

Nano Fe₂O₃, Clinoptilolite and H₃PW₁₂O₄₀ as Efficient Catalysts for Solvent-Free Synthesis of 5(4*H*)-Isoxazolone under Microwave Irradiation Conditions

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Uma abordagem rápida e sem solvente envolvendo a exposição de reagentes puros a radiação de micro-ondas em conjunto com o uso dos catalisadores clinoptilolita, H₃PW₁₂O₄₀ e nanopartículas de Fe₂O₃ é descrita. Neste trabalho, a condensação de cloridrato de hidroxilamina, acetato de sódio, acetoacetato ou benzoilacetato de etila e aldeídos apropriados pelo emprego dos catalisadores forneceu 5(4*H*)-isoxazolona em etapa única. A quantidade de catalisador, efeito de temperatura e reutilização dos catalisadores foram monitorados. Entre os catalisadores, o catalisador de nanopartículas de Fe₂O₃ apresentou melhor desempenho que os demais do ponto de vista de rendimento e tempo de reação. Os presentes protocolos oferecem várias vantagens, tais como tempo de reação curto, rendimento razoável, condição de reação suave e fácil reciclagem dos catalisadores.

A quick and solvent-free approach involving the exposure of neat reactants to microwave irradiation in conjunction with the use of clinoptilolite, H₃PW₁₂O₄₀ and Fe₂O₃ nanoparticle catalysts is described. In this work, condensation of hydroxylamine hydrochloride, sodium acetate, acetoacetic or benzoyl acetic ethyl ester and appropriate aldehydes by employing catalysts gave 5(4*H*)-isoxazolone only in one step. Catalyst amount, temperature effects and catalysts reusability were monitored. Among the catalysts, Fe₂O₃ nanoparticles had better performance than other catalysts from viewpoint of yield and reaction time. The present protocol offers several advantages, such as short reaction time, reasonable yield, mild reaction condition and recycling catalysts with a very easy workup.

Keywords: Fe₂O₃ nanoparticles, clinoptilolite, HPA, 5(4*H*)-isoxazolone, multicomponent reactions

Introduction

Heterocyclic compounds are acquiring more importance in recent years due to their pharmacological activities.¹ Nitrogen, sulfur, oxygen containing five/six membered heterocyclic compounds have occupied enormous significance in the field of medicinal chemistry.^{2,3} Oxazoles play very important role in the manufacturing process of various biologically active drugs as anti-cancer,⁴ anti-microbial, anti-diabetic and anti-obesity.^{5,6}

5-Isoxazolone derivatives have been associated with diverse pharmacological activities and they have been used in the dye chemistry.⁷⁻¹⁰ Recently, heterogeneous catalysts have attracted the attention of researchers due to their economic and industrial significance and published reports indicate that they scored over homogeneous catalysts. Amongst various heterogeneous catalysts, heteropolyacids (HPAs), zeolites and nanoscale catalysts are the most attractive ones.¹¹

Heteropolyacids are very interesting solid acid catalysts and they can act as green and ecofriendly catalysts.¹² Catalysis by HPAs and related compounds is a field of increasing importance in worldwide. The reactions, in which they can

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be used from dehydration, cyclization and esterification up to amine oxidation or olefin epoxidation, may find wide applications in the field of industrial chemical productions, such as fragrances, pharmaceuticals and foods.¹³⁻¹⁹ Clinoptilolite [(Na,K,Ca)₃Al₃(Al,Si)₂Si₁₃O₃₆-12H₂O] is one of the most useful natural zeolites. Clinoptilolite is a aluminosilicate framework, whose structure is characterized by cavities and channels, where exchangeable cations and water molecules are hosted.²⁰ These structural features are responsible for the wide industrial applications of zeolites as catalysts and selective absorbers.²¹⁻²⁵ They are used in many applications such as chemical sieves,²⁶ gas absorbers²⁷ and feed additives,²⁸ odor control agents and as water filters for municipal and residential drinking water and aquariums.²⁹ They can easily absorb ammonia and other toxic gases from air and water, and thus can be used as filters, for health reasons and for odor removal.³⁰ Metal oxide promoted reactions at heterogeneous conditions is a proficient field of chemistry which is highlighted by the use of various nanosized catalysts.³¹⁻³³ Metal oxide surfaces exhibit both acid and base properties. These dualities make metal oxides excellent adsorbents and activators of organic compounds. The promising factors which govern the catalytic activity of metal oxides are their metal cation nature, morphology, particle size and surface area. Recent developments on the nanoscience have provided great opportunity for the surface modification and chemical composition of nanosized metal oxides.³⁴⁻³⁷

