Alumina sulfuric acid (ASA), tungstate sulfuric acid (TSA), molybdate sulfuric acid (MSA) and xanthan sulfuric acid (XSA) as solid and heterogeneous catalysts in green organic synthesis: a review

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Abstract

In this comprehensive review, we report on the sulfonic acid functionalized solid acids such as alumina sulfuric acid (ASA), tungstate sulfuric acid (TSA), molybdate sulfuric acid (MSA) and xanthan sulfuric acid (XSA) as green and heterogeneous catalysts in a wide range of organic transformations. Recently, the use of sulfonic acid functionalized solid acids as catalyst in organic synthesis has become an efficient and green strategy for the selective construction of organic motifs. The sustainable advantage of sulfonic acid functionalized solid acids is that it can be recovered and reused several times without loss of their efficiency. In this review, we attempt to give an overview of the use of ASA, TSA, MSA, XSA as catalysts in the synthesis of various organic compounds having industrial as well as pharmaceutical applications.

Keywords: Alumina sulfuric acid, tungstate sulfuric acid, molybdate sulfuric acid, xanthan sulfuric acid, heterogeneous catalysts, solid acid catalyst

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1. Introduction

Organic synthesis generally involves the use of various solvents and catalysts, which may be toxic, hazardous, corrosive and inflammable. These chemical processes are largely harmful to the environment. Nowadays, it has become a major issue that has been brought forward at the global level. Apart from the atmospheric pollution, the use of solvents in an industrial process may also cause occupational health hazards. Furthermore, completion of the reaction, some reagents or catalysts, which are used in many chemical processes, are converted into another

form and are not recycled efficiently. In view of the seriousness of chemical pollution, the use of a wide range of volatile, toxic, corrosive and inflammable chemicals are being re-examined, leading to a search for the design and development of environmentally benign green organic transformations.

According to the green chemistry principles,[1] modern organic synthesis should be carried out using methodologies that maximize conversion of reactants into products, generate low amounts of waste or by-products as far as possible, utilize minimum energy requirements, and reduce the use of toxic, corrosive and hazardous chemicals.

Nowadays, organic transformations by using solid, heterogeneous and reusable catalysts have been developed, because of environmental and economic regulations.[2-6] Homogeneous catalysts such as sulfuric acid (H_2SO_4), hydrofluoric acid (HF), hydrobromic acid (HBr), hydrochloric acid (HCl) and tri-fluoroacetic acid (CF_3COOH) are frequently used in organic synthesis.[7] However, these acid catalysts are toxic, harmful, corrosive and difficult to handle. Also, their disposals cause the problems for the chemical industries.[8] In the case of homogeneous catalysts recovery and separation of the catalyst from the reaction mixture is very difficult.[9] In addition, during the reaction or work-up process, loss of catalyst is a significant problem in many organic transformations. If a recyclable heterogeneous catalyst and solvent free conditions are used for many organic transformations, then both ecological and economic profiles will improve. Therefore, in recent years more development has been carried out in the field of heterogeneous solid acids catalyzed organic synthesis.[10-19] Solid heterogeneous acids have many advantages over conventional acids such as simplicity in handling, decreased reactor and plant corrosion problems and reusability. Also, wastages and by-products can be minimized.[20-23]

Development of novel heterogeneous catalysts to facilitate various organic transformations is an intense area of research in recent years. Therefore, many efforts have been made by scientists constantly to introduce new and novel heterogeneous catalyzed organic synthesis by using alumina sulfuric acid (ASA), tungstate sulfuric acid (TSA), molybdate sulfuric acid (MSA) and xanthan sulfuric acid (XSA) (Figure 1), which are more efficient, economical and compatible with the environment. Also, these catalysts can be recovered and reused many times, without decreasing their activity. The present article is intended to review briefly the recent research progress made concerning the synthesis of different organic compounds catalyzed by heterogeneous solid acids.
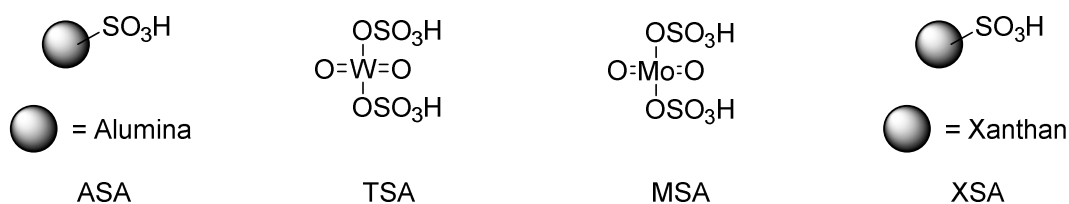
**Figure 1.** Structure of ASA, TSA, MSA, XSA.

2. Alumina Sulfuric Acid (ASA)

Alumina sulfuric acid (ASA) has been developed as a solid Bronsted acid catalyst for the synthesis of a variety of organic and heterocyclic compounds. ASA can be readily prepared by adding chlorosulfonic acid (0.35 mL, 5.25 mmol) to activated neutral alumina (15 g) under stirring condition with removal of the liberated HCl gas under reduced pressure. Then the reaction was kept at this condition for 1 h at room temperature, washed successively with water, followed by ethanol and dried at 130 $^{\circ}$C for 3 h.[24-26] ASA is a white solid which can be stored for a long period of time without a decrease in activity.

    ASA is a solid, heterogeneous catalyst and after completion of an organic transformation, it can be recovered and reused several times without loss of efficiency.

2.1. Synthesis of benzimidazoles and quinoxalines

Pramaniket et al.[27] have developed an efficient and eco-friendly synthesis of 2-aryl-1-arylmethyl-1H-benzimidazoles via the condensation of different aldehydes with $ortho$-phenylenediamine in the presence of alumina sulfuric acid (ASA) as a recyclable solid, heterogeneous acid catalyst in ethanol at room temperature (Scheme 1a). The effects of various solvents such as ethanol, n-hexane, diethyl ether, ethyl acetate, dichloromethane, methanol, water and toluene have also been studied by the authors. However, the reactions using ethanol gave the best yield of the products. In addition, the authors also carried out a comparison of ASA with different acid catalysts such as $HClO_4$-SiO_2, PPA (polyphosphorous acid)-SiO_2, $NaHSO_4$-SiO_2, Al_2O_3, Zeolite and Conc. H_2SO_4. It was found that these acids did not give good results as compared to ASA. Also, the ASA could be recovered after completion of the reaction, while homogeneous catalysts couldn't be recovered. The authors have also reported the synthesis of quinoxaline from $ortho$-phenylenendiamine and 1,2-diketone in the presence of ASA in ethanol at room temperature, which afforded high yield of the product (Scheme 1b).

R = H, Me
R' = H, Me, OMe, NO$_2$, Cl, OH, pyridyl, furyl   77-91 %
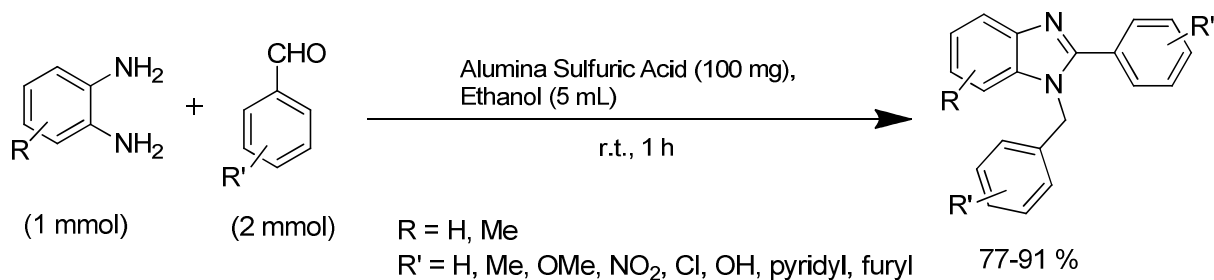
Scheme 1a. Synthesis of benzimidazole derivatives catalyzed by ASA.
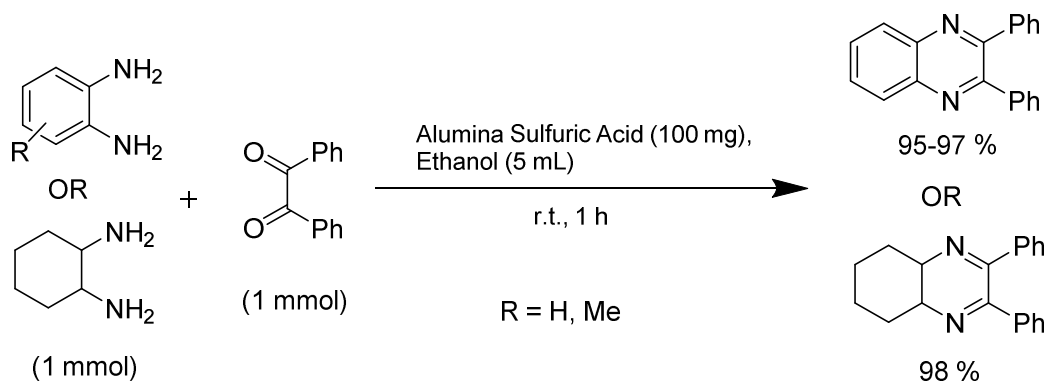
Scheme 1b. Synthesis of quinoxaline derivatives catalyzed by ASA.

