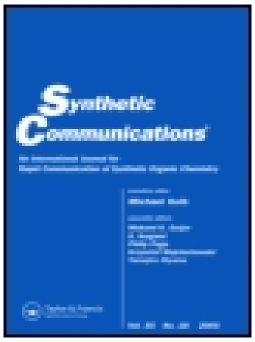

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Synthetic Communications
An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Shu Guo, Renyou Zeng & Caiye Li (2016): Nitrite Containing Resin as an Efficient and Recyclable Catalyst for Aerobic Oxidation of Oximes to Carbonyl Compounds, Synthetic Communications

To link to this article: http://dx.doi.org/10.1080/00397911.2016.1211290

Nitrite Containing Resin as an Efficient and Recyclable Catalyst for Aerobic Oxidation of Oximes to Carbonyl Compounds

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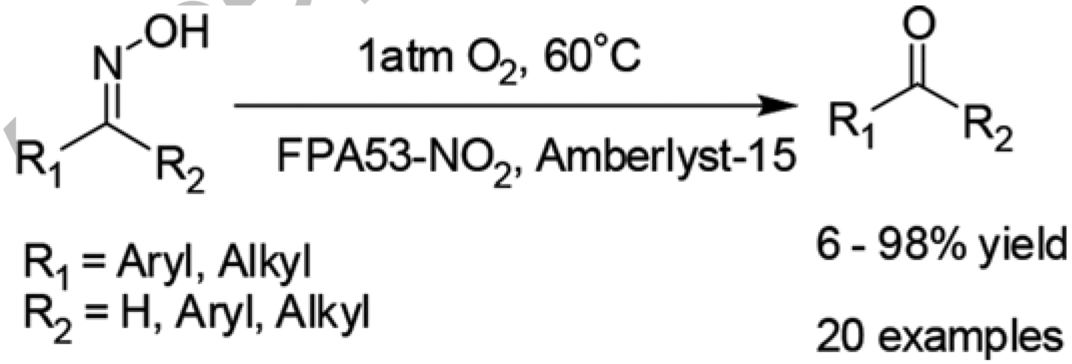
Abstract

Using novel nitrite containing resin as NO source, Amberlist-15 as cocatalyst, aerobic oxidation of oximes to corresponding carbonyl compounds with molecular oxygen as a clean oxidant reagent was developed. It was distinguished from the previous related reports, and the experimental result indicated that additional water obviously decreased the yield. This process provided a better choice for oxidative deoximation with many advantages, such as higher yield, simple procedure, high catalytic performance, and recyclable catalyst.

GRAPHICAL ABSTRACT



KEYWORDS: Nitrite Containing Resin; Aerobic oxidation; Deoximation Reaction; Recyclable catalyst

INTRODUCTION

Oximes serve as important synthetic intermediates as they are extensively used for purification, characterization and also protection of carbonyl containing molecules. Hence many reagents and methods have been devised for the deprotection of oximes. There were reports that Amberlyst-15 supported nitrosonium ion as an effective oxidative reagent was applied in cleavage of oximes to the corresponding carbonyl compounds.[1] An adapted process using catalytic amounts of $NaNO_2$ and the reuse of Amberlyst-15 as reagent was developed to the same aerobic oxidation.[2] Above two reports indicated that the organic solvent / water as a mixed solvent would enhance the reaction rate. Herein, we report our new approach that an aerobic oxidation system which introduced novel FPA53 containing nitrite functional group resin (FPA53-NO_2) and Amberlyst-15 as the catalyst and molecular oxygen as the environmentally friendly oxidation for regeneration of carbonyl compounds from oximes. However, as far as our research was concerned, there was evidence to show that the protic solvent including water, was a negative activator to inhibit the generation of NO_2, an actual oxidizing agent for aerobic oxidation of oximes.

