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Review Article

FERRIC HYDROGENSULFATE AS AN ACIDIC AND SOLID SUPPORTED CATALYST IN ORGANIC SYNTHESIS: A REVIEW

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ABSTRACT

Ferric Hydrogensulfate (FHS) has been used in many organic procedures as a solid acid catalyst. FHS is an inexpensive catalyst and prepared by simple process. It is easy to store, handle, eco-friendly with high reactivity and reusability. It is used in various organic preparations to give corresponding product in excellent yield with high selectivity. FHS supported on silica is known as Silica supported Ferric Hydrogensulfate (SFHS) which is also used as acidic catalyst for various organic transformations. Some important applications of FHS and SFHS in organic reactions are discussed in this review.

Keywords: Ferric hydrogensulfate, Solid acid catalyst, Silica supported catalyst, Solvent-free conditions, Reusable catalyst.

1. INTRODUCTION

In the last couple of decades more attention was given by scientist on the development of new methods for the synthesis of organic compounds using eco-friendly catalyst. These methods include use of catalyst such as solid catalyst [1], solid supported catalyst [2], reusable catalyst [3], heterogeneous catalyst [4] and bio-catalyst [5]. These catalysts are the best alternative to homogeneous protic acids as it is easy to store, easy to handle, less toxic, eco-friendly with high reactivity and reusability. Catalysts which fulfill these conditions are silica hydrogensulfate (FHS) and silica ferric hydrogensulfate (SFHS).

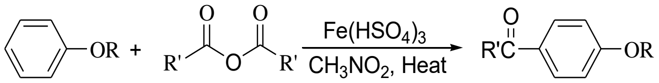
2. APPLICATIONS OF FHS AND SFHS IN ORGANIC SYNTHESIS

2.1. Acylation of alkoxy benzenes

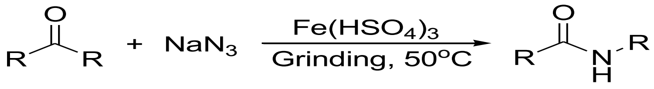
Friedel-Crafts acylation of alkoxy benzenes was carried out by Salehi et al. from aliphatic acid anhydride using catalytic amounts of ferric hydrogensulfate in nitromethane. Alkyl benzenes and aryl halides; as well as aromatic anhydrides, remain intact under these conditions [6] (Scheme 1).

2.2. Schimdt reaction

A new, efficient and convenient method has been developed by Hossein Eshghi for the one-pot synthesis of amides from ketones and sodium azide in the presence of ferric hydrogensulfate at solvent free and grinding condition. Chemoselectivity, high yield, simple operation solvent free condition and short reaction time are the advantages of this method [7] (Scheme 2).



Scheme 1: Acylation of alkoxy benzenes



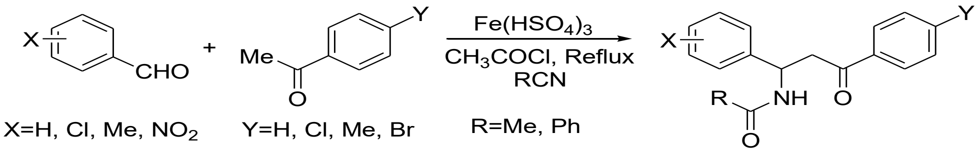
Scheme 2: Conversion of ketones to amides

2.3. Synthesis of β-amido ketones and esters

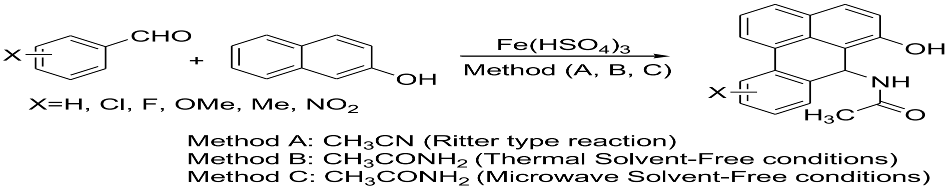
Shaterian et al. carried out one pot four component condensation of benzaldehyde derivatives, enolizable ketones, acetyl chloride and acetonitrile/benzonitrile for the synthesis of β-amido ketones and esters using ferric hydrogensulfate as a catalyst at reflux condition. This method offers advantages such as good yield, shorter reaction time, easy work up and recyclability of catalyst [8] (Scheme 3).