2.2. Nitration of aromatic compounds

Hosseini-Sarvari et al.[28] have discovered a novel and safe protocol for nitration of phenols, anilines and other aromatic compounds in the presence of alumina sulfuric acid (ASA) as a catalyst and $Mg(NO_3)_2.6H_2O$ as a nitrating agent in neat water as a solvent (Scheme 2). With this protocol nitrated products were obtained in excellent yields. In a comparative study, the authors employed this reaction using toluene or dichloromethane (DCM) under reflux conditions; however, in such cases the reaction proceeded with low yield. In addition, no products were obtained when the reaction was carried out at room temperature or without water or catalyst. Different metal nitrates have ~~also~~ been employed in this reaction, but $Mg(NO_3)_2.6H_2O$ gave the best results as compare to others. It is interesting to note that in the presence of ASA, the amino group was protonated and therefore acted as a deactivating group. Furthermore, di-nitration and tri-nitration of phenol was also carried out by the authors. The use of water as a solvent makes this method green and clean.
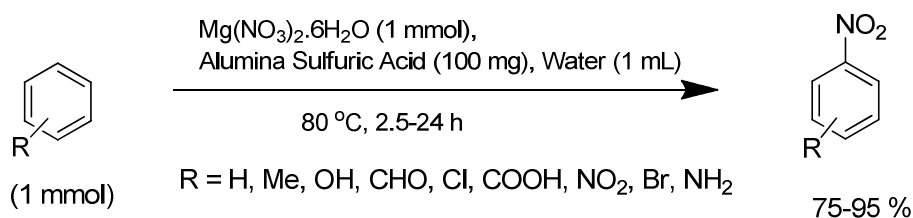
Scheme 2. Nitration of aromatic compounds catalyzed by ASA.

2.3. Synthesis of 2,5-disubstituted 1,3,4-oxadiazoles

Teimouri and co-workers[29] have disclosed an efficient method for the synthesis of 2,5-disubstituted 1,3,4-oxadiazoles by the condensation of different aromatic carboxylic acids and benzoyl hydrazides in the presence of natural alumina, alumina sulfuric acid (ASA), nano-alumina and nano-alumina sulfuric acid (nano-ASA) as a solid heterogeneous catalyst. These reactions were performed under microwave irradiation (dedicated microwave oven) and solvent-

free conditions (Scheme 3). Shorter process times, easy work-up process, mild reaction conditions, and high yields of the products are the advantages of this protocol. Here, microwave irradiation considerably decreased the reaction times and increased the yield of the products as compared to the conventional methods. In addition, the product was obtained in very low amount when catalyst was not used in this reaction. The authors have carried out this reaction with various alumina based catalysts such as natural alumina, nano-γ-alumina, ASA and nano-γ-ASA. However, the nano-γ-ASA showed the best activity in this synthesis. Higher yield of the products and recoverability of catalyst make this method green and an environmentally friendly.
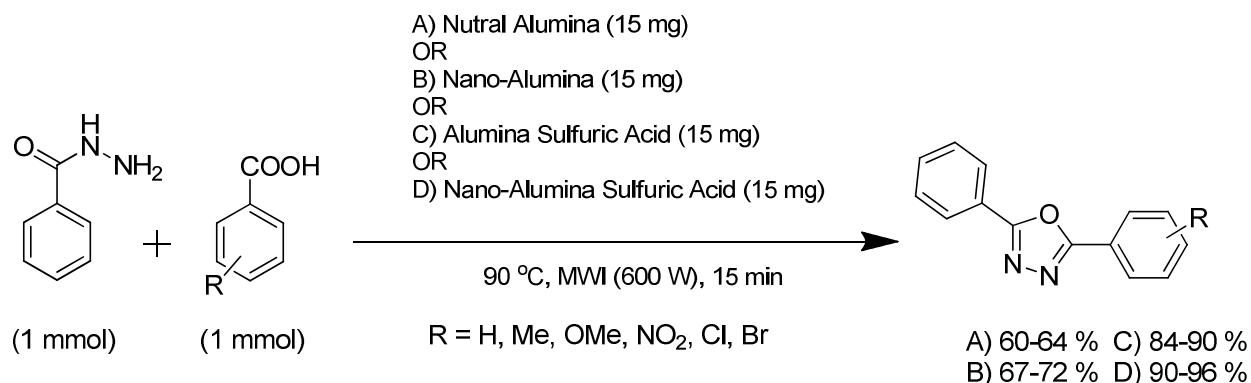
Scheme 3. Synthesis of 2,5-disubstituted 1,3,4-oxadiazoles catalyzed by ASA.

2.4. Chemoselective dithioacetalization and oxathioacetalization

Shaterian et al.[30] have described an efficient and green synthesis of dithiolane, dithiane, and oxathiolane derivatives from their corresponding carbonyl compounds using a catalytic amount of alumina sulfuric acid (ASA) in acetonitrile at room temperature (Scheme 4). Protection of aldehydes in the presence of ketones was selectively carried out by this protocol. The authors synthesized 2-phenyl-1,3-dithiane using benzaldehydes and 1,3-propanedithiol in the presence of different amounts of ASA as a catalyst under various of solvents, such as diethyl ether, dichloromethane, chloroform, ethyl acetate and acetonitrile. However, the best result was obtained in acetonitrile with 50 mg. of ASA.
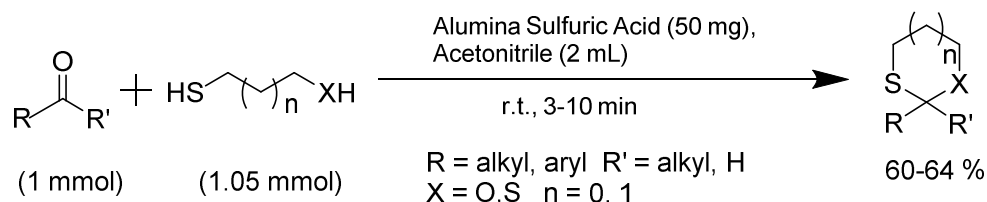
Scheme 4. Chemoselective dithioacetalization and oxathioacetalization catalyzed by   ASA.

2.5. ortho-Silylation of alcohols, oximes and phenols

Shaterian et al.[31] have developed ortho-Silylation of a wide range of alcohols, phenols and oximes in the presence of hexamethyldisilazane (HMDS) at room temperature, which afforded high yields of the products (Scheme 5). The primary alcohols were converted selectively into their corresponding ortho-silylated products in the presence of secondary and tertiary alcohols. In a comparative study, authors carried out this reaction with various catalysts such as lithium perchlorate, iodine and cupric sulfate pentahydrate. However, the reactions using ASA gave the best product yields.
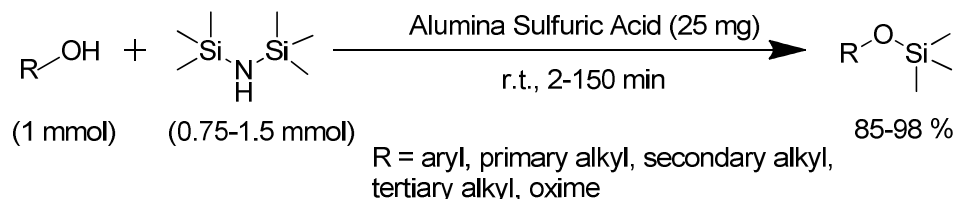
Scheme 5. ortho-Silylation of alcohols, oximes and phenols catalyzed by ASA.