EXPERIMENTAL

The IR spectra were determined on a Nicolet Avatar360 FTIR Spectrometer (KBr pellets), ^{1}HNMR and ^{13}CNMR spectra were recorded with a Bruker AV400 (400MHz) spectrometer. GC were performed on a GC9790 (Zhejiang Fuli Analytical Instrument Co., Ltd) using a capillary column of HP-5 (25m×0.32mm×0.25um). Amberlite FPA53 (weakly basic anion exchange resin, moisture holding capacity 56-64 %), Amberlyst 15 (H form, dry) resin and 732 strongly acidic cation exchange resin (the same as Amberlite IR120 H Form resin, water content 50–55%, ion-exchange capacity: 3.2 mmol/g) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD and used in original form. All solvent was freshly distilled.

Preparation Of FPA53 Containing Nitrite Functional Group (FPA53-NO$_2$)

The FPA53-NO$_2$ was prepared as follow. 5.0 g Amberlite PFA53 was added to 15 ml alcohol, and was stirred at RT for 10 min. Then 5 g phosphoric acid (85% w/w) was slowly added to the suspension of FPA53. After 6 h stirred, the solution was filtered out. The resin beads were thoroughly rinsed with deionized water until given a neutral solution by pH paper detecting. Then sodium nitrite (3.5 g, 0.05 mol), deionized water (15 ml) and the treated polymer beads with phosphoric acid were introduced into a flask, and the stirring was continued for 4 hours at 40℃. The light yellow polymer beads was filtered and washed many times with deionized water until no yellow AgNO$_2$ precipitation was observed by dripping 0.1 M silver nitrate aqueous solutions in the eluent. Again sodium nitrite (3.5 g, 0.05 mol) and deionized water (15 ml) was added and the process was repeated a second time for another 4 h at 40℃. In succession, the resin was dried in a vacuum oven at 40℃ for 4 hours. By this time, the golden resin beads containing nitrite functional group (FPA53-NO_2) were prepared.

As a comparison, FPA53 loaded $NaNO_2$ also was prepared in the meanwhile. Involved procedure was in agreement with process of preparing FPA53-NO_2 except for protonation of tertiary amine by phosphoric acid.

General Experimental Procedure For Deoximation To The Corresponding Carbonyl Compounds

Oximes (1.0 mmol), Amberlyst-15 (0.02 g), FPA53-NO_2 (0.02 g) and solvent (1.5 mL) were introduced into a 25 cm high and 90 mL autoclave with a glass tube inside equipped with magnetic stirring. Then the autoclave was charged with oxygen to 0.1 MPa. The reaction mixture was stirred at desirable temperature for special time. Progress of the reaction was monitored by TLC or GC. After the reaction, The resin (Amberlyst-15 and FPA53-NO_2) were separated from the reaction mixture by filtration and was extracted with 3 mL CH_3CN (2×1.5ml). The solvent was removed under reduced pressure. The residue was further purified by column chromatographyon silicagel (300 mesh) with hexane / ethylacetate to give the corresponding carbonyl compounds.

RESULTS AND DISCUSSION

FTIR spectrum of FPA53, FPA53 loaded $NaNO_2$ and FPA53-NO_2 were collected and given in Fig. 1. FPA53 and FPA53 loaded $NaNO_2$ showed almost no difference absorption peaks both in number and intensity. The similarities suggested very low loading level of $NaNO_2$ due to no bonding interaction between the resin and $NaNO_2$. The above estimate also was confirmed by measuring the capacity of FPA53 loaded $NaNO_2$ based on nitrite content by spectrophotometer. The detected result showed loading amount of nitrite was much lower as 6.5 mg per gram of dry resin.[3] However, the quantization to FPA53-NO_2 by the same spectrophotometer was unreliable because of the decomposition in the presence of water under acidic conditions. What should happen next is to find a accurate and useful detection methodology to determine nitrite content of FPA53-NO_2.

