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A REVIEW: MICROWAVE ASSISTED ORGANIC REACTION USING SIO$_2$-SO$_3$H AS CATALYST

Sandro L. Barbosa
Department of Pharmacy, Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM, Campus JK Diamantina/MG, Brazil

Milton de S. Freitas
Department of Pharmacy, Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM, Campus JK Diamantina/MG, Brazil

Sávio Eduardo Oliveira Miranda
Department of Pharmacy, Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM, Campus JK Diamantina/MG, Brazil

Iolanda Araújo Rodrigues
Department of Pharmacy, Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM, Campus JK Diamantina/MG, Brazil

Maria Luíza Pereira e Oliveira
Department of Pharmacy, Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM, Campus JK Diamantina/MG, Brazil

Yuno Raphael Ferreira Araújo
Department of Pharmacy, Universidade Federal dos Vales do Jequitinhonha e Mucuri-UFVJM, Campus JK Diamantina/MG, Brazil

Natália de Souza Freitas
Department of Pharmacy, Universidade
Federal dos Vales do Jequitinhonha e
Mucuri-UFVJM, Campus JK
Diamantina/MG, Brazil
Diamantina/MG, Brazil

Adria Tayna Souza Fernandes
Department of Pharmacy, Universidade
Federal dos Vales do Jequitinhonha e
Mucuri-UFVJM, Campus JK
Diamantina/MG, Brazil

Lucas Pacônio Silva
Department of Pharmacy, Universidade
Federal dos Vales do Jequitinhonha e
Mucuri-UFVJM, Campus JK
Diamantina/MG, Brazil

Hélvia Nancy Fuzer Lira
Department of Pharmacy, Universidade
Federal dos Vales do Jequitinhonha e
Mucuri-UFVJM, Campus JK
Diamantina/MG, Brazil
Universidade Tecnológica Federal do Paraná
- UTFPR - Campus Apucarana
Apucarana - PR

Stanlei I. Klein
Department of General and Inorganic
Chemistry, Institute of Chemistry, São Paulo
State University-Unesp
Araraquara/SP

Alexandre P. Wentz
Centro Universitário SENAI-CIMATEC
Salvador, BA, Brazil

Abstract: This review presents a summary of reactions performed using microwave irradiation. These green processes have resulted through the use of the SiO_2-SO_3H catalyst (surface area of $115\ m^2/g$, pore volumes of $0.38\ cm^3/g$ and $1.32\ mmol\ H^+/g$) and readily recyclable solvents. Yields were often higher than those obtained by conventional methods. The review also focuses on the principle of microwave activation, two types of microwave reactors (domestic microwave and Monowave 300 microwave oven) and their characteristics.

Keywords: Microwave irradiation, reaction activation, hydrophilic sulfonated silica catalyst, SiO_2-SO_3H; organic reactions, green chemistry.

INTRODUCTION

Several are methods of activation of chemical reactions, chemists have restored to using a wide variety of techniques such as photochemical, electrochemical, sonochemical, enzymatic and microwave methods. The first application of microwave irradiation in chemical synthesis was published in 1986 [1].

Microwave irradiation has gained popularity in the past decade as a powerful tool for rapid and efficient synthesis of a variety of compounds because of selective absorption of microwave energy by polar molecules [2]. The application of microwave radiation to enhance the reaction rate and improve the yield of product in chemical synthesis has been quite successful in the formation of a variety of carbon-heteroatom bonds. The studies described below were taken from various original publications by our group. The data regarding the characterization of the catalyst can also be found in these publications.

MICROWAVE ASSISTED ESTERIFICATION REACTIONS

SOLVENT FREE ESTERIFICATION REACTIONS USING LEWIS ACIDS IN SOLID PHASE CATALYSIS [3].

The first study of microwave-assisted organic reactions performed by our research group involved the use of different Lewis acids as catalysts. A clean, efficient and rapid method for esterification reactions for sterically (biodiesels) or otherwise inactive (aromatic) precursors was developed using catalysts supported in a solid phase under "solvent free" conditions, and whose reactions were promoted by MW irradiation.