## 2.6. Biginelli type condensation reaction

Shaterian and co-workers[32] have discovered an efficient and green procedure for the synthesis of substituted dihydropyrimidinones/thiones derivatives through the condensation of various aldehydes and 1,3-diketo compounds with urea or thiourea using alumina sulfuric acid (ASA) as a recyclable catalyst under microwave irradiation (domestic microwave oven, samsung, model KE300R) in short periods of time (Scheme 6). In addition, by this protocol a wide range of multi-substituted 3,4-dihydropyrimidinones/thiones derivatives were synthesized. Thus, this method is considered to have a wide synthetic utility. In addition, Besoluk et al.[33] have also developed the same protocol for the synthesis of substituted dihydropyrimidinones/thiones derivatives in excellent yield in the presence of alumina sulfuric acid as a reusable catalyst. Compare to conventional acid catalysts, ASA gave the best results and could be easily recovered and reused.
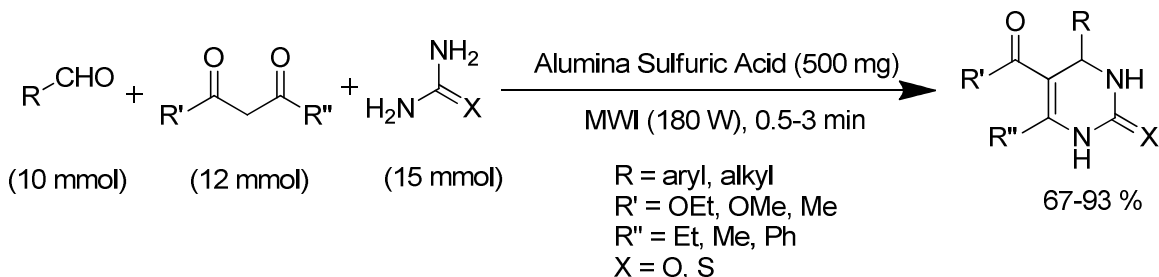
Scheme 6. Biginelli type condensation reaction catalyzed by ASA.

2.7. Pechmann condensation reaction

Amoozadeh et al.[34] have discovered high yielding methodology for the synthesis of coumarin derivatives through the Pechmann condensation reaction using alumina sulfuric acid (ASA) under solvent-free condition at 100 °C (Scheme 7). In a comparative study, the authors carried out this reaction with various catalysts, such as ASA, neutral alumina, acidic alumina, Al_2O_3/H_3PO_4, Al_2O_3/HNO_3, Al_2O_3/H_2SO_4, $Al_2O_3/HClO_4$ and H_2SO_4. However, the reactions using ASA gave the best product yields. Furthermore, 4-methyl-2*H*-benzo[*h*]chromen-2-one could be efficiently synthesized from naphthol-1-ol.
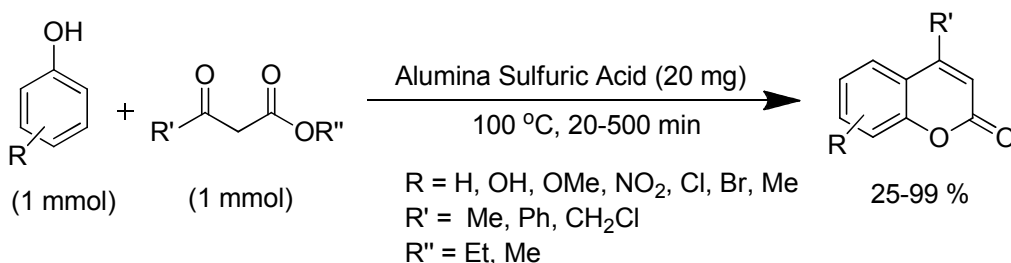
Scheme 7. Pechmann condensation reaction catalyzed by ASA.

2.8. Synthesis of Xanthenedione derivatives

Pramanik and co-workers[35] have developed a green synthesis of 9-aryl-1,8-dioxododecahydroxanthenes and 9-aryl-3,3,6,6-tetramethyl-1,8-dioxooctahydroxanthenes in high yield, through the chemoselective cyclocondensation of various aryl and heteroaryl aldehydes with 1,3-diketones using alumina sulfuric acid (ASA) as a recyclable catalyst. All reactions were carried out in ethanol under reflux condition (Scheme 8). In a comparative study, the authors carried out this reaction with various acidic catalysts such as ASA, conc. H_2SO_4/alumina, neutral alumina, cellulose sulfuric acid (CSA), conc. H_2SO_4, SiO_2, PPA-SiO_2, $HClO_4/SiO_2$, $NaHSO_4/SiO_2$ and NaCl/alumina. However, the high yield and selectivity of products were observed in the case of ASA. Various organic solvents such as hexane, diethyl ether, tetrahydrofuran (THF), Acetone, ethyl acetate, methanol, dichloromethane (DCM), 1-propanol and water were also employed in this reaction, but they did not give the best results as compared to ASA. By this protocol, a wide range of xanthenedione derivatives was synthesized in high yield.
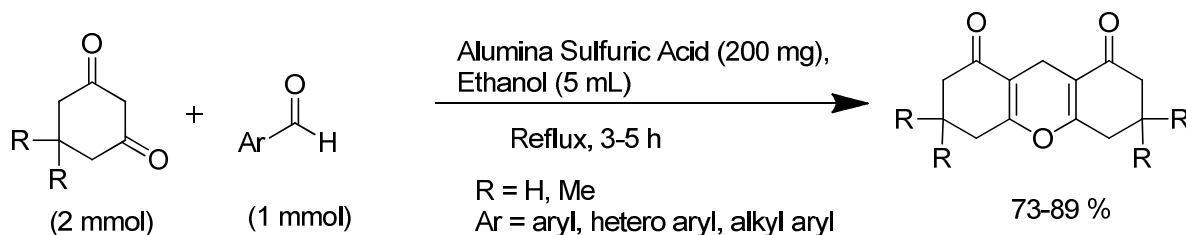

Scheme 8. Synthesis of xanthenedione derivatives catalyzed by ASA.

2.9. Synthesis of 1,4-dihydropyridines

Arslan and co-workers[36] have described a multi-component condensation of various aldehydes, 1,3-dicarbonyl compounds and ammonium acetate for the synthesis of 1,4-dihydropyridines in excellent yield using alumina sulfuric acid (ASA) as a catalyst in methanol under reflux condition (Scheme 9). The yields of the products and time of the reaction depended on the type of reagent used in this reaction. Instead of ethyl acetoacetate, dimedone shows good results due to the acidity of the methylenic protons. In addition, substrates containing electron-withdrawing and electron-releasing groups undergo reaction smoothly in this transformation.
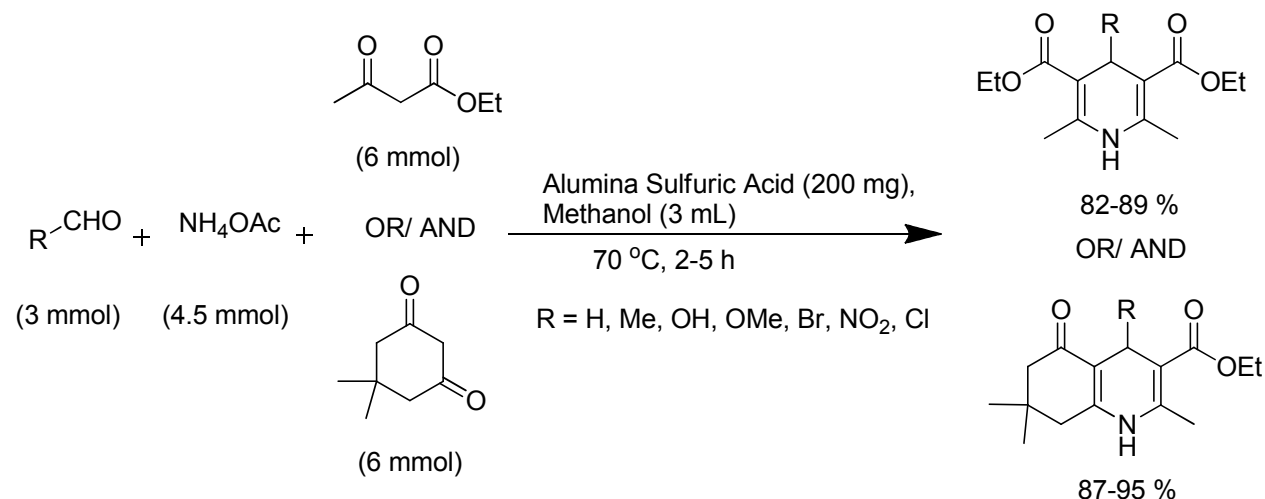
Scheme 9. Synthesis of 1,4-dihydropyridines catalyzed by ASA.