From Fig. 1, the infrared absorption at about 1035 cm^{-1} was corresponded to C-N stretching vibration of tertiary amine in FPA53 and FPA53 loaded $NaNO_2$. There was reason to assume that the blueshift of C-N stretching vibration from 1035 cm^{-1} to 1062 cm^{-1} could be attribute to convert tertiary amine into tertiary aminium salt. A broad and weak absorption peak appeared at 2553cm^{-1} was likely related to N-H stretching vibration of R_3NH^+. The intensity of N-O symmetric stretching of nitrate at 1268 cm^{-1} almost have not significantly increase in FPA53 loaded $NaNO_2$. However, a strong absorption peak at 1268 cm^{-1} showed that FPA53-NO_2 had higher nitrite content and it could be attributed to form a stronger bonding interaction between FPA53 and nitrite.

First, acetophenoneoxime was used as a model substrate and efficiency of a variety of solvents and catalytic conditions were investigated. The results were listed in Table 1.

In this catalyzed system, FPA53-NO_2 was served as an efficient NO source, which was immediately oxidized by oxygen to form NO_2 as an oxidant to oxidize oxime. We found that an acidic condition could make the release of NO more effective. In this work, Amberlist-15, a strongly acidic cation exchange resin, was arranged to provide a recycled acidic source. The trace water of Amberlyst-15 (about 1.5% water content) actually was an essential composition for release a little proton which helped to establish a smooth acid reaction environment. From Table 1, the results confirmed that the lack of Amberlist-15 made the oxidation almost was not carried out (Table 1, entry 1). When adding 0.01 g Amberlist-15, the desired product was obtained in 45.5% yield (Table1, entry 2). Increasing the amount of Amberlist-15 to 0.02 g, an excellent yield of acetophenone was obtained at 60℃ for 2 h (100% GC yield, Table 1, entry 3). When air was used instead of O_2, the yield decreased to 42.7% (Table1, entry 4). Shorten reaction hours and lowing reaction temperature, obvious deteriorated results could also be observed (Table1, entry 5-6). When CH_3CN was replaced with DMF (an weakly basic aprotic solvent), an offset in the acidity of Amberlyst-15 drastically reduced the yield of acetophenone to 1.5% (Table1, entry 11).

The possible mechanism of the deoximation reaction has been described.[1-2] In the existence of molecular oxygen, NO is oxidized to NO_2. The latter was deemed to be actual oxidizing agent for oxidating oximes to the corresponding carbonyl compounds in this reaction.[4-6] In the presenting of active hydroxyl, NO could be rapidly oxidized by oxygen to nitrosonium (NO^+), which reacted with nucleophilic centers such as ROH to produce RONO alkylnitrite,[7] or reacts with water to form nitric and nitrous acids respectively.[8] Both of the process inhibited formation of NO_2, and resulted in an unexpectedly low yield (Table1, entry 7 and entry 10). The result also was supported by other experimental evidence. From Table1, entry 9 we could find that CH_2Cl_2, a aprotic solvent with a low water content make the conversion of oxime completely. When the same amount of 732 resin (50–55% water content) was used instead of Amberlist-15 (1.5% water content), a significant decrease of yield was observed because of quenching the formation of actives ingredients by containing excess water (Table1, entry 8). It was suggested that the solvent that contain excess active hydroxyl, such as alcohols and water or basic solvent should be excluded from this reaction.

