

Nafion-H[®]: Its catalytic applications

Compiled by Fatemeh Karimi

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

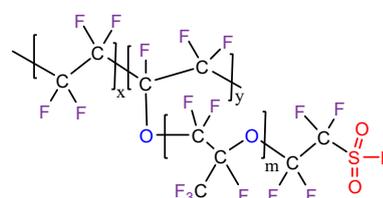
Introduction

Nafion-H[®] as a perfluorinated sulfonic acid resin which had been synthesized by Dr. Walther Grot at DuPont in the late 1960's for the first time [1]. The general chemical formula of Nafion-H[®] is shown as below in the Scheme 1 [2].

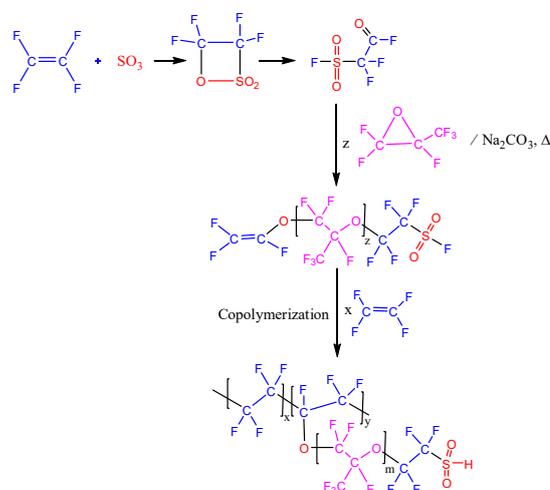
Nafion-H[®] had been prepared *via* the polymerization of its corresponding starting materials as depicted in the Scheme 2 [3, 4].

Nafion-H[®] as an important solid super acid catalyst, which its acidity is comparable to that of 96–100% sulfuric acid ($H_0 \approx 12$) [5, 6]. Due to its strong acidity, superior physical, chemical and thermal stability, high catalytic activity, non-corrosive and non-toxic nature, selectivity in the reactions, easy recoverability, and eco-friendly nature as compared with other available heterogeneous acid catalysts, it had been widely used as a multipurpose heterogeneous catalyst in the organic synthesis such as esterification [7], acetylation of alcohols [8], trans alkylation (Friedel–Crafts reaction) [9–11], ethers synthesis [12,13], aldol condensation [14], Fries arrangements [15], oxidations [16], acylation [17], nitration [18], acetal synthesis [19], and in the Diels–Alder reaction [20]. Applications of Nafion-H[®] in the chemical processes have been comprehensively reviewed [21]. Herein, I

tried to highlight the catalytic applications of Nafion-H[®] in the several organic methodologies.



Scheme 1. Structure of Nafion-H[®].



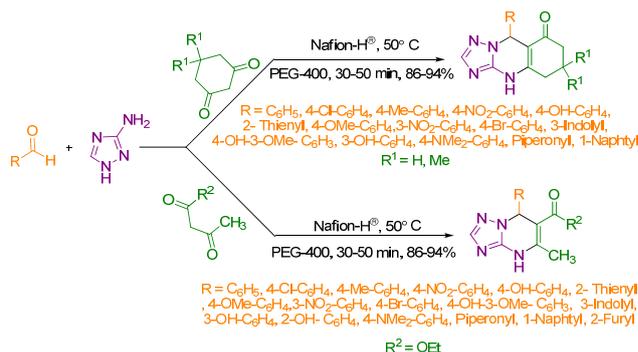
Scheme 2. Preparation of Nafion-H[®].

Abstracts

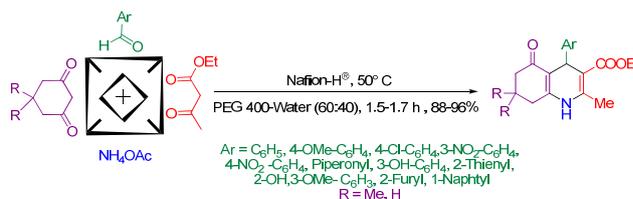
(A) In 2016, Nafion-H[®] has been used as an eco-friendly and reusable catalyst for the synthesis of bis(indolyl)methanes by the condensation of indoles and aromatic aldehydes using PEG-400:water system as a reaction media. The reported protocol represents a simple, green, efficient, and rapid route for the preparation of desired molecules with excellent yields [22].



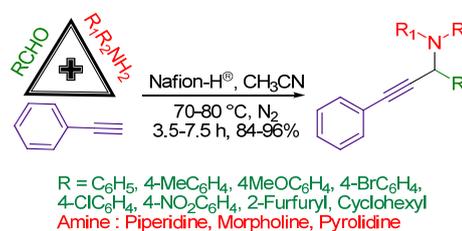
(B) In 2013, Kidwai and co-workers, reported the application of Nafion-H[®] as a recyclable and environmentally benign catalyst for the convenient synthesis of a series of [1,2,4] triazolo [5,1-b] quinazolinones and [1,2,4] triazolo[1,5-a] pyrimidines *via* cyclocondensation reaction of 3-amino-1,2,4-triazole, various aldehydes and 1,3-dicarbonyl compounds derivatives in PEG-400 as solvent at 50 °C [23].