2.10. Strecker reaction

Teimouri et al.[37] have discovered a condensation of different aldehydes, amines and trimethylsilyl cyanides for the synthesis of α-aminonitriles derivatives using natural alumina, alumina sulfuric acid (ASA), nano-γ-alumina, nano-alumina sulfuric acid (nano-ASA) (Scheme 10). All these reactions were performed under microwave irradiation (dedicated microwave oven) without the use of any organic solvents. The authors have described and compared the catalytic activity of natural alumina, ASA, nano-γ-alumina, and nano-ASA, and it was found that, nano-ASA showed better activity in terms of the yield of the products and time of the reaction. The temperature and the MWI power played important roles in this reaction. At higher or lower temperatures, the reaction rate was decreased.
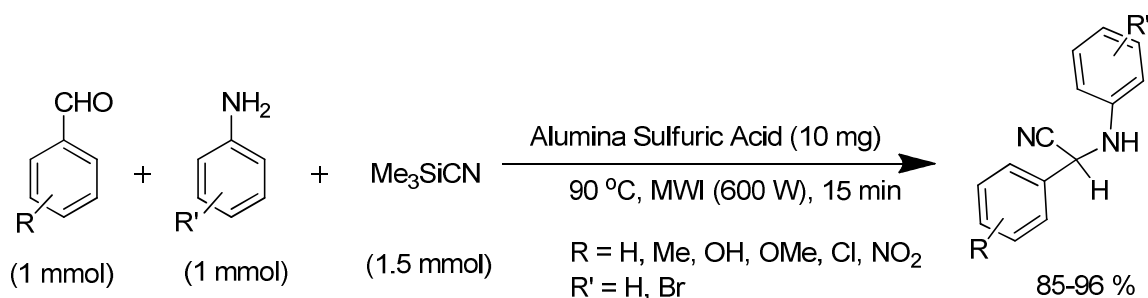
Scheme 10. Strecker reaction catalyzed by ASA.

3. Tungstate Sulfuric Acid (TSA)

TSA is a yellow colored solid, heterogeneous catalyst, which decomposed at 285 ^{o}C. For the preparation of TSA, take *n*-hexane (25 mL) in a 100 mL round-bottomed flask, equipped with an ice bath, and 0.59 g (2.0 mmol) of anhydrous sodium tungstate was added. To the stirred mixture, 0.266 mL (4.0 mmol) of chlorosulfonic acid was added drop wise during 30 min. This solution was stirred for 1.5 h and the reaction mixture was cautiously poured into 25 mL of chilled distilled water with agitation. The yellow solid which separated was filtered and the catalyst was washed with distilled water 5 times or until the filtrate showed a negative test for the chloride ion, and dried at 120 ^{o}C for 5 h.[38,39] It can be stored indefinitely without loss of their efficiency.

   TSA is a recyclable, nonhygroscopic and eco-friendly catalyst and can be reused several times without the loss of activity.

3.1. Synthesis of *α*-substituted *β*-naphthols derivatives
Kamaei et al.[40] have disclosed an efficient and solvent-free synthesis of *α*-substituted *β*-naphthols using tungstate sulfuric acid (TSA) at 100 ^{o}C in a short period of time (Scheme 11). This eco-friendly method has some advantages such as excellent yields, less reaction time, use of recyclable catalyst, and easy work-up.
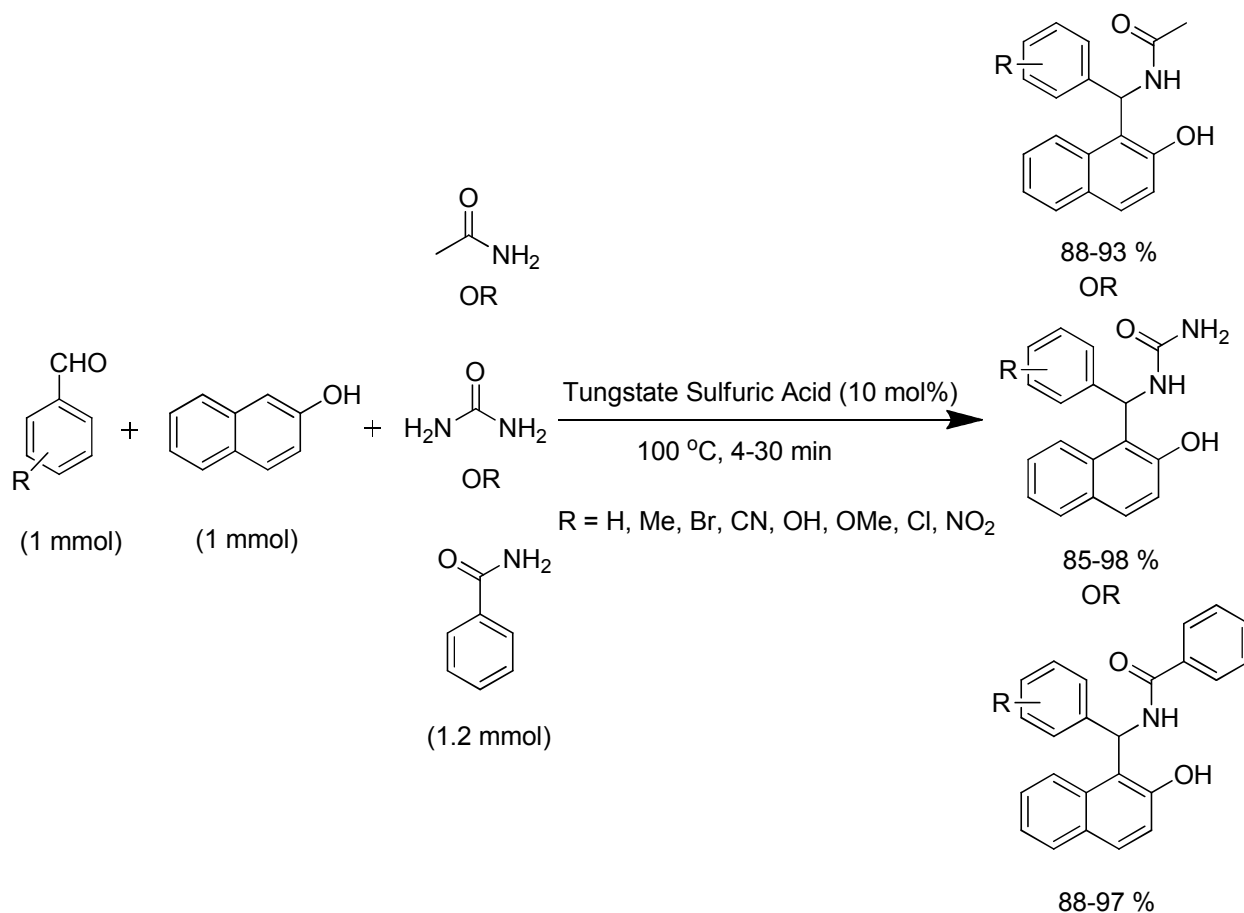
Scheme 11. Synthesis of α-substituted β-naphthols derivatives catalyzed by TSA.

3.2. Synthesis of benzoxazoles and benzothiazoles

Farahi et al.[41] have developed a green protocol for the synthesis of benzoxazole and benzothiazole derivatives through the reactions of orthoesters with *ortho*-aminophenols or *ortho*-aminothiophenols respectively in high yields (Scheme 12). All these reaction were carried out in the presence of tungstate sulfuric acid (TSA) under solvent free condition at 80-90 °C. In a comparative study, authors employed various catalysts such as ZnCl₂, MgBr₂ and H₂SO₄ in this reaction, but they did not give good results. In addition, solvent free conditions give better results.
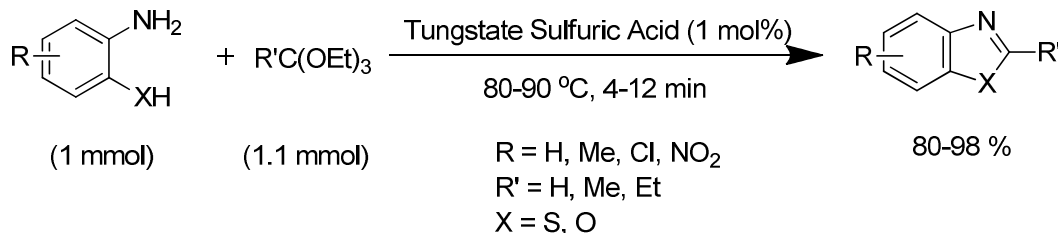
Scheme 12. Synthesis of benzoxazoles and benzothiazoles catalyzed by TSA.

3.3. Biginelli condensation reaction

Karami et al. have[42] discovered an efficient protocol for the synthesis of 3,4-dihydropyrimidine-2-(1*H*)thione derivatives via condensation of β-dicarbonyls, various aldehydes and thiourea using tungstate sulfuric acid (TSA) (Scheme 13). These all transformations were performed under solvent-free conditions at 80 °C. Both electrons-releasing and electron-withdrawing groups on the aryl aldehyde reacted smoothly in this method. Here, the reaction temperature affected the yield of the products.
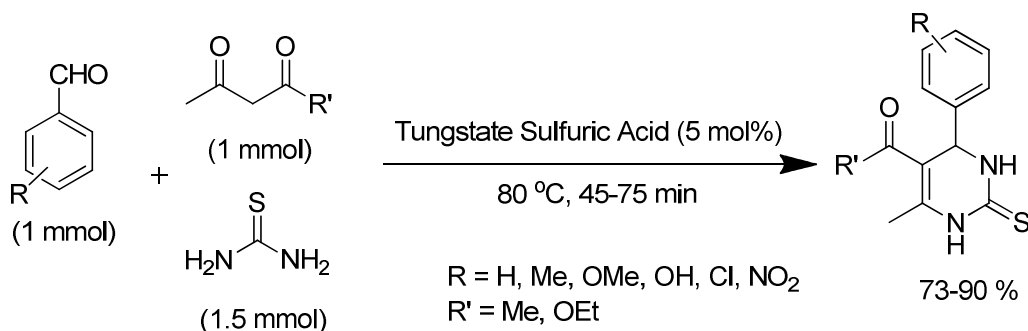
Scheme 13. Biginelli condensation reaction catalyzed by TSA.