To evaluate the scope of this catalytic system, a variety of oxime including various aromatic aldoximes as well as aliphatic and aromatic ketoximes were subjected to these reaction conditions. The results were summarized in Table 2. Not only the ketoximes bearing electron withdrawing groups (such as Cl, Br, F, Ph, NO_2) on the arene ring, but also bearing electron donating groups (including of H, CH_3, OCH_3) could easily be almost completely converted to the corresponding ketones (Table2, entries1-7). Meanwhile, for the sterically hindered benzophenoneoxime and 9-fluorenoneoxime, excellent yields could also be achieved (Table 2, entries 9 and 10). Deoximation reaction of aliphatic oximes were a bit more difficult, and normally requires longer reaction times. After 6 h reaction time, benzylacetone oxime, DL-Camphor oxime and 1,3-diphenylacetone oxime could respectively give the corresponding ketone with gentle yields from 32% to 83% (Table 2, entries 11-13). Unexpectedly, cyclohexanoneoxime give the corresponding ketones in poor yields (Table 2, entry 14). It is possible that the conjugate effect or hyper conjugation effect of the aromatic ketoximes make the intermediate to possess higher stability than those of the aliphatic ketoximes.[1, 9] Similarly, when some aldoximes, that is, benzaldehyde oxime derivatives were subjected to the standard reaction conditions, moderate yields (60%- 85%) were obtained with 4 h reaction time (Table 2, entries 15-19). However, an aliphatic aldoxime, cinnamaldehyde oxime only got 6% yield (Table 2, entry 21). These results might indicate that the aldoximes are more stable than ketoximes under the reaction conditions. Moreover, for the ketoximes or aldoximes containing active hydroxyl, it is little surprise that no corresponding carbonyl compounds could be obtained (Table 2, entry 8 and 20). As was mentioned earlier, NO can easily produce RONO with hydroxyl and inhibit formation of NO_2.

In order to check recycle ability of the resin catalyst, the catalyst recycles successive runs were carried out as following procedures. First, in the presence of FPA53-NO_2 (0.02 g) and Amberlyst-15(0.02 g), 1 mmol acetophenoneoxime and 1.5 ml acetonitrile were allowed to test with 1 atm molecular oxygen, at 60℃ for 2h. At the end of one oxidation run, the autoclave was cooled down and the organic phase was removed by a pipette. The residue was further extracted twice with acetonitrile (2×1.5 ml). The solid phase was kept in the autoclave, and then fresh 1 mmol acetophenoneoxime and another 1.5 ml acetonitrile was added. Subsequently, the autoclave was pressurized with 1 atm O_2 again and was heated under the same reaction conditions for the next cycle. The results of the catalyst recycle were shown in Fig. 2.

The catalyst maintained its good level of efficiency and the yield of acetophenone were hold above 95% even after being reused for six runs (Fig. 2). The obvious decrease in yield could be observed in the seventh reaction cycle, indicating the catalyst owned relatively stable activity in the recycle.

CONCLUSIONS

In conclusion, we have prepared a novel nitrite containing resin FPA53-NO_2, which was accompanied with amberlyst-15 formed a simple, efficient and reused system for aerobic oxidation of oximes to corresponding carbonyl compounds with molecular oxygen as a clean oxidant reagent. The method has advantages in terms of yield, heterogeneous nature, green and reproducible reagents, short reaction times and easy work-up. To this catalytic system, solvent selection is of critical importance, and the protonic solvent, basic solvent and excess water existed in the reaction system must be avoided.

FUNDING

We are thankful to the Natural Science Foundation of Hainan (No.214025) for their funding in this research work.

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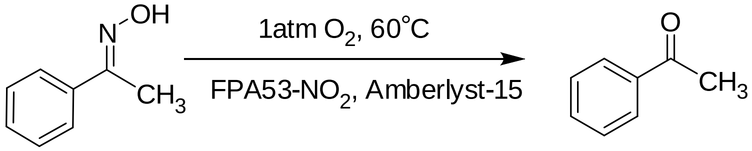
Table 1. The FPA53-NO_2 catalyzed deoximation reaction of acetophenoneoxime with Amberlist-15 and molecular oxygen under different reaction conditions [a]