2.4. Synthesis of 1-amidoalkyl-2-napthols

Synthesis of 1-amidoalkyl-2-napthols was achieved using multi-component reaction of β-napthol, aromatic aldehydes and acetamide in the presence of ferric hydrogensulfate under solvent free and microwave condition by Shaterian et al. 1-Amidomethyl-2-napthols can be converted into important biological drug like active 1-aminomethyl-2-napthols derivatives by amide hydrolysis [9] (Scheme 4).



Scheme 3: Synthesis of β-amido ketones and esters



Method A: CH_3CN (Ritter type reaction)
Method B: CH_3CONH_2 (Thermal Solvent-Free conditions)
Method C: CH_3CONH_2 (Microwave Solvent-Free conditions)

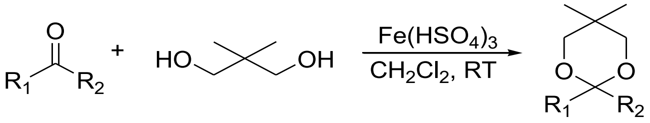
Scheme 4: Synthesis of 1-amidoalkyl-2-napthols

2.5. Synthesis of acetyl/ketal

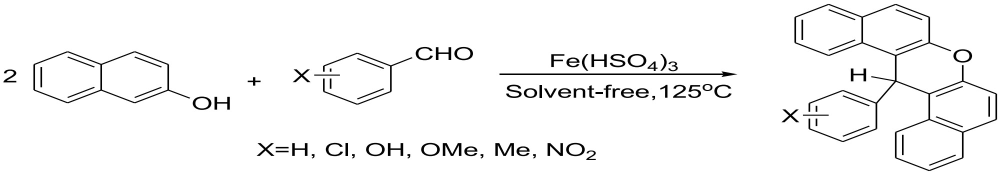
Ferric hydrogensulfate has been used as an efficient catalyst for acetalization and ketalization of carbonyl compounds with neopentyl glycol at room temperature by Eshghi et al. Same catalyst is used for the deprotection of acetals to the corresponding carbonyls in aqueous acetone [10] (Scheme 5).

2.6. Synthesis of aryl 14H-dibenzo[a,j]xanthenes

Preparation of aryl 14*H*-dibenzo [a, j] xanthenes derivatives were achieved by Shaterian and Ghashang by condensation of β-napthols and substituted benzaldehydes under solvent free conditions using ferric hydrogensulfate at 125°C. Easy workup procedure and greener conditions are the advantages of this method [11] (Scheme 6).



Scheme 5: Formation of acetyl/ketal



Scheme 6: Preparation of aryl 14*H*-dibenzo [a,j] xanthene derivatives

2.7. Oxidative coupling

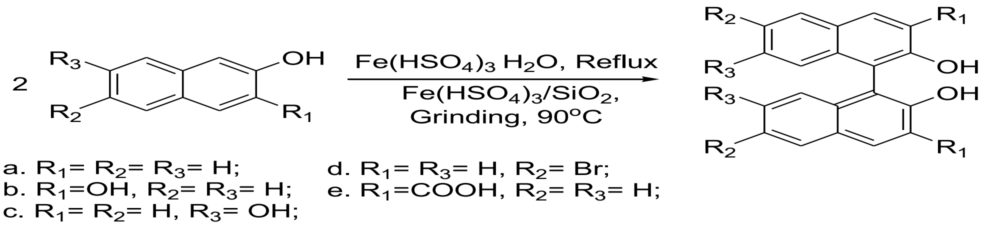
The symmetric oxidative coupling of 2-napthol derivatives with ferric hydrogen sulfate in water and silica ferric hydrogensulfate in solvent free condition at 90°C were carried out by Eshghi et al. This reaction follows principles of green chemistry [12] (Scheme 7).

2.8. Synthesis of 1,8-dioxo-octahydroxanthenes

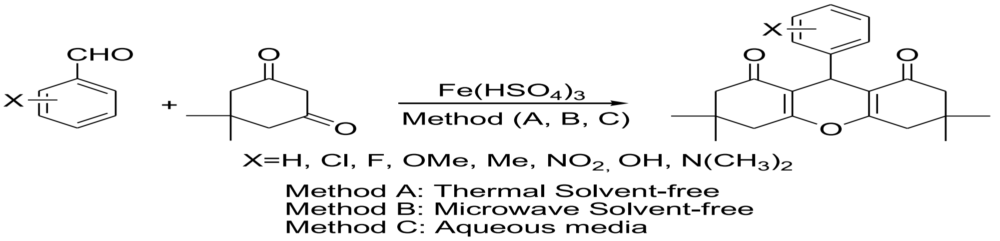
Shaterian et al. carried out silica ferric hydrogensulfate catalyzed synthesis of 1, 8-dioxo-octahydroxanthenes via condensation reaction between aromatic aldehydes and dimedone under solvent-free thermal and microwave irradiation as well as in aqueous media condition. The catalyst was easily separated and recycled several times without loss of reactivity [13] (Scheme 8).