3.4. Rapid deoximation of oximes

Karami et al.[43] have reported deoximation of a variety of oximes oxidized to their parent carbonyl compounds in excellent yield under the mild conditions using heterogeneous wet TSA/KMnO$_4$ in dichloromethane (DCM) (Scheme 14). Various oximes were deoximated to their parent carbonyl compounds efficiently by this method.
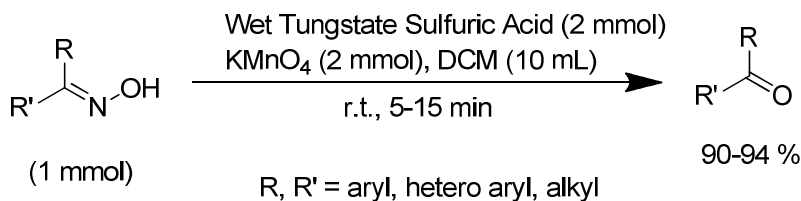
Scheme 14. Rapid deoximation of oximes catalyzed by TSA.

3.5. Synthesis of 1,3-dithiane and 1,3-dithiolane derivatives

Karami et al.[44] have disclosed an efficient protocol for the thioacetalization of aliphatic and aromatic carbonyl compounds using tungstate sulfuric acid (TSA) as an eco-friendly catalyst under solvent-free conditions at 80 °C or by grinding at room temperature to afford 1,3-dithianes and 1,3-dithiolanes (Scheme 15). Here, the reaction mechanism shows that TSA is a strong, solid acid and it can activate the carbonyl group to enhance the rate of the reaction. Several aromatic and aliphatic carbonyl compounds with electron-releasing or electron-withdrawing substituents

afforded good to excellent yields of the products. The grinding technique required less time to complete the reaction as compared to conventional heating conditions.
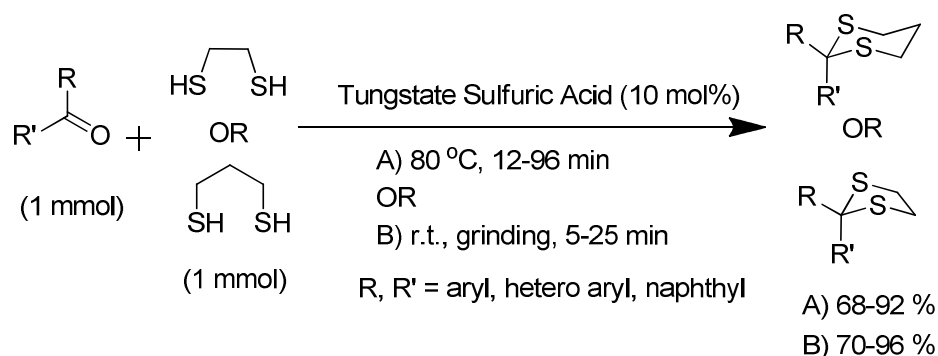
Scheme 15. Synthesis of 1,3-dithiane and 1,3-dithiolane derivatives catalyzed by TSA.

3.6. Oxidation of thiols to disulfides and oxidative demasking of 1,3-dithianes

Karami et al.[45] have developed a combination of tungstate sulfuric acid (TSA) and NaNO₂ as an oxidant for the transformation of thiols to disulfides in dichloromethane (DCM) at room temperature in high yields (Scheme 16a). The selective oxidative deprotection of 1,3-dithianes to their corresponding carbonyl compounds using tungstate sulfuric acid (TSA) in combination with KMnO₄ in dichloromethane (DCM) under reflux condition has also been investigated by the authors (Scheme 16b).
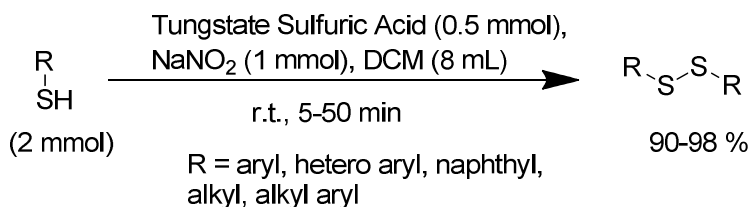
Scheme 16a. Oxidation of thiols to disulfides catalyzed by TSA.
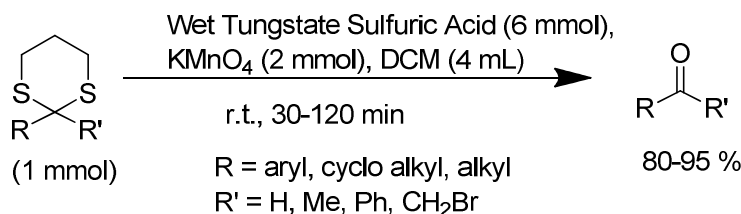
Scheme 16b. Oxidative demasking of 1,3-dithianes catalyzed by TSA.

3.7. N-Nitrosation of secondary amines

Karami et al.[46] have described an efficient and fast method for N-nitrosation of versus *C*-nitrosation or *O*-nitrosation of various secondary amines using TSA/NaNO$_2$ in dichloromethane (DCM) at room temperature (Scheme 17). The mechanism proposed by the authors reveals that the reaction proceeds through the formation of NO$^+$ by the reaction of wet TSA and NaNO$_2$, which then reacts wit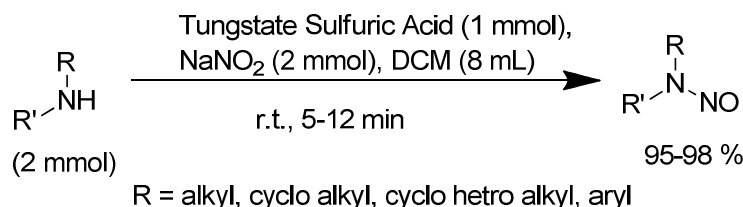h various secondary amines affording the corresponding nitroso products in excellent yield. In addition, mild and eco-friendly reaction conditions, easily accessible reagents and a simple work-up process are the advantages of this protocol.

Scheme 17. N-Nitrosation of secondary amines catalyzed by TSA.

3.8. Synthesis of benzimidazoles

Karami et al.[47] have discovered an eco-friendly and high yielding protocol for the synthesis of benzimidazoles through a condensation reaction of *ortho*-phenylenediamines with orthoesters by employing tungstate sulfuric acid (TSA) under solvent-free conditions at 80 °C (Scheme 18).
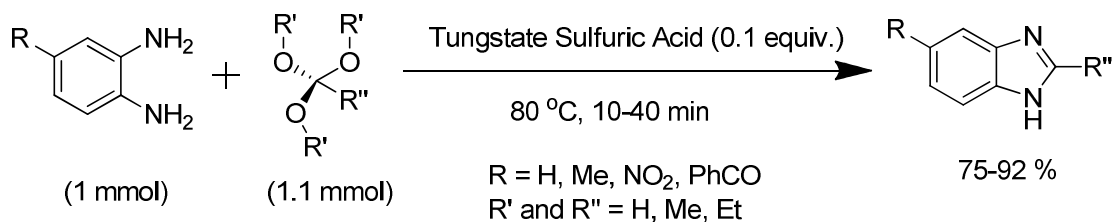
Scheme 18. Synthesis of benzimidazoles catalyzed by TSA.

3.9. Synthesis of polycyclic aromatic phenazines and quinoxalines

Karami and co-workers[48] have been developed high yielding synthesis of quinoxalines and phenazines by the condensation of 1,2-dicarbonyl compounds and *ortho*-phenylenediamines in the presence of tungstate sulfuric acid (TSA) without the use of any solvent (Scheme 19). All reactions were performed at ambient temperature. Here, 5 mole% TSA was sufficient for completion of the reaction. However, by using higher amounts of catalyst, the product yield and time of the reaction did not improve.
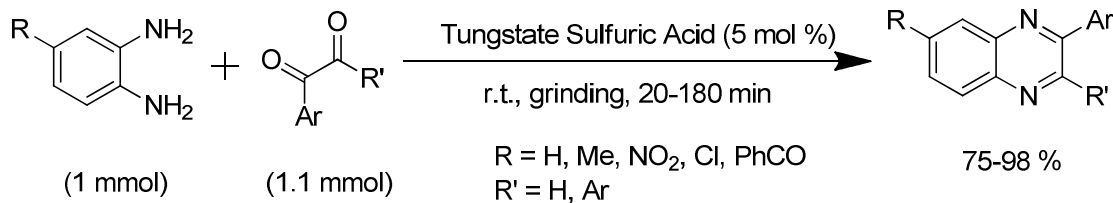
Scheme 19. Synthesis of polycyclic aromatic phenazines and quinoxalines catalyzed by TSA.