Entry	**Solvent**	**FPA53-NO_2 (g)**	**Amberlist-15 (g)**	**Time (h)**	**Yield [a] (%)**
1	CH_3CN	0.02	-	2	< 1
2	CH_3CN	0.02	0.01	2	45.5
3	CH_3CN	0.02	0.02	2	100 (98 [b])
4	CH_3CN	0.02	0.02	2	42.7 [c]
5	CH_3CN	0.02	0.02	1	68.7
6	CH_3CN	0.02	0.02	2	53.7 [d]
7	CH_3CN	0.02	0.02	2	24.9 [e]
8	CH_3CN	0.02	0.02	2	41.6 [f]
9	CH_2Cl_2	0.02	0.02	2	100
10	C_2H_5OH	0.02	0.02	2	1.5
11	DMF	0.02	0.02	2	1.7

[a] Reaction condition: acetophenoneoxime (1 mmol, 0.137 g), solvent (1.5 mL), O_2 (1atm), at 60℃

[b] Yield is based on the gas chromatography (GC) with area normalization.

[c] Values in parentheses is the isolated yield

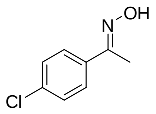
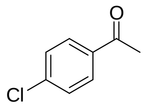
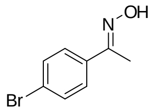
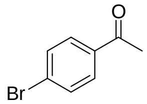
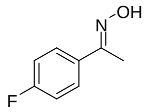
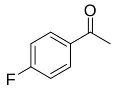
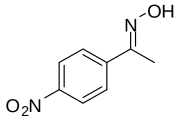
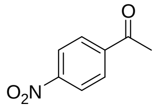
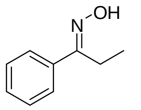
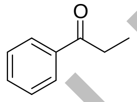
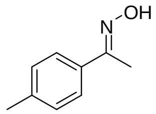
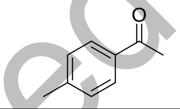
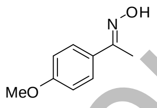
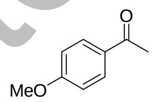
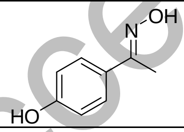
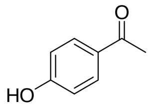
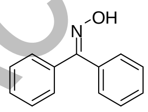
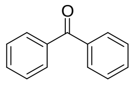
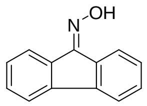
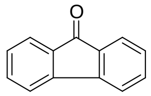
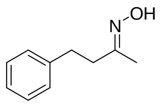
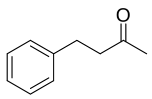
[d] Air (1atm) was used instead of O_2 (1atm)

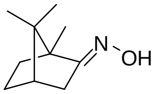
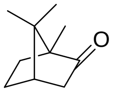
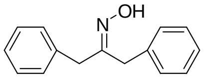
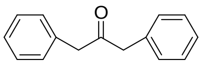
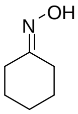
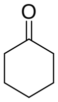
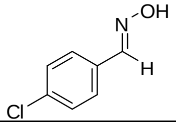
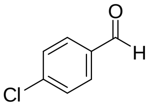
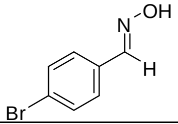
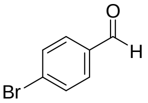
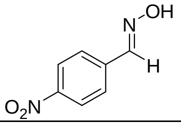
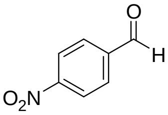
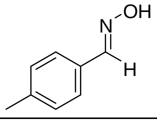
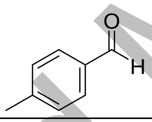
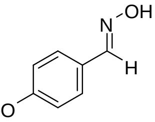
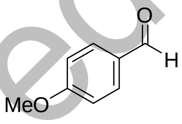
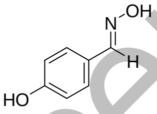
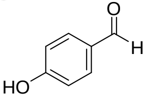
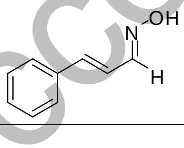
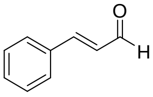
[e] Reaction temperature is at 50℃

[f] 0.1 mL of water was added

[g] The same amount of 732 resin was used instead of Amberlist-15.