2.9. Synthesis of 1H-tetrazoles and amides

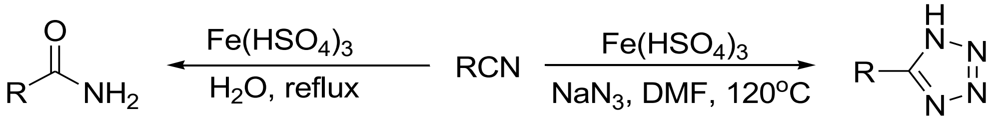
Ferric hydrogensulfate catalyzed synthesis of 5-substituted 1 *H*-tetrazoles via [2+3] cycloaddition of nitriles and sodium azide is carried out in dimethyl formamide at 120°C by Eshghi et al. Hydrolysis of nitriles to primary amines is also carried out by ferric hydrogensulfate in aqueous medium at reflux condition [14] (Scheme 9).



Scheme 7: Oxidative coupling of 2-napthols



Scheme 8: Preparation of 1, 8-dioxo-octahydro-xanthene derivatives



Scheme 9: Conversion of nitriles to 1*H*-tetrazoles and amides

2.10. Synthesis of 1,3-diaryl-3*H*-benzo [*f*] chromenes

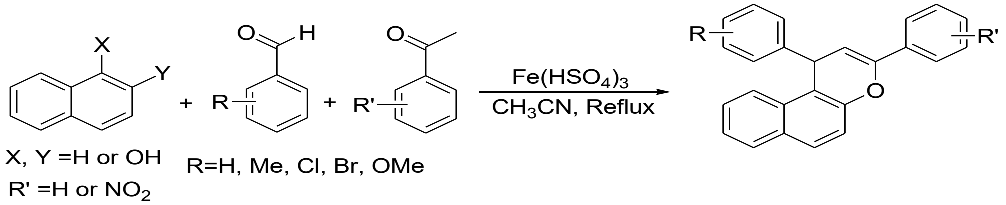
Damavandi amd Sandaroos carried out the synthesis of 1, 3-diaryl-3*H*-benzo [*f*] chromenes by one pot condensation of napthols, aromatic aldehydes and acetophenones in the presence of ferric hydrogensulfate as the catalyst at reflux condition in acetonitrile [15] (Scheme 10).

2.11. Synthesis of propargylamines

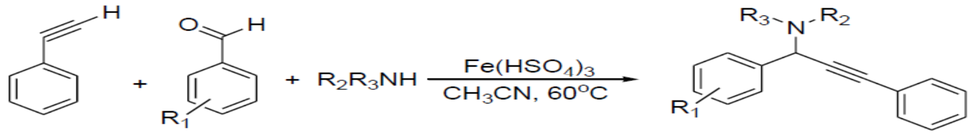
Coupling reaction of phenylacetylene, aldehyde and amine derivatives in the presence of ferric hydrogensulfate is carried out by Eshghi et al. for the synthesis of propargylamines in acetonitrile at 60°C. This method provides the wide range of substrate applicability [16] (Scheme 11).

2.12. Intra-molecular cyclization

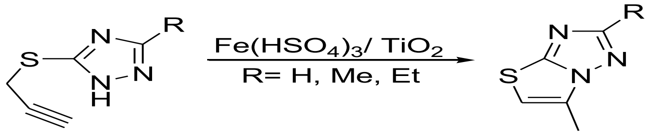
Intra-molecular cyclization of 5-alkyl-3-propargylmercapto-1, 2, 4-triazole derivatives to corresponding 6-methyl thiazolo[3,2-b][1,2,4]triazoles was performed in the presence of ferric hydrogensulfate supported on nano titanium dioxide as solid acid by Hedayati et al. in acetic acid at reflux condition [17] (Scheme 12).