The supports/catalysts (80% w/w) utilized were SiO2/ZnCl2, SiO2/FeSO4, Al2O3/ZnCl2, Al2O3/FeSO, Nb2O5/ZnCl2, Nb2O5/FeSO4, activated charcoal/ZnCl2, and activated charcoal/FeSO4.

The solid phase catalytic system involving a Lewis acid metal compound and an inorganic solid oxide, can perform esterifications with high yields, in a medium which is free from undesired organic solvents and other hazardous components, such as strongly acidic solutions. The catalysts can be recycled, and the reactions were complete within minutes when promoted by microwave irradiation. However, these catalysts were not effective when the reaction involved benzylic alcohols. The benzylic alcohol derivatives did not exhibit effective nucleophilicity when these catalysts were used.

NIOBIUM TO ALCOHOL MOLAR RATIO CONTROL OF THE CONCURRING ESTERIFICATION AND ETHERIFICATION REACTIONS PROMOTED BY NBCL5 AND AL2O3 CATALYSTS WITH MICROWAVE IRRADIATION [4]

Alcohols and acids can be connected to produce ethers or esters by varying the alcohol to catalyst molar ratio, in a new etherification and esterification method using $NbCl_5/Al_2O_3$ catalyst under "solvent free" conditions and promoted by MW (microwave) irradiation. A "two sites" mechanism for the reaction was proposed in an attempt to clarify the tendency for the catalyst to be dependent on the alcohol alone during the esterification process.

This work explores the fact that NbCl5, even when exposed to air for a short period, can form an efficient esterification system when mixed in situ with Al2O3 and the mixture to be esterified is subjected to microwave irradiation. This system is almost as efficient as the powerful microwave-driven catalyst ZnCl2 supported on SiO2 reported previously [3]. However, it is more effective than $ZnCl_2$ when the alcohol partner of the reaction bears an aromatic ring. This behavior, and the cross pairs of reactions attempted, point to the fact that the niobium-aluminum pair is independent of the type of acid used, but directly dependent on the steric and electronic characteristics of the alcohol to be esterified, indicating a new mechanistic route for this type of reaction, which is probably different from the classical Fischer mechanism.

The reactions of various aliphatic acids and benzoic acid with different alcohols in the presence of the $Al_2O_3/NbCl_5$ catalyst and in the absence of solvent were studied. Yields of esters varying from 54 to 91% were observed in a 5-min period using a domestic 300 Watt microwave oven at temperatures up to 80 ºC, including 85% yields of benzyl acetate and benzyl benzoate.

SYNTHESIS OF BENZYL BENZOATE AND DIBENZYL ETHER USING MICROWAVE IRRADIATION (DOMESTIC OVEN) WITH A SIO_2-SO_3H CATALYST [5].

In this work, a sulfonated silica gel, with a surface area of 115 m^2/g, pore volumes of 0.38

cm^3/g and 1.32 mmol H$^+$/g was prepared from the sodium silicate obtained from the reaction of construction sand and sodium carbonate, and sulfonated with concentrated sulfuric acid. At 7% (w/w), it promoted the Fischer-Speier esterification of benzoic acid with benzyl alcohol in 93% yields within 5 min, and at higher concentrations, dibenzyl ether was produced selectively and quantitatively in solvent-free reactions induced by microwave irradiation.

In all the reactions involving SiO$_2$-SO$_3$H, the amounts of benzoic acid (0.6839 g, 5.6 mmol) and benzyl alcohol (0.1081 g, 1.0 mmol) used were standardized. The amount of catalyst employed in each run was adjusted to maintain a constant mass-to-mass ratio to the alcohol. All the reactions were irradiated in an unmodified MW oven (900 GHz/360 W) using an unstoppered 125-mL two-necked round bottom flask, and the final temperature of the slurries did not exceed 73 °C.

