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# Nano $SiO_2/H_2SO_4$ as catalyst for the Beckmann rearrangement and deoximation of aldoximes

Marziyeh Bagheri, Mostafa Karimkoshteh*

*Department of Chemistry, Faculty of Science, Urmia University, Urmia 57159-165, Iran.*

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## ABSTRACT

Nano silica-$H_2SO_4$ is an efficient and mild catalysis system for the regeneration of aldehyde from aldoximes. Ketoximes are converted to amides by Beckmann rearrangement in the presence of nano silica-$H_2SO_4$. The reactions are carried out in solvent-free conditions under microwave irradiation (600 W) within 50-120 sec in good yields.

***Keywords***: *Oxime, Nano $SiO_2$, Amide, Carbonyl compound*.

## 1. Introduction

Oximes are extensively used for purification and characterization of carbonyl compound [1] as well as preparation of amides via the Beckmann rearrangement [2]. The important role of oximes as intermediates in conversion of aldehyde and ketones into the carbonyl compounds [3] and amides [4] has provided motivation to develop several reagents and catalystssuch as $Nb_2O_5$ [5], Ti/montmorillanite [6], sulfonic acid [7], chlorosulfonic acid [8], cyanuric chloride [9], $SOCl_2/\beta$-cyclodextrin [10], pivaloyl chloride [11] andphosphonate [12]. However, some of these methods suffer from different disadvantages such as tedious work-up procedure, drastic reaction conditions, long reaction times, undesired chemical yields and use of expensive and toxic reagents. Therefore, a milder, more selective, non-hazardous and inexpensive reagent is still required for such transformation.

The coupling of microwave irradiation with the use of catalysts on mineral supported reagents, under solvent-free conditions, provide unique chemical processes with special attributes such as enhanced reaction rates, higher yields, greater selectivity, and ease of manipulation. Microwave irradiation as an unconventional energy source has been widely used to perform many kinds of chemical reactions [13]. Nanoparticles exhibit high catalytic activity and chemical selectivity under mild conditions [14]. As one common type of nanoparticles, silica ($SiO_2$) particles have been utilized increasingly as catalysts [15,16]. Because of large surface area, nano$SiO_2$ show unusual physicochemical properties compared with those bulk particles [17,18]. Through infrared spectroscopy method, $SiO_2$ nanoparticle exist a large number of hydroxyl groups on its surface, and forms the deviation from the steady state of the silicon oxide structure as shown in Scheme 1 [19].

Various methods for the preparation of nano $SiO_2$ are employed such as micro emulsion processing, combustion synthesis and sol-gel processing [20].

Hear we wish to report the use of $H_2SO_4$/nano silica as an efficient system in the oximes reactions (Scheme 1).

## 2. Experimental

All microwave assisted reactions were carried out in a Yusch household microwave oven (1000 W). All substrates and reagents were obtained from commercial sources of the highest quality and were used without further purification. Nano $SiO_2$ is prepared in high purity according to the reported procedures in literature [21]. The products were characterized by comparison of their melting or boiling points with authentic samples. NMR and IR spectra were recorded on 300 MHz

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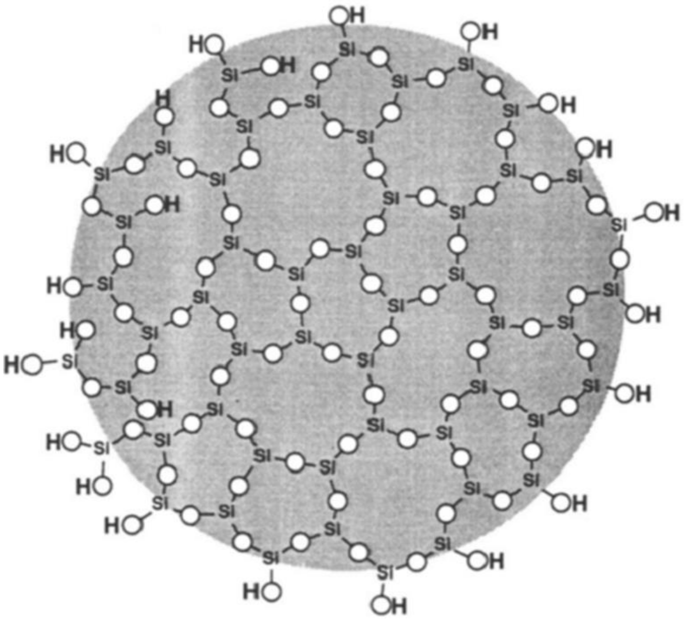
[*] Corresponding author: E-mail: karimkoshteh@gmail.com



**Scheme 1.** [18]

Bruker Avance and Thermo Nicolet Nexus 670 FT-IR spectrometer, respectively. The aryl oximes were recrystallized in ethanol/water.