Scheme 10: Synthesis of 1, 3-diaryl-3*H*-benzo[*f*]chromene derivatives



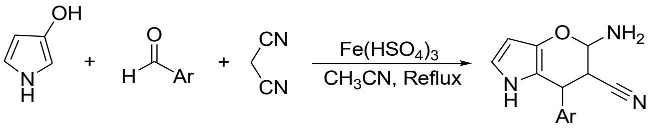
Scheme 11: Synthesis of propargylamines



Scheme 12: Cyclization of 5-alkyl-3-propargyl-mercapto-1, 2, 4-triazoles

2.13. Synthesis of 4*H*-pyrano[3,2-*b*]pyrroles

Sandaroos and Damavandi developed a new approach for the synthesis of 4*H*-pyrano[3,2-*b*] pyrrole derivatives from condensation of 3-hydroxypyrrole, malanonitrile and various aldehydes using ferric hydrogensulfate as a catalyst in acetonitrile at reflux condition [18] (Scheme 13).



Scheme 13: Synthesis of 4*H*-pyrano [3,2-*b*] pyrrole derivatives

2.14. Synthesis of 1,8-dioxodecahydroacridines

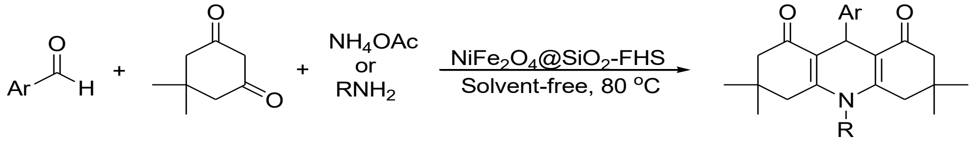
A new magnetically separable catalyst consisting of ferric hydrogensulfate supported on silica-coated nickel ferrite nanoparticles was prepared by Khojastehnezhad et al. and used for the synthesis of 1,8-dioxodecahydroacridine derivatives from aromatic aldehydes, dimedone and ammonium acetate/aromatic primary amine under solvent free condition at 80°C. This catalyst is readily recovered by simple magnetic decantation and recycled several times with no significant loss of catalytic activity [19] (Scheme 14).

2.15. Cyclization of chalcones

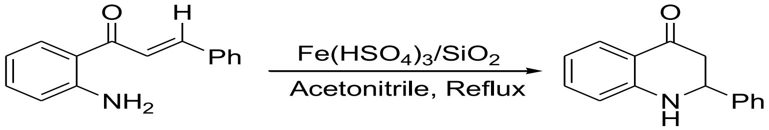
Intramolecular cyclization of 2-aminochalcones was carried out to the corresponding 2,3-dihydroquinolin-4(1*H*)-ones using silica ferric hydrogensulfate by Eshghi et al. The catalyst is reusable without significant decrease in its activity after four times recycling [20] (Scheme 15).

2.16. Hantzsch condensation

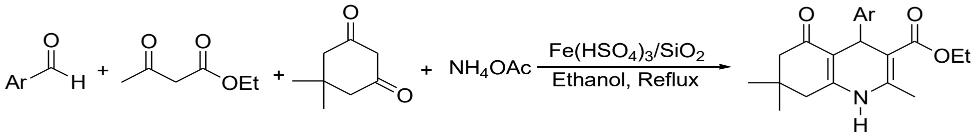
Pandit et al. carried out the synthesis of polyhydroquinoline derivatives via Hantzsch condensation reaction between aromatic aldehydes, dimedone, ethyl acetoacetate and ammonium acetate in the presence of catalytic amount of silica ferric hydrogen sulfate in ethanol. Catalyst can be easily recovered and reused without significant loss up to five times [21] (Scheme 16).



Scheme 14: Synthesis of 1,8-dioxodecahydroacridine derivatives



Scheme 15: Intramolecular cyclization of 2-aminochalcones



Scheme 16: Synthesis of polyhydroquinoline derivatives

2.17. Esterification and transesterification

Taufiq-Yap et al. carried out production of biodiesel by simultaneous esterification and transesterification of mixed waste vegetable oils with methanol using ferric hydrogen sulfate as a catalyst. The process is carried out at 205°C with a stirring speed of 350 rpm [22].

3. CONCLUSION

In this review, applications of ferric hydrogensulfate and silica ferric hydrogensulfate have been studied. Wide variety of compounds can be synthesized by FHS and SFHS through one or multi-component reaction It has been discussed by various examples that ferric hydrogen sulfate can be used as a catalyst in the synthesis of heterocycles by conventional, microwave irradiation, solvent free conditions and in aqueous media. From the various discussions it is concluded that FHS and SFHS are easy to handle, non toxic, efficient and reusable catalyst for various organic transformations.

4. ACKNOWLEDGEMENT

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Conflict of Interest

The author declares no conflict of interest, financial or otherwise.

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