The maximum yield of benzyl benzoate was achieved (98.97%) at a catalyst/alcohol ratio of 7.0%, but a new spot in the TLC monitoring plates and a corresponding new peak in the GC/MS chromatogram were observed at this concentration, indicating the formation of dibenzyl ether (1.03%). Further experiments indicated that higher yields of ether could be obtained with higher ratios of catalyst; at 20% (w/w), only the ether was formed. The maximum yield of ether-free benzoate (93.61%) was obtained with a catalyst load of 6%.

The mild conditions for the preparations of benzyl benzoate and dibenzyl ether facilitated the recovery of the catalyst, which was filtered from the reaction mixture, washed with ether and dried at 150 °C. The quantity of sulfonic groups on the catalyst (0.20 mmol H/g) was sufficient to promote a very high yield of ester or the ether. This yield was probably influenced by the high water tolerance of the catalyst, which is a characteristic of its textural parameters. The small surface area and large pores of the catalyst also facilitated the quantitative and selective preparation of dibenzyl ether [5].

PREPARATION OF THE PHENYL ESTERS USING MICROWAVE IRRADIATION WITH A SIO$_2$-SO$_3$H CATALYST [6].

On a 10% (w/w) basis, the SiO$_2$-SO$_3$H catalyst was very efficient for catalyzing the esterification of carboxylic acids with phenol, which is not a very good nucleophile. The reaction processes were performed using conventional heating and microwave irradiation. The yields were higher in the microwave-irradiated esterification. The catalyst could be used for three esterification reactions in both processes.

In all the reactions involving SiO2-SO3H, the amounts of carboxylic acid (1.0 mmol) and phenol (0.0941 g, 1.00 mmol) were uniform. All the reactions were heated with a heating mantle (5 h, the final temperature of the slurries did not exceed 120 °C) or by irradiation (5 or 9 min) in an unmodified MW oven (900 GHz/360 W) using an unstoppered 125-mL two-necked round bottom flask. The final temperature of the slurry did not exceed 73 °C.

The processes of esterification using the modified silica were accomplished without solvent, and they were irreversible because the silanol groups present in the solid catalyst adsorbed the water produced. The unnecessary use of different organic solvents, and the abolishment of the use of excesses of acid or alcohol are the added bonuses from this irreversibility.

The phenol esters of formic acid, acetic acid, the nicotinic and salicylic aromatic acids, and the oxalic acid diester were prepared using a domestic microwave oven in the presence of

the SiO$_2$-SO$_3$H catalyst. A large number of different acylation methods exist [7,8], but the vast majority suffers from the production of side products, harsh reaction conditions, the use of air sensitive or toxic promoters, and reaction times on the order of days [7]. Moreover, alcohols that are poor nucleophiles, such as phenol, require anhydride activators in addition to requiring prolonged acylation periods.

Yields of phenyl benzoate greater than 96% were obtained with this catalyst using microwave irradiation, and the catalyst could be reused three times before deactivation. The presence of extra functional groups in the acids, such as the pyridine nucleus in nicotinic acid or the hydroxyl group in salicylic acid, lead to a decrease in the activity without affecting the formation of the respective phenyl esters. The high polarity of the reactants and the strong Bronsted character of the catalyst lead to a high reagent-catalyst affinity, and this affinity appeared to increase when the reaction medium suffers the effect of microwave radiation, resulting in good to excellent yields (64 to 80%) of the esterification products of the otherwise unreactive phenol. The diphenyl ester of oxalic acid, an important intermediate for the production of diphenyl carbonate, was obtained directly with this catalyst using phenol and oxalic acid, using both simple heating (70%) or microwave irradiation (74%), thereby precluding the necessity of prior preparation of the methyl or ethyl oxalic acid ester intermediates and their subsequent transesterification with phenol. The reactions performed using conventional heating conditions required five hours of heating to obtain yields of esters comparable to those obtained within five minutes of heating by microwave radiation.