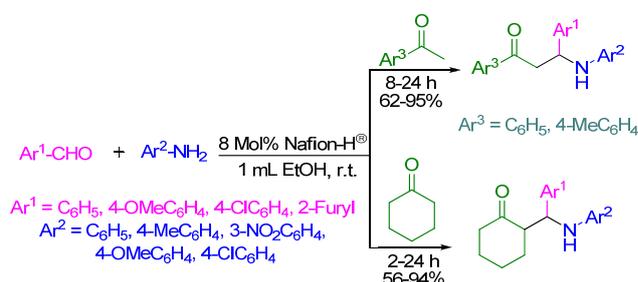
(C) In another investigation, one-pot reaction of dimedone, aldehydes, ethylacetoacetate and ammonium acetate have been efficiently catalyzed by heterogeneous Nafion H[®] in PEG-400:water to give the corresponding polyhydroquinoline compounds in excellent yields [24].



(D) Kidwai and co-workers, reported a one-pot, three-component coupling reaction of aldehydes, amines, and alkyne (A³-coupling) *via* C-H activation using Nafion-H[®] as a recyclable and environmentally benign catalyst. The described method avoids the use of heavy metals, co-catalysts and produces the propargylamines in excellent yields [25].



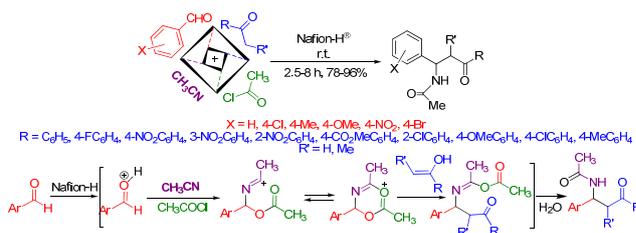
(E) In 2011, Nafion-H[®] had been applied for the one pot three-component Mannich reaction of various aldehydes, amines, and ketones in ethanol at ambient temperature. Not only the catalyst exhibits superior potential of recyclability over the studied reaction, but also diastereoselective products had been obtained in Mannich reaction of aliphatic ketones [26].



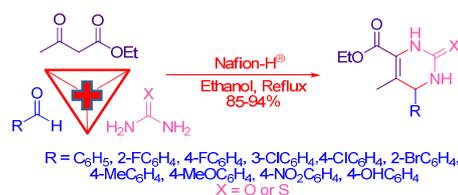
(F) In 2008, the synthesis of α -aminonitriles by a direct three component Strecker reaction of aldehydes and some ketones had been prepared using Nafion-H[®] as an effective and environmentally friendly heterogeneous catalyst. This methodology has the advantages such as efficient reusability of the catalyst, simple and clean reactions, and high yields of products [27].



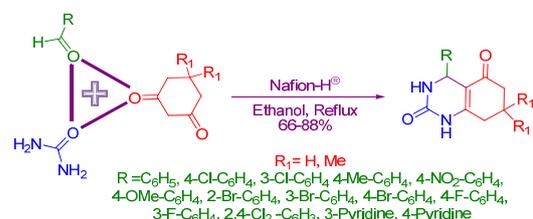
(G) In 2007, multi component condensation of an aryl aldehyde, acetyl chloride, acetonitrile and enolizable ketone in the presence of Nafion-H[®], as an efficient, environment friendly heterogenous and recyclable catalyst for the one-pot synthesis of β -acetamido ketones in high yields [28].



(H) In another assay, Nafion-H[®] has been successfully applied as a robust catalyst for the single step synthesis of dihydropyrimidinones in ethanol under reflux conditions as an eco-friendly and high yielding methodology. This adopted protocol for Biginelli reaction has the advantages of reusability of the catalyst, high yields and easy work-up [29].

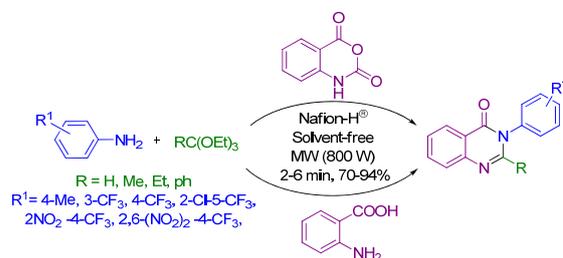


(I) In another exploration, Lin and co-workers have developed a convenient, efficient and eco-friendly method for the synthesis of octahydroquinazolinone derivatives by the multicomponent reactions of cyclic diketones, urea and aldehydes over Nafion-H[®] with good yields and selectivity.