Table 2. The FPA53-NO_2 catalyzed Aerobic deoximation reaction of Ketooximes and Aldoximes to Carbonyl Compounds in the presence of Amberlist-15 [a]

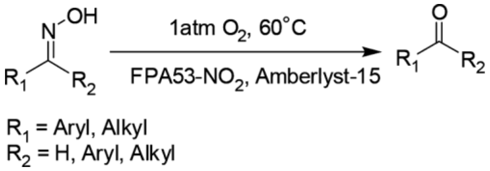
Entry	**Substrate**	**Product**	**Time (h)**	**Yield [b] (%)**
1			2	97
2			2	98
3			2	97
4			2	98
5			2	98
6			2	97
7			2	97
8			2	0
9			2	98
10			2	98
11			6	59

12			6	83
13			6	32
14			6	19
15			4	60
16			4	75
17			4	73
18			4	79
19			4	85
20			4	0
21			4	6

[a] Reaction condition: oxime (1 mmol), Amberlyst 15 (0.02 g), FPA53-NO_2 (0.02 g), acetonitrile (1.5 mL), O_2 (1atm), at 60℃

[b] Based on isolated yield

Scheme 1. FPA53-NO_2 and Amberlyst-15 catalyzed aerobic Deoximation



Scheme 2. process of preparing FPA53-NO_2

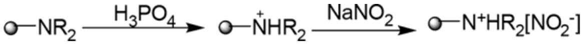


Figure 1. FTIR spectrum of FPA53, FPA53 loaded $NaNO_2$ and FPA53-NO_2

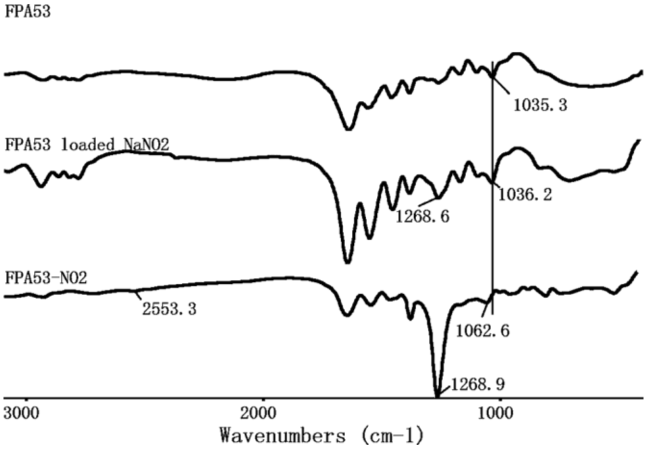
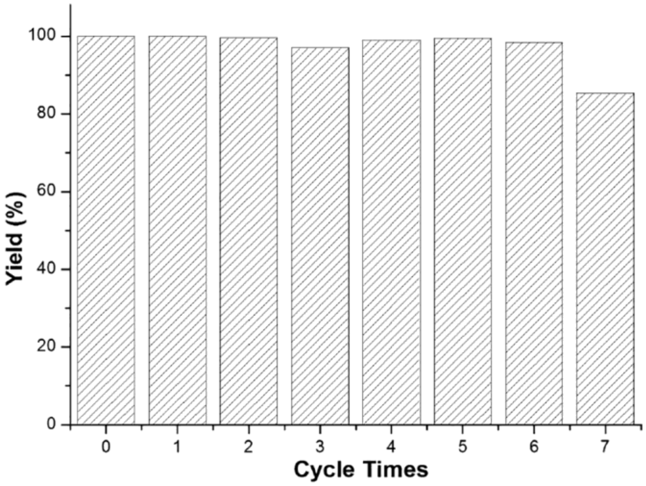


Figure 2. Reuse of Resins for Deomixation of acetophenoneoxime [a]



[a] Based on GC yield