MICROWAVE ASSISTED DEHYDRATION REACTION OF D-FRUTOSE

DEHYDRATION OF D-FRUCTOSE TO 5-HYDROXYMETHYL-2-FURFURAL IN DMSO USING A HYDROPHILIC SULFONATED SILICA CATALYST IN A PROCESS PROMOTED BY MICROWAVE IRRADIATION [9]

SiO$_2$-SO$_3$H, was used as a catalyst in a 10% (w/w) ratio for the preparation of 5-hydroxymethyl-2-furfural (HMF) from fructose. A 100% conversion was achieved using a domestic microwave reactor. The MW reactions were carried out in 10-mL G-10 vials of an Anton Paar Monowave 300 single-mode MW synthesis reactor, powered by an 850 W magnetron and equipped with a temperature sensor and magnetic stirring during 10 min at 150 °C in DMSO. A 100% selectivity for HMF at a molar ratio of fructose:DMSO equal to 1:56 was observed. The catalyst could be reused three times.

5-Hydroxymethyl-2-furfural (HMF), which can be obtained from the dehydration of sugars, has a high potential as a renewable raw material for the production of a variety of important molecules containing or derived from the furan ring, including biofuels, solvents, drugs, and biopolymer monomers [10-12]. Thus, several studies have described the synthesis of HMF by catalytic dehydration of fructose [13-27], However, the utilization of these systems suffers from several drawbacks. Apart from the general non-selectivity of the processes due to degradation of HMF via rehydration and polymerization reactions, the use of mineral acids involves material corrosion, difficulties in the separation of the acid from the reaction mixture, and, of course, the high toxicity of the acids themselves [17,28-31]. Therefore, the development of more environmentally friendly and convenient solid acid catalysts to replace the liquid acid catalysts is highly desirable.

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Apart from the catalyst, the choice of solvent for the dehydration reaction is also very important. The commonly applied solvents are water, methanol, DMSO and ionic liquids [12,17,30,32]; water/organic solvent biphasic systems are also important for the increase in the conversion rates and selectivity, but the current methods require large amounts of solvents because of the high solubility of HMF in water and the poor partitioning into the organic phase, which sometimes requires additional salting-out techniques for the separation of the product [25].

The preparation of HMF from fructose with DMSO as the solvent and the hydrophilic SiO_2–SO_3H catalyst was achieved using microwave irradiation in processes under ambient atmosphere; MW irradiation has been widely used in the production of HMF [26], and recently, in its oxidation to value-added acid derivatives using solid catalysts containing Ru [33] or Ag [34].

Microwave irradiation was used as an energy source for reaction activation because of its advantages over conventional heating methods [23,24]. As expected, conventional heating of the reaction mixture required longer reaction times and furnished lower yields than microwave heating, except for a reaction in which no solvent was added to the mixture of catalyst and HMF.

Musau and Munavu used DMSO as the sole dehydrating agent using conventional heating [35]. This work shows that, as expected, the use of MW irradiation speeds the overall process, and the excellent mark of 100% HMF conversion could be achieved in only 30 min.

The synergic DMSO/SiO2-SO3H hexose-dehydration reaction might be at its optimum level under MW irradiation because the excellent 100% fructose conversion was again achieved, but with only 10 min of irradiation, and no products other than HMF were formed (by GC/MS analysis). This result compares very favorably with that of Watanabe et al. [36], who observed a very good 94% fructose conversion, but a smaller 73% HMF yield, obtained by the catalytic dehydration of fructose in acetone-water mixtures in the presence of a sulfonic acid resin catalyst at the same temperature of 150 °C and with MW irradiation.