### *2.1. A typical procedure for the conversion acetophenoneoxime to acetanilide.*

A mixture of nano $SiO_2$ (0.3 g, 5 mmol) and $H_2SO_4$ (0.196 g, 2 mmol) was ground in a mortar. Then, Acetophenoneoxime (0.135 g, 1 mmol) was added to the mixture and grinding of the reaction mixture was continued for a moment. The mortar was covered with a watch glass and put inside of the oven (60% power amplitude ≈ 600W) for 50 sec. The progress of the reaction was monitored by TLC (eluent; $CCl_4/Et_2O$: 5/2). At the end of the reaction, distilled water (5 ml) was added to the reaction mixture and neutralized with 10 ml of an aqueous solution of sodium hydroxide (5%) and then extracted with diethyl ether (3×5 mL). The extracts were combined and dried over $Na_2SO_4$. After evaporation of the solvent the acetanilide was obtained, in 95% yield (0.128 g, Table 3: entry 1). white solid, m.p. 113–115$^o$C. IR (KBr, $\nu_{max,}$ cm$^{-1}$): 3294 (N-H), 1662 (CONH), 1602, 1551, 1493, 755, 698. $^1$HNMR (300 MHz, $CDCl_3$, ppm) δ: 2.12 (s, 3H), 7.08 (t, 1H, *J* = 8.0 Hz), 7.23 (t, 2H, *J* = 8.0 Hz), 7.52 (d, 2H, *J* = 8.0 Hz), 8.54 (br. s, 1H, NH). $^{13}$C NMR (75 MHz, $CDCl_3$, ppm) δ: 168.9 (C=O), 138.1, 128.8, 124.2, 120.2, 24.1 ($CH_3$).

## 3. Results and discussion

The literature review shows that the sol-gel process is widely used to produce pure silica particles due to its ability to control the particle size, size distribution and morphology through systematic monitoring of the reaction parameters [22]. So we prepared nanosilica with this method (diagram 1).

We found that $H_2SO_4$ in the presence of nano $SiO_2$ dramatically performs deoximation and Beckmann rearrangement of various aldoximes and ketoximes to the corresponding carbonyl and amide compounds under solvent-free conditions (Scheme 2). In order to

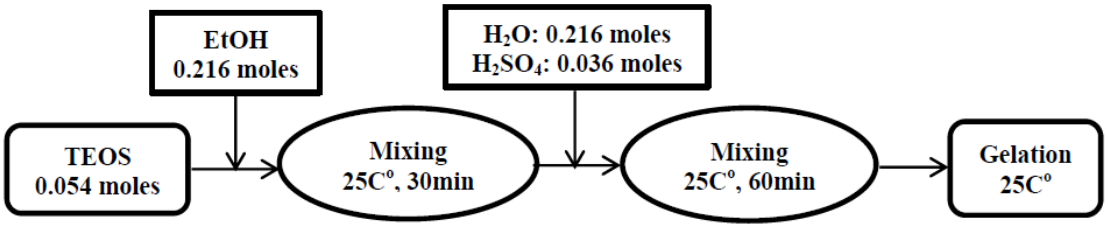


**Diagram 1.** [21]

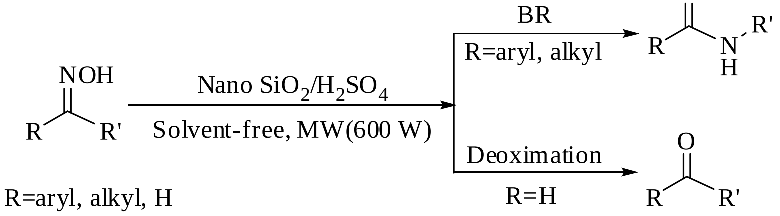
**Table 1**. Experimental optimization for the conversion of benzaldehyde oxime to benzaldehyde with nano $SiO_2/H_2SO_4$ system. [a]

| Entry | Molar ratio Subs./nano $SiO_2/H_2SO_4$ | Condition[b] | Time (min) | Solvent | Conversion (%) |
|---|---|---|---|---|---|
| 1 | 1/-/1.5 | Solvent-free/MW | 2 | - | 0 |
| 2 | 1/3/- | Solvent-free/MW | 2 | - | 0 |
| 3 | 1/3/1.5 | R.T. | 60 | THF | 0 |
| 4 | 1/3/1.5 | Reflux | 60 | $CH_3CN$ | 0 |
| 5 | 1/3/1.5 | Reflux | 60 | $H_2O$ | 0 |
| 6 | 1/3/1.5 | Solvent-free/oil bath | 60 | - | 10 |
| 7 | 1/3/2 | Solvent-free/oil bath | 60 | - | 10 |
| 8 | 1/4/1.5 | Solvent-free/oil bath | 60 | - | 10 |
| 9 | 1/3/1.5 | Solvent-free/MW | 50sec | - | 100 |
| 10 | 1/3/1 | Solvent-free/MW | 50sec | - | 98 |
| 11 | 1/3/2 | Solvent-free/MW | 50sec | - | 100 |
| 12 | 1/4/1.5 | Solvent-free/MW | 50sec | - | 100 |

[a] All reactions were carried out with 1 mmol of benzaldehyde oxime:

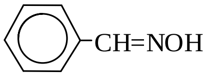
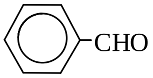