3.10. Synthesis of calix[4]resorcinarene derivatives

Karami and co-workers[49] have discovered a facile and simple method for the preparation of novel calix[4]resorcinarene derivatives through the condensation of aryl aldehydes with resorcinol using tungstate sulfuric acid (TSA) under solvent-free conditions at 120 ^{o}C (Scheme 20). The use of excessive amounts of the catalyst does not increase the yield of the products and reaction time. This eco-friendly method has many advantages, such as high yield, lesser reaction time, use of safe and recoverable catalyst, and workup.
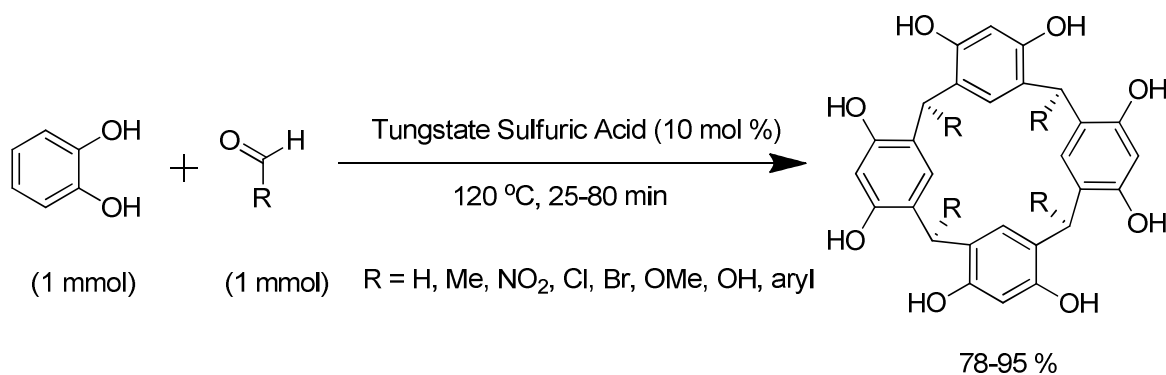
Scheme 20. Synthesis of calicx[4]resorcinarene derivatives catalyzed by TSA.

4. Molybdate Sulfuric Acid (MSA)

MSA is prepared according to following method: anhydrous sodium molybdate (20 mmol, 4.118 g) was added to dry n-hexane (25 mL) in a 100 mL round bottom flask equipped with ice bath and overhead stirrer. Chlorosulfonic acid (0.266 mL, 40 mmol) was then added drop wise to the flask during 30 min and stirred for 1.5 h. The reaction mixture was gradually poured into 25 mL of chilled distilled water with agitation. The molybdate sulfuric acid was separated as a bluish solid by filtration, washed with cold distilled water five times until the negative test for chloride ion for filtrate, and dried at 120 ^{o}C for 5 h.[52] MSA is environmentally benign, easy to handle and is stable in reaction media. It can be stored for a longer time without loss of activity. Also it is

easily recovered after completion of the reaction and it can be reused several times without loss of activity.

4.1. Synthesis of 2,3,4,5-tetrasubstituted pyrroles

Tamaddon et al.[50] have discovered the solvent-free preparation of 2,3,4,5-tetrasubstituted pyrroles through the [2+2+1] strategy via condensation of 1,3-dicarbonyls, benzoin derivatives and ammonium acetate in the presence of catalytic amounts of molybdate sulfuric acid (MSA), which afforded high yields of the products (Scheme 21). Solvents like ethanol, water, dichloromethane and acetonitrile were examined by the authors. However, ethanol gave better results as compared to the other solvents. In a comparative study, various catalysts such as $ZrOCl_2$, $ZnCl_2$, $MgBr_2$, $CuCl_2$, H_2SO_4, HCl, CH_3COOH and MSA were employed in this reaction, but MSA proved to be the best performing catalyst. Here, the mechanism shows that the 1,3-dicarbonyl compound reacts initially with NH_4OAc to form an imine intermediate, then it condenses with activated benzoin by MSA to produce a cyclic intermediate, which could be dehydrated to produce the corresponding tetra substituted pyrroles.
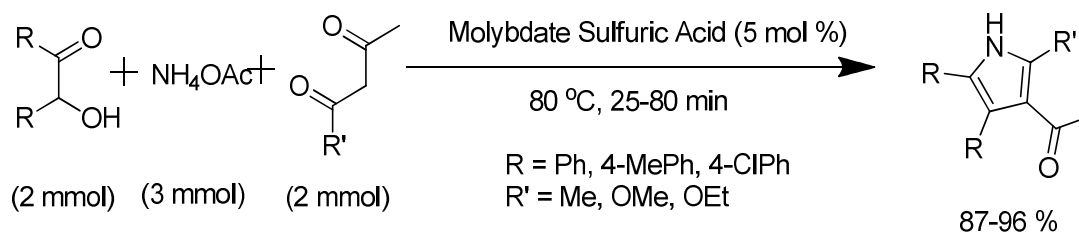
Scheme 21. Synthesis of 2,3,4,5-tetrasubstituted pyrroles catalyzed by MSA.

4.2. Synthesis of gem-bisamide

Tamaddon et al.[51] have developed another protocol for the high yielding synthesis of gem-bisamides and bisurides through condensation of two moles of amides, nitriles, carbamates or urea with aldehydes in the presence of molybdate sulfuric acid (MSA) and silica sulfuric acid (SSA) as catalysts in ethyl acetate at 80-90 ^{o}C (Scheme 22). Best results were obtained by using MSA and SSA in terms of yield, selectivity and reaction time as compared to commercial sulfuric acid. Both electrons-donating and electron-withdrawing groups on aldehydes, amides, urea and carbamates gave the *N,N*-arylidene and alkylidene bisamides in high yields. The mechanism of this transformation suggests that initially MSA or SSA activates the carbonyl group of aldehyde for reaction with amide to form a hemiamidal intermediate. Subsequently, this hemiamidal dehydrates to an acyliminium intermediate and it condenses with another molecule of amide to form the gem-bisamide.
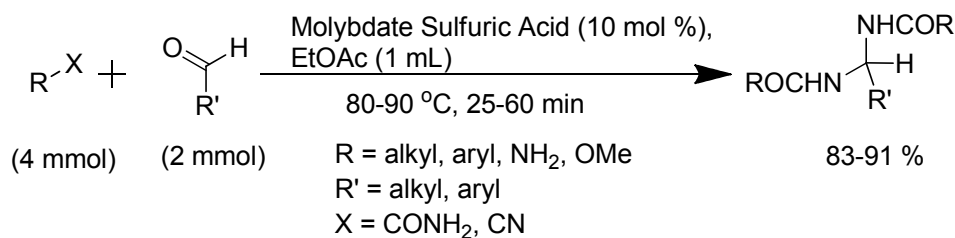
Scheme 22. Synthesis of gem-bisamide catalyzed by MSA.

4.3. Synthesis of disulfides

Montazerozohori and co-workers[52] have reported a mild method for the synthesis of symmetric disulfides from a variety of thiols using sodium nitrite and wet molybdate sulfuric acid (MSA) in dichloromethane or methanol at room temperature (Scheme 23).
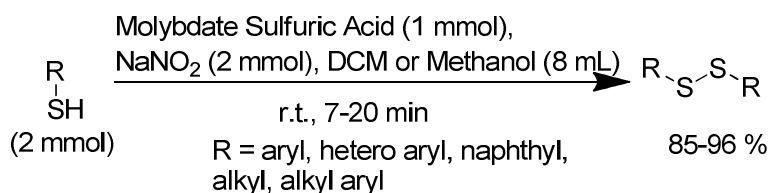
Scheme 23. Synthesis of disulfides catalyzed by MSA.