The use of microwave irradiation decreased the time required for the production of HMF by dehydration of fructose with DMSO at 150 °C by fourfold and resulted in 100% conversion and 100% selectivity. Addition of the hydrophilic catalyst SiO2-SO3H to that system reduced the reaction time a further threefold, while maintaining the excellent mark of 100% fructose conversion and 100% selectivity to HMF. The catalytic system also seems to be promising for the preparation of oxobis(5-methyl-2-furaldehyde) ether from HMF. By increasing the contact times of the fructose conversion reactions, the condensation to oxobis(5-methyl-2-furaldehyde) indeed occurs after the hexose was 100% converted to HMF. No other side-product was observed.

MICROWAVE ASSISTED KETALIZATION AND ALDOLIZATION REACTIONS

KETALIZATION OF KETONES TO 1,3-DIOXOLANES AND CONCURRENT SELF-ALDOLIZATION CATALYZED BY AN AMORPHOUS, HYDROPHILIC SIO2-SO3H CATALYST WITH MICROWAVE IRRADIATION [37]

The amorphous, mesoporous SiO2-SO3H catalyst was very efficient for the protonation of ketones on a 10% (w/w) basis, and the catalyst-bound intermediates could be trapped by polyalcohols to produce ketals in high yields or suffer aldol condensations within minutes under low-power microwave

irradiation. The same catalyst could easily reverse the ketalization reaction.

Of particular interest for this work, both SiO2-SO3H [38] and SiO_2-CH_2-CH_2-CH_2-SO_3H [39] have been used with success for ketalization reactions using conventional heating with reaction times extending up to 12 h. An example involves the preparation of the cyclohexanone ketal in 90% yield using toluene as the solvent and heating at reflux temperature for 3 h [39]. However, these experimental conditions yielded only about 50% of the acetophenone ketal, against 93% yield (10 h reflux) using the propyl-modified catalyst. During our attempts to carry out the ketalization reactions using conventional heating, it became clear that concurrent reactions occurred using our SiO2-SO3H catalyst, namely, etherification and aldol condensation [39]. The same reaction was performed using SiO_2-SO_3H as the catalyst in the absence of solvent using low-power microwave irradiation from a domestic microwave oven (360 W). The temperature of the slurry did not exceed 73 ºC, and a 99.9% yield was obtained within only 2 min.

All the ketalization reactions could be reversed by the addition of water to the ketals in the presence of SiO2-SO3H, as has already been pointed out by Rajput *et al.* [40]. Under microwave irradiation, this reaction takes only 2 min to complete. For the hydrolysis of the ketals, the amount of catalyst was adjusted to 20% (w/w) in relation to the ketal (1.00 mmol), and an excess of water (10.00 mL) was added to minimize the auto-condensation reactions of the ketone products.

The formation of six-membered ketals seemed to be favored over the formation of 1-3-dioxolanes, especially those of the seemingly less reactive benzophenone. Cyclohexanone readily self-condensed in the presence of the sulfonated catalyst, but this reaction became negligible at 2:1 or higher ratios of glycol to ketone. However, at these higher ratios, the condensation of the alcohol became important. In the absence of a ketone, ethylene glycol was converted to bis(ethylene glycol) in 96% yield. The catalyst could be used three times, with very little loss in activity under microwave irradiation conditions.

The mesoporous sulfonated silica with a small surface area, large pore diameters and high hydrophilicity presented a higher affinity for ketones than for alcohols and easily promoted aldol condensations when used in concentrations from 7 to 24% (w/w) relative to the concentrations of ketones. In the presence of the poly-alcohols ethylene glycol, glycerol, trimethylolpropane and neopentyl glycol, the ketones acetophenone, *p*-methylacetophenone and benzophenone were converted to the respective ketals in reasonable to good yields. However, benzophenone failed to react with glycerol; pure alkyl ketones such as cyclohexanone were more easily condensed and ketalized. In the absence of ketones, ethylene glycol was smoothly converted to bis(ethylene glycol). All the reactions occurred within minutes under solvent-free conditions using microwave irradiation at 360 W.

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