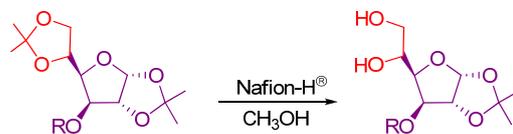


The reusability of catalyst, high yields and easy purification of products are important advantages of presented methodology [30].

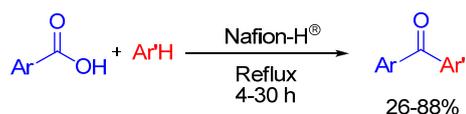
(J) It is reported that eco-friendly and recoverable Nafion-H[®] catalyst could be used efficiently for the synthesis of 2,3-disubstituted 4-(3H)-quinazolinones by the three-component coupling of isatoic anhydride/anthranilic acid, orthoesters, and amines with good yields under solvent-free and microwave irradiation conditions in short reaction times [31].



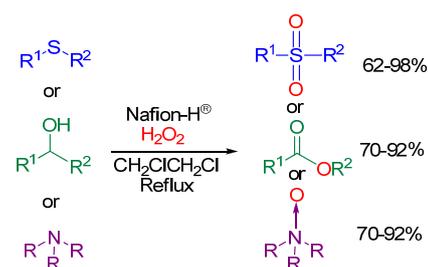
(K) A versatile chemoselective hydrolysis of terminal isopropylidene acetals has been carried out by Nafion-H[®] in methanol at ambient temperature in 68-96% yield for 2-4 h [32].



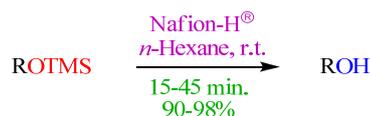
(L) Aroylation of aromatic hydrocarbons with aryl carboxylic acids over Nafion-H[®] as catalyst has been carried out by Prakash and co-workers. In all reaction of this report, the aromatics play the dual role as the substrate as well as the solvent. Reactions were performed under reflux conditions (175-180 °C) and products obtained in 26-88 % yield [33].



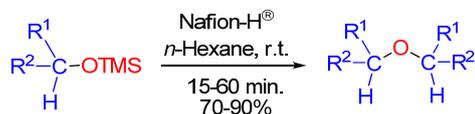
(M) Jain and Sain have outlined highly efficient method for the oxidation of sulfides to sulfone, tertiary amines to *N*-oxides, secondary alcohols to esters/lactones and aldehydes to methyl ester using 30% hydrogen peroxide and Nafion-H[®] as recyclable heterogeneous catalyst [34].



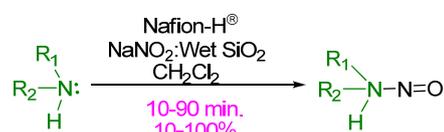
(N) Zolfigol and co-workers had been developed a simple, convenient and efficient method for the conversion of trimethylsilyl ethers into their corresponding alcohols in the presence of Nafion-H[®] with good to excellent yields [35].



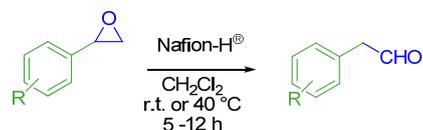
(O) In another attempt, primary and secondary trimethylsilyl ethers had been converted to their corresponding ethers over Nafion-H[®] under mild and heterogeneous conditions. Rearrangement, elimination and ether cleavage reactions had not been reported. They had believed that the described heterogeneous system may be useful for industrial applications [36].



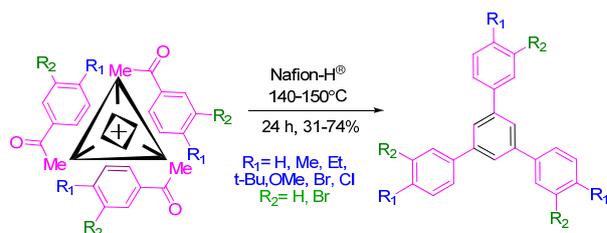
(P) In 2003, Zolfigol *et al.* had been used Nafion-H[®] and sodium nitrite in the presence of wet SiO₂, as an effective nitrosating agent for the *N*-nitrosation of secondary amines under mild and heterogeneous conditions in good to excellent yields. The cheapness and the availability of the reagents, easy and clean work-up, chemoselectivity and high yields made the reported method attractive for the large-scale operations. Also the simple reported procedure is highly selective and *C*-nitrosation and hydroxy oxidation side-products had not observed [37].



(Q) The isomerization of various styrene derivatives was found to be quantitative after treatment with Nafion-H[®] at room temperature or at 40 °C [38].



(R) In 1990, Nafion-H[®], had been applied as a convenient and reusable catalyst for the condensation of acetophenones to provide 1,3,5-triarylbenzenes under relatively mild conditions. Reactions are clean, so that the water formed as by-product did not deactivate the catalyst [39].



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