H₃PW₁₂O₄₀, clinoptilolite and Fe₂O₃ nanoparticles were selected as catalysts because there are no reports on their use for multicomponent synthesis of 5(4H) isoxazolone.

Experimental

Material and methods

Melting points were obtained on a Gallenkamp melting point apparatus. Infrared (IR) spectra were recorded on a Mattson 1000 FT-IR spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Bruker DRX-500 Avance spectrometer using tetramethylsilan (TMS) as an internal standard. Mass spectra were obtained by Shimadzu QP 1100EX. The microanalyses for C, H and N were performed on a Perkin-Elmer elemental analyzer. The used commercial microwave reactor was an Ethos 1600 Microwave Lab Station (Italy). All reagents and solvents were purchased from Merck Chemical Company except for γ -Fe₂O₃ which was bought from Nano Pars Lima Company. All materials were used without further purification. The size and structure of γ -Fe₂O₃ were also evaluated

using transmission electron microscopy (Zeiss EM10 C Germany). TEM image shows that nanoparticle size is 40 nm with spherical morphology (Figure 1).

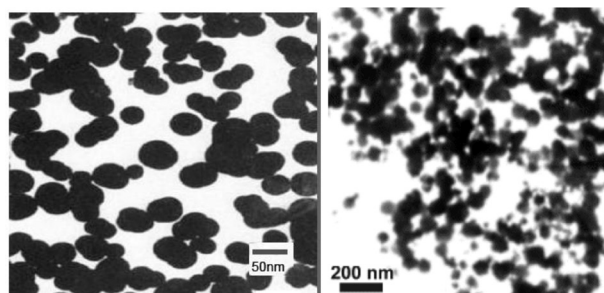


Figure 1. TEM image of γ -Fe₂O₃.

Method A: synthesis of 5(4H)-isoxazolone, using H₃PW₁₂O₄₀

Hydroxylamine hydrochloride (1 mmol), sodium acetate (1 mmol), acetoacetic ester or benzoyl acetic ester (1 mmol), appropriate aldehydes (1 mmol) and H₃PW₁₂O₄₀ (5 mol%) were all poured into a beaker, the obtained suspension was irradiated by a microwave oven at a power output of 300 W for an appropriate time. After irradiation, the mixture was cooled down to room temperature, washed with cold water and filtered. Filtrate was evaporated under reduced pressure, and then the solid catalyst was collected, dried and reused. The filtered crud product was recrystallized from ethanol (96%).

Method B: synthesis of 5(4H)-isoxazolone, using clinoptilolite

Hydroxylamine hydrochloride (1 mmol), sodium acetate (1 mmol), acetoacetic ester or benzoyl acetic ester (1 mmol), appropriate aldehydes (1 mmol) and clinoptilolite (2.5 mol%) were all irradiated by a microwave oven (300 W) for an appropriate time. After irradiation, the mixture was washed three times with chloroform and filtered. The filtrate was evaporated under reduced pressure to give isoxazolone which was then recrystallized from ethanol 96%. The filtered catalyst was repeatedly washed with chloroform and reused.

Method C: synthesis of 5(4H)-isoxazolone, using nano Fe₂O₃

Nano Fe₂O₃ (1 mol%) was added to a mixture of hydroxylamine hydrochloride (1 mmol), sodium acetate (1 mmol), acetoacetic ester or benzoyl acetic ester (1 mmol) and appropriate aldehydes (1 mmol). The resulting mixture was then reacted in an orbital shaker incubator for the appropriate reaction time. After the reaction completion, as indicated by thin layer chromatography (TLC), the reaction mixture was diluted using ethanol 96% and then heated. Nanoparticles were separated from hot ethanol by filtration. The filtrate was cooled to give 5(4H)-isoxazolone. The crud product was then recrystallized from ethanol

96%. Filtered nanoparticles were washed twice with dichloromethane, dried and reused without any significant deactivation even after five runs.

