-depressive agents [53]. Generally, benzodiazepines are synthesized by the condensation of *o*-phenylenediamines with α,β -unsaturated carbonyl compounds or β -haloketones or with ketones. Many reagents have been tried for this reaction including polyphosphoric acid, BF₃-etherate, NaBH₄, Yb(OTf)₃, MgO/POCl₃ and more recently with acetic acid under microwave conditions [54–56]. In continuation to our efforts in finding new applications for solid acid catalysts in the area of fine chemicals synthesis, we have carried out this reaction with promoted zirconia catalysts [57]. In the presence of promoted ZrO₂ catalysts, *o*-phenylenediamines reacted smoothly with various ketones and produced the corresponding 1,5-benzodiazepine derivatives in good to excellent yields under solvent free conditions (Scheme 7). Enhanced reaction rates and selectivities were obtained for all the reactions in the presence of sulfated zirconia catalyst. Results of this reaction are summarized in Table 8.

4. Conclusions

The following conclusions can be drawn from this study: (1) The zirconia sample calcined at 923 K is in crystalline form with monoclinic ZrO₂ phase dominating over the tetragonal phase. (2) Incorporation of sulfate, molybdate, and tungstate promoters showed significant influence on the physicochemical properties of zirconia. (3) In the case of Pt/Mo-ZrO₂ catalyst a complete tetragonal phase was observed. (4) Surface areas of all the promoted catalysts are higher than that of pure ZrO₂. Among all the promoted catalysts, sulfated zirconia exhibited high surface area. (5) Ammonia-TPD results reveal that among all the investigated promoters, sulfate ion shows strong influence on the acidic properties of zirconia followed by molybdate. (6) Raman

spectrum of the W-ZrO₂ catalyst exhibited shoulder peaks in high frequency region, indicating the presence of geometrically different WO_x species. The Zr(MoO₄)₂ compound formation was noted from Raman results in the case of Mo-ZrO₂ catalyst. (7) The sulfate, molybdate, and tungstate promoted zirconia catalysts have been employed to catalyze various acid catalyzed organic synthesis and transformation reactions. All the investigated catalysts showed unique catalytic activities under very mild reaction conditions. Further studies are essential to determine the exact nature of the acid sites present on these oxides. Although much about the generation of active sites is unresolved, the catalytic activity of these materials is remarkable.

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