4.4. Synthesis of quinoxaline and phenazine derivatives

Karami et al.[53] have discovered an efficient synthesis of quinoxaline and phenazine derivatives by the reaction of 1,2-diketones and *ortho*-pheneylenediamines using a catalytic amount of molybdate sulfuric acid (MSA) in ethanol as solvent at room temperature (Scheme 24a-b). This protocol is considered to have a wide synthetic utility because of the wide variety of 1,2-diketones and *ortho*-pheneylenediamines that were employed in this reaction.
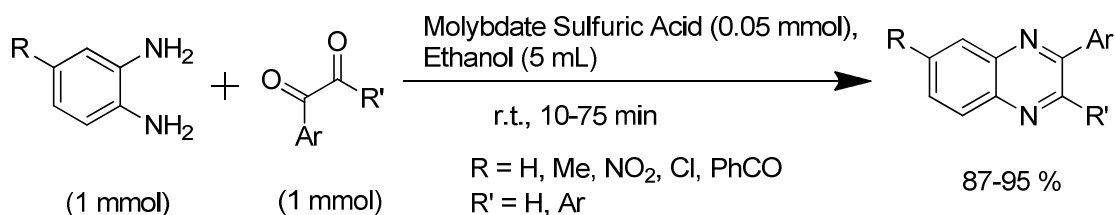
Scheme 24a. Synthesis of quinoxaline derivatives catalyzed by MSA.
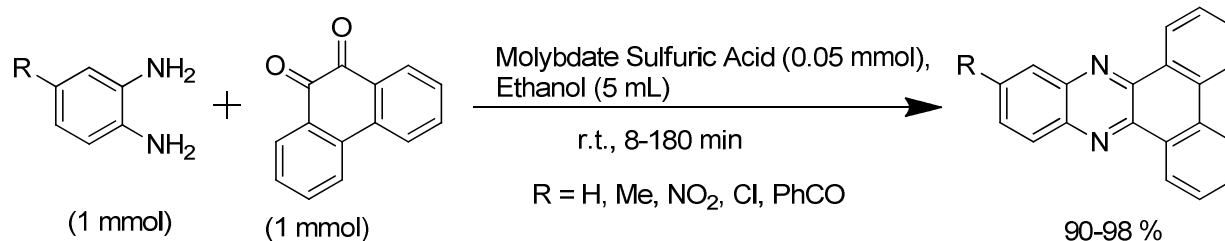
Scheme 24b. Synthesis of phenazine derivatives catalyzed by MSA.

4.5. Synthesis of N-nitroso compounds

Montazerozohori et al.[54] have described an environmental friendly procedure for the synthesis of N-nitroso compounds in excellent yield from a variety of secondary amines employing wet molybdate sulfuric acid (MSA) and sodium nitrite ($NaNO_2$) in dichloromethane (DCM) at room temperature (Scheme 25). Furthermore, N-nitrosation was observed selectively instead of *C*- or O-nitrosation.

Scheme 25. Synthesis of N-nitroso compounds catalyzed by MSA.

5. Xanthan Sulfuric Acid (XSA)

Xanthan is the most abundant bacterial exo-polysaccharide in the world and is produced through fermentation. It has been widely studied in the last few years, as it is a biodegradable material and a renewable re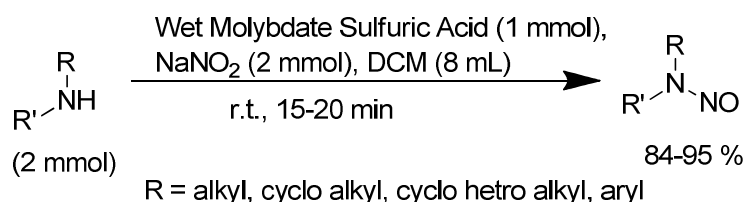source. In addition, it is very stable under a wide range of temperatures and pH conditions. The xanthan sulfuric acid (XSA) catalyst was prepared by following method: To a magnetically stirred mixture of 5.0 g xanthan in 20 mL $CHCl_3$, chlorosulfonic acid (9 mmol, 1.0 g) was added dropwise at 0 ^{o}C during 2 h. After addition was complete, the mixture was stirred for 2 h until HCl was removed from the reaction vessel. The mixture was then filtered and washed with 30 mL methanol or acetonitrile and dried at room temperature to afford 5.26 g xanthan sulfuric acid as white powder.[55]

   Xanthan sulfuric acid is a heterogeneous catalyst and it is recovered and reused many times without loss of activity.

5.1. Synthesis of bis(indolyl)methane derivatives

Siddiqui and co-workers[56] have developed a solvent free procedure for the synthesis of bis(indolyl)methanes by using indole and aromatic aldehydes in the presence of xanthan sulfuric acid (XSA) by grinding at room temperature to afford the products in high yield (Scheme 26). Various catalysts such as zinc acetate, $NiCl_2$, $AlCl_3$, benzenesulfonic acid, sulfuric acid, sulfamic acid, L-proline and $Zn(L\text{-proline})_2$ were employed in this reaction in a comparative study; however, they did not give good results. In addition, different solvents like methanol, ethanol, acetonitrile, 1,2-dichloroethane, acetic acid and iso-propanol were examined by the authors for optimization of the yield of the products and reaction time. It was found that the solvent free condition proved to be the best for this reaction.
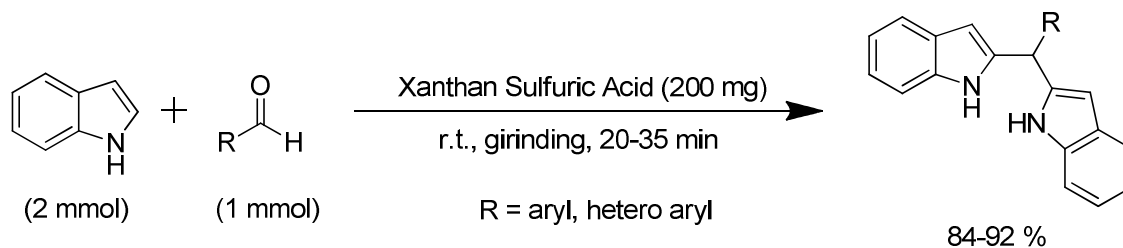
Scheme 26. Synthesis of bis(indolyl)methane derivatives catalyzed by XSA.

5.2. Synthesis of *N*-substituted pyrroles

Rahmatpour[57] has disclosed a solvent-free protocol for the synthesis of various of *N*-substituted pyrroles by the reaction of 2,5-hexanedione with various amines or diamines in the presence catalytic amount of xanthan sulfuric acid (XSA) at room temperature (Scheme 27). In this protocol, all the products were obtained in excellent yields. The use of a non-hazardous, inexpensive, readily available and reusable bio-supported proton source catalyst makes this protocol green and environmentally friendly. This transformation was carried out by employing various solvents such as dichloromethane, chloroform, carbon tetrachloride and acetonitrile, but solvent free conditions were found to be the most favorable for this transformation in terms of the yield of the products. In addition, an excessive amount of catalyst did not increase the yield of the products in this protocol.
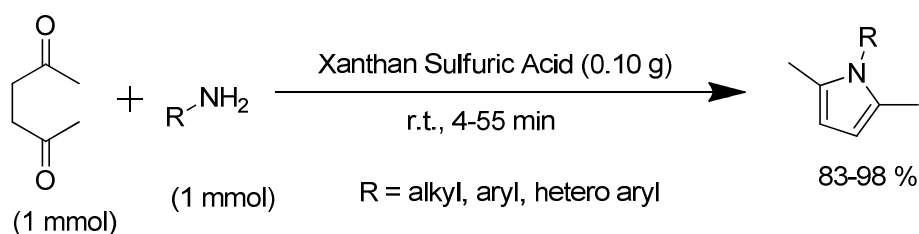
Scheme 27. Synthesis of N-substituted pyrroles catalyzed by XSA.

5.3. Pechmann condensation reaction

Kuarm et al.[58] have disclosed a solvent-free preparation of substituted coumarins via Pechmann condensation of various phenols and ethyl acetoacetate derivatives using catalytic amounts of xanthan sulfuric acid (XSA) at room temperature (Scheme 28). The lower yield of the product was obtained, when lower amounts of catalyst were used. In the absence of catalyst the yield of the product was very poor. However, best results were obtained when 10 mole % of XSA was used as a catalyst. Various catalysts such as silica sulfuric acid, methane sulfonic acid and sulfuric acid in acetic acid were used in this reaction, but they were not as efficient as XSA.
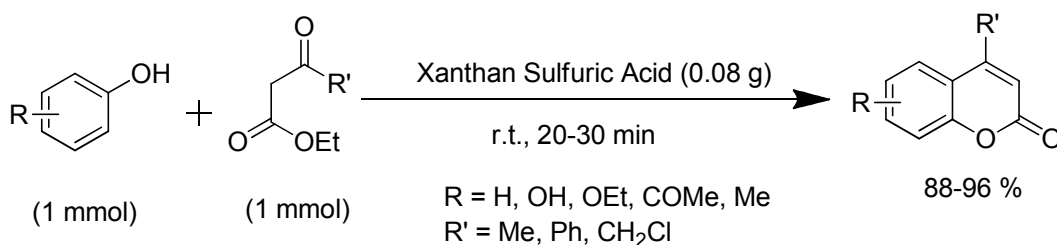
Scheme 28. Pechmann condensation reaction catalyzed by XSA.