3-Methyl-4-(1-phenylmethylidene)-5-isoxazolone (3a), C₁₁H₉NO₂)

Yellow crystal; mp 144-145 °C; IR (KBr) ν /cm⁻¹ 1753, 1636; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.32 (s, 3H, CH₃); 7.47 (s, 1H, vinyl); 7.53 (dd, 2H, *J* 7.6, 7.4 Hz, ArH); 7.61 (dd, 1H, *J* 7.4, 7.4 Hz, ArH); 8.37 (d, 2H, *J* 7.5 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 12.0, 120.0, 129.4, 132.7, 134.2, 134.4, 150.5, 161.7, 168.3; MS *m/z* 187 (68%, M⁺), 186 (100%), 128 (85%), 90 (65%).

4-[1-[4-(Dimethylamino)phenyl]methylidene]-3-methyl-5-isoxazolone (3b), C₁₃H₁₄N₂O₂)

Red crystal; mp 208-209 °C; IR (KBr) ν /cm⁻¹ 1729, 1636; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.26 (s, 3H, CH₃); 3.17 (s, 6H, 2CH₃); 6.73 (d, 2H, *J* 9.2 Hz, ArH); 7.23 (s, 1H, vinyl); 8.42 (d, 2H, *J* 8.5 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 12.1, 40.5, 111.6, 111.9, 121.9, 138.0, 149.6, 154.7, 162.0, 170.5; MS *m/z* 230 (100%, M⁺), 215 (6%), 172 (11%), 144 (31%); CHN (C₁₃H₁₄N₂O₂) calc. (%) C (67.84), H (6.08), N (12.17); found (%) C (67.71), H (5.94), N (12.33).

4-[1-(4-Methoxyphenyl)methylidene]-3-methyl-5-isoxazolone(3c), C₁₂H₁₁NO₃)

Yellow crystal; mp 160-161 °C; IR (KBr) ν /cm⁻¹ 1753, 1612; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.32 (s, 3H, CH₃); 3.96 (s, 3H, OCH₃); 7.05 (d, 2H, *J* 9 Hz, ArH); 7.38 (s, 1H, vinyl); 8.47 (d, 2H, *J* 9 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 12.1, 56.1, 115.1, 116.8, 126.3, 137.4, 149.7, 161.7, 165.0, 169.2; MS *m/z* 217 (100%, M⁺), 202 (8%), 159 (28%).

3-Methyl-4-[1-(4-methylphenyl)methylidene]-5-isoxazolone(3d), C₁₂H₁₁NO₂)

Yellow crystal; mp 132-133 °C; IR (KBr) ν /cm⁻¹ 1753, 1636; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.32 (s, 3H, CH₃); 2.49 (s, 3H, CH₃); 7.35 (d, 2H, *J* 8.1 Hz, ArH); 7.43 (s, 1H, vinyl); 8.32 (d, 2H, *J* 8.2 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 12.0, 22.5, 118.9, 130.3, 130.4, 134.6, 146.1, 150.3, 161.6, 168.6; MS *m/z* 201(100%, M⁺), 186 (67%), 145 (50%), 128 (81%); CHN (C₁₂H₁₁NO₂) calc. (%) C (71.66), H (5.47), N (6.96); found (%) C (71.78), H (5.46), N (6.81).

3-Methyl-4-[1-(2-thienyl) methylidene]-5-isoxazolone (3e), C₉H₇NO₂S)

Yellow brown crystal; mp 148-149 °C; IR (KBr) ν /cm⁻¹ 1753, 1612; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.32 (s, 3H,

CH₃); 7.29 (dd, 1H, *J* 4.9, 3.9 Hz, thienyl); 7.66 (s, 1H, vinyl); 7.96 (d, 1H, *J* 5 Hz, ArH); 8.13 (d, 1H, *J* 8.5 Hz, thienyl); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 11.9, 115.0, 129.3, 136.9, 139.6, 140.0, 141.9, 161.1, 169.1; MS *m/z* 193 (100%, M⁺), 135 (32%), 108 (18%); CHN (C₉H₇NO₂S) calc. (%) C (55.96), H (3.62), N (7.25); found (%) C (55.85), H (3.57), N (7.39).

4-[1-(4-Fluorophenyl)methylidene]-3-methyl-5-isoxazolone (3f), C₁₁H₈NO₂F)

Yellow crystal; mp 139-140 °C; IR (KBr) ν /cm⁻¹ 1727, 1623; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.31 (s, 3H, CH₃); 7.24 (dd, 2H, *J* 8.5, 8.5 Hz, ArH); 7.42 (s, 1H, vinyl); 8.47 (dd, 2H, *J* 8.38, 5.58 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 12.0, (116.8, 117.0²*J*_{CF} 22.01 Hz), 119.6, 129.29, 137.1, 137.2, 148.7, 161.5, (167.4, 168.4¹*J*_{CF} 131.05 Hz); MS *m/z* 205 (100%, M⁺), 146 (78%), 147 (54%), 108 (39%), 120 (35%); CHN (C₁₁H₈NO₂F) calc. (%) C (64.41), H (3.90), N (6.83); found (%) C (64.28), H (3.85), N (6.75).

3-Phenyl-4-(1-phenylmethylidene)-5-isoxazolone (3g), C₁₆H₁₁NO₂)

Yellow crystal; mp 193-194 °C; IR (KBr) ν /cm⁻¹ 1753, 1636; ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.29 (dd, 2H, *J* 7.7, 7.5 Hz, ArH); 7.76-7.66 (m, 7H, vinyl, ArH), 8.37 (d, 2H, *J* 7.6 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 119.2, 127.8, 129.2, 129.4, 129.7, 131.5, 132.8, 134.4, 134.6, 153.2, 164.4, 168.5; MS *m/z* 249 (100%, M⁺), 205 (57%), 191 (65%), 102 (100%).

4-[1-[4-(Dimethylamino)phenyl]methylidene]-3-phenyl-5-isoxazolone (3h), C₁₈H₁₆N₂O₂)

Red crystal; mp 142-143 °C IR (KBr) ν /cm⁻¹ 1729, 1636; ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.19 (s, 6H, 2CH₃); 6.74 (d, 2H, *J* 9.2 Hz, ArH); 7.41 (s, 1H, vinyl); 7.57-7.63 (m, 5H, ArH), 8.42 (d, 2H, *J* 8.1 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 40.6, 110.4, 111.9, 122.2, 129.1, 129.3, 129.4, 130.7, 138.4, 152.1, 154.9, 165.2, 170.8; MS *m/z* 292 (100%, M⁺), 234 (5%), 144 (18%), 117 (30%).

4-[1-(4-Methoxyphenyl)methylidene]-3-phenyl-5-isoxazolone (3i), C₁₇H₁₃NO₃)

Yellow crystal; mp 166-167 °C; IR (KBr) ν /cm⁻¹ 1753, 1612; ¹H NMR (500 MHz, DMSO-*d*₆) δ 3.96 (s, 3H, OCH₃); 7.04 (d, 2H, *J* 8.9 Hz, ArH); 7.56 (s, 1H, vinyl); 7.70-7.64 (m, 5H, ArH), 8.45 (d, 2H, *J* 8.9 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 56.2, 115.1, 115.8, 126.4, 128.2, 129.2, 129.6, 131.2, 137.7, 152.5, 164.8, 165.3, 169.4; MS *m/z* 279 (100%, M⁺), 221 (14%), 132 (16%).

4-[1-(4-Methylphenyl)methylidene]-3-phenyl-5-isoxazolone (**3j**, C₁₇H₁₃NO₂)

Yellow crystal; mp 181-182 °C; IR (KBr) ν /cm⁻¹ 1753, 1636; ¹H NMR (500 MHz, DMSO-*d*₆) δ 2.49 (s, 3H, CH₃); 7.36 (d, 2H, *J* 8.2 Hz, ArH); 7.59-7.65 (m, 6H, vinyl, ArH), 8.30 (d, 2H, *J* 8.2 Hz, ArH); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 2.5, 118.0, 128.0, 129.2, 129.7, 130.3, 130.5, 131.4, 134.8, 146.4, 153.2, 164.6, 168.8; MS *m/z* 263 (100%, M⁺), 248 (44%), 219 (49%), 205 (44%), 116 (68%).

3-Phenyl-4-[1-(2-thienyl)methylidene]-5-isoxazolone (**3k**, C₁₄H₉NO₂S)

Yellow crystal; mp 189-190 °C; IR (KBr) ν /cm⁻¹ 1753, 1612; ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.31 (dd, 1H, *J* 4.6, *J* 4.5 Hz, thienyl); 7.59-7.66 (m, 5H, ArH), 7.83 (s, 1H, vinyl); 8.01 (d, 1H, *J* 5 Hz, thienyl); 8.11 (d, 1H, *J* 3.7 Hz, thienyl); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 113.9, 128.0, 128.9, 129.3, 129.8, 131.4, 137.1, 140.6, 142.0, 142.5, 163.8, 169.4; MS *m/z* 255 (100%), 211 (42%), 105 (97%).

Results and Discussion

In this work, it is reported good catalytic activities for HPA, clinoptilolite and nano Fe₂O₃ for the synthesis of 5(4H) isoxazolone by microwave irradiation using a commercial microwave reactor. Initially, the reaction of benzaldehyde (1 mmol), hydroxylamine hydrochloride (1 mmol), sodium acetate (1 mmol) and acetoacetic ester (1 mmol) was chosen as a model of reaction for the optimization of catalyst amount (Table 1). Results summarized in Table 1 show the influence of the catalyst concentration on the reaction process. 5 mol% HPA, 2.5 mol% clinoptilolite and 1 mol% nano Fe₂O₃ gave maximum yields. It is noteworthy to mention that in the absence of the catalyst, only small amounts of the product were obtained and the microwave irradiation decreased just the reaction time. These results indicate

Table 1. Influence of the catalyst concentration on the synthesis of **3a**

entry	Catalyst / mol%	Yield / % (a/b/c)
1	1	48/44/75
2	2.5	56/60/71
3	5	63/52/64
4	10	60/56/61
5	15	55/51/50
6	no catalyst	14

Reactions were performed using: hydroxylamine hydrochloride (1 mmol), sodium acetate (1 mmol), acetoacetic ester (1 mmol), benzaldehyde (1 mmol). a: H₃PW₁₂O₄₀ (5 mol%); b: clinoptilolite (2.5 mol%); c: nano Fe₂O₃ (1 mol%) under microwave irradiation at a power output of 300 W.

that the catalysts exhibit a high catalytic activity in this transformation.

During the optimization of the reaction conditions, the effect of temperature was monitored. The product yields were not good even after 5 h under thermal heating condition but the yields were excellent by microwave irradiation. Thus, microwave irradiation has been employed to reduce the reaction time and rate enhancement, and to increase yields (Table 2). Reusability of the catalysts was examined under identical reaction conditions. The recycled catalysts were used five times to obtain 5(4H)-isoxazolone without appreciable decreasing in yields (Table 3).

Table 2. Influence of the temperature on the synthesis of **3a**

entry	Temperature / °C	Yield / % (a/b/c)
1	25	20/10/25
2	40	23/15/33
3	60	34/22/52
4	90	45/36/55
5	microwave (reaction time: Table 1)	63/60/75

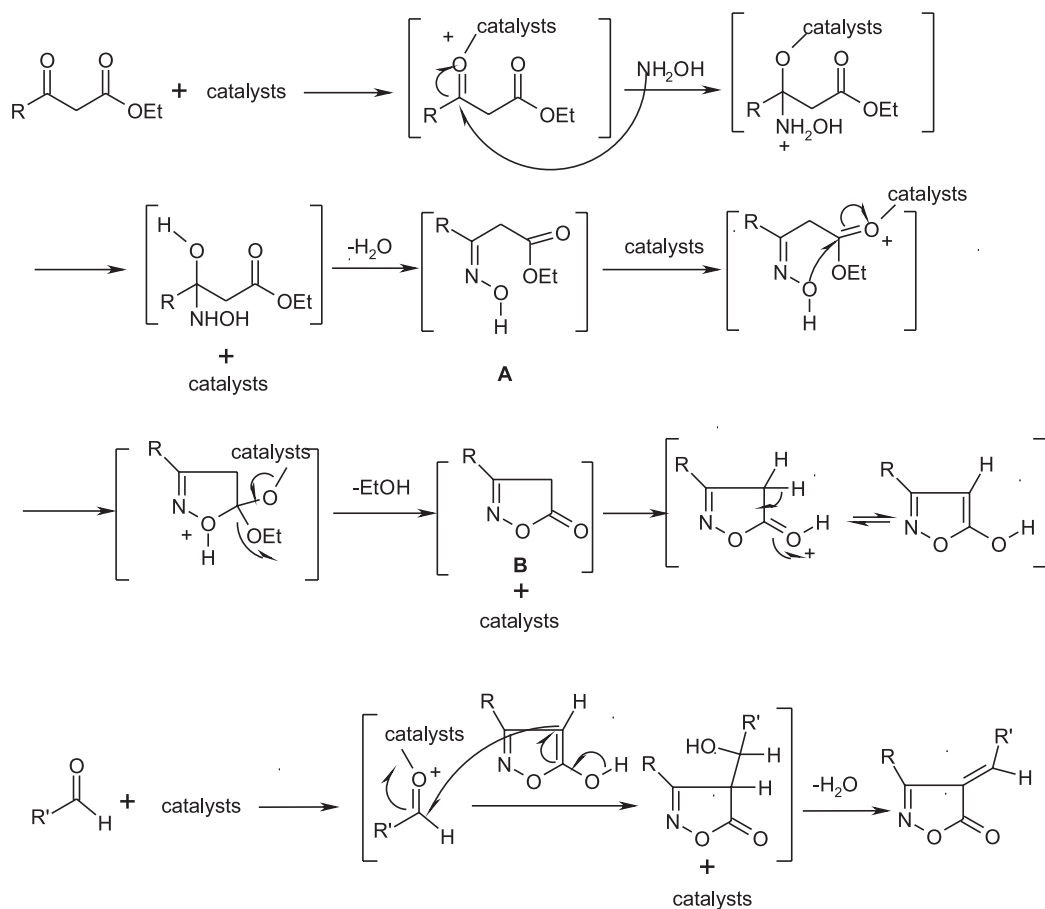
Reactions were performed using: hydroxylamine hydrochloride (1 mmol), sodium acetate (1 mmol), acetoacetic ester (1 mmol), benzaldehyde (1 mmol). a: H₃PW₁₂O₄₀ (5 mol%); b: clinoptilolite (2.5 mol%); c: nano Fe₂O₃ (1 mol%) under thermal heating condition for 5h and microwave irradiation at a power output of 300 W.

Table 3. Reusability of catalysts for synthesis of **3a**

Run	Yield / % (a/b/c)
1	63/60/75
2	63/60/75
3	62/58/75
4	62/57/74
5	62/56/72

Reactions were performed using: hydroxylamine hydrochloride (1 mmol), sodium acetate (1 mmol), acetoacetic ester (1 mmol), aldehydes (1 mmol). a: H₃PW₁₂O₄₀ (5 mol%); b: clinoptilolite (2.5 mol%); c: nano Fe₂O₃ (1 mol%) under microwave irradiation at a power output of 300 W.

The results presented in Table 4 show the scope and generality of the methods (Scheme 1). One of the salient features of these methods is that electron poor or rich aldehydes give good yields and purities. These catalysts are the most attractive ones because of their flexibility in modifying the acid strength, environmental compatibility, low toxicity and experimental simplicity. From these, Fe₂O₃ nanoparticle is the most promising catalyst because of its ease of handling, ease of recovery and high catalytic activities. This catalyst is highly preferred as it offers



Scheme 2. Plausible mechanism for synthesis of 5(4H)-isoxazolone.

Supplementary Information

Supplementary information (spectra of synthesized compounds) is available free of charge at <http://jbcs.sbgq.org.br> as a PDF file.

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