5.4. Synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ols)

Kuarm et al.[59] have reported an efficient protocol for the synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ols) via the condensation of 1-phenyl-3-methylpyrazol-5-one and various aldehydes by employing catalytic amounts of xanthan sulfuric acid (XSA) in ethanol under reflux conditions (Scheme 29).
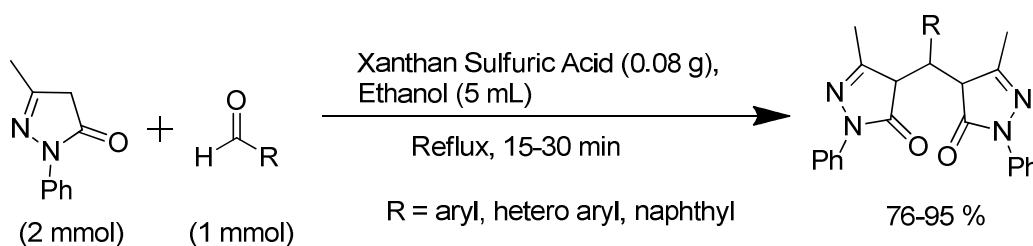
Scheme 29. Synthesis of 4,4'-(arylmethylene)bis(1*H*-pyrazol-5-ols) catalyzed by XSA.

5.5. Synthesis of 14-Aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-dione

Kuarm et al.[60] have discovered an efficient protocol for the high yielding synthesis of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones through the condensation of 2-hydroxynaphthalene-1,4-dione, 2-naphthol and various aromatic aldehydes in the presence of xanthan sulfuric acid (XSA) as a recyclable catalyst in ethanol at 50 °C (Scheme 30).
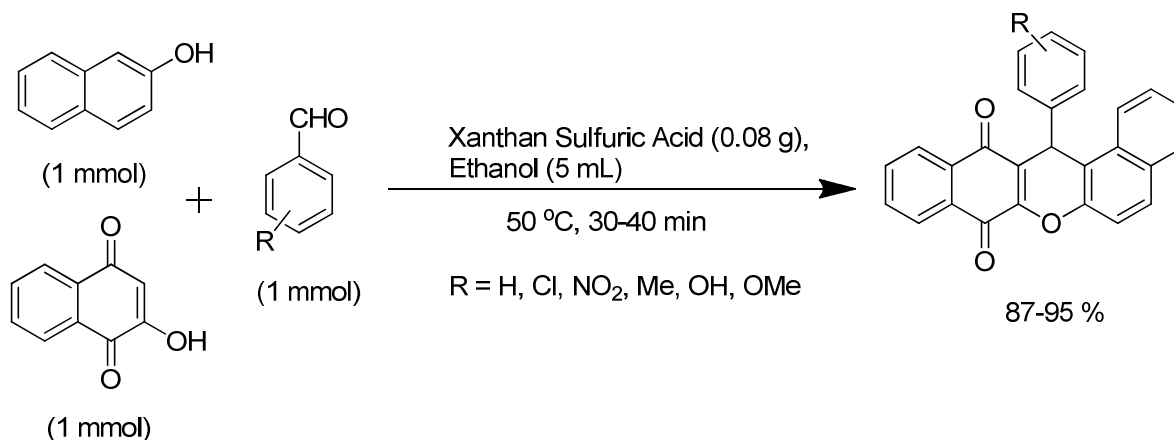
Scheme 30. Synthesis of 14-Aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-dione catalyzed by XSA.

5.6. Synthesis of *α*-amino phosphonates

Sun et al.[61] have described an solvent-free procedure for the development of α-amino phosphonates via condensation of various aldehydes, diethyl phosphate and amine by using catalytic amount of xanthan sulfuric acid at the 60 ^{o}C (Scheme 31). The effects of catalyst loading and temperature of the reaction on the yield of the products and rate of the reaction were also investigated by the authors. A wide range of α-amino phosphonates have been obtained by this protocol, making it have a potentially a wide synthetic utility.

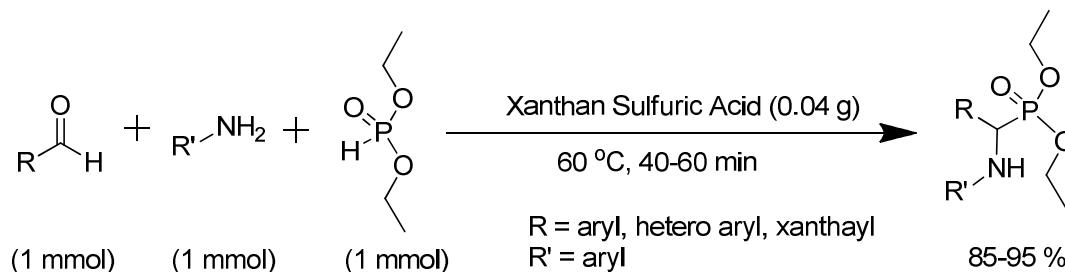**Scheme 31.** Synthesis of *α*-amino phosphonates catalyzed by XSA.

5.7. Biginelli condensation reaction

Kuarm et al.[62] have disclosed a solvent-free method for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones via a one-pot, three-component Biginelli condensation reaction of aldehydes, amines, and urea/thiourea at the 40 ^{o}C (Scheme 32). Various solvents such as methanol, acetonitrile, dichloromethane, toluene and ethanol were employed in a comparative study. However, solvent free conditions were found to be preferable for this transformation in terms of the yield of the products.
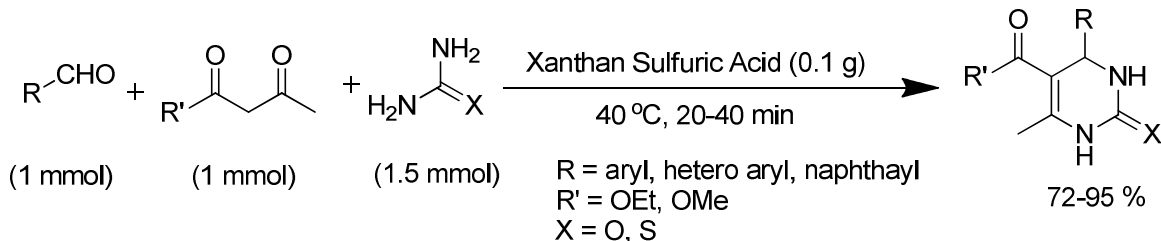
Scheme 32. Biginelli condensation reaction catalyzed by XSA.

5.8. Synthesis of *α*-amino nitriles

Shaabani et al.[63] have discovered the condensation reaction of aldehydes or ketones, amines and trimethylsilylcyanide in the presence of a catalytic amount of xanthan sulfuric acid (XSA) at room temperature, which afforded *α*-amino nitriles in excellent yields (Scheme 33). The results showed that the efficiency and the yield of the products in acetonitrile were found to be higher compared with other solvents such as water, ethanol, methanol, dichloromethane and toluene or under solvent-free conditions.
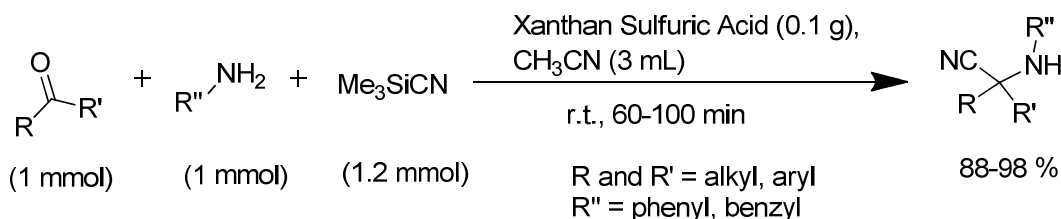
Scheme 33. Synthesis of α-amino nitriles catalyzed by XSA.

6. Conclusions

This review summarizes the development of green organic transformations catalyzed by sulfuric acid based solid, heterogeneous catalysts. In recent years, alumina sulfuric acid (ASA), tungstate sulfuric acid (TSA), molybdate sulfuric acid (MSA) and xanthan sulfuric acid (XSA) have been explored for improving selectivity, purity and high yields of organic compounds. Particularly, ASA and TSA are widely used in efficient synthesis methodologies of many organic transformations. Moreover, recoverability and reusability of these four catalysts make all process environmentally friendly, cost-effectiveness and green. It should be noted that though great progress has been achieved in this field over the last few years, this research area has still further possibilities for growth and, no doubt, we will see an increasing number of new and novel procedures for the synthesis of various organic compounds catalyzed by solid heterogeneous catalysts.

7. Acknowledgements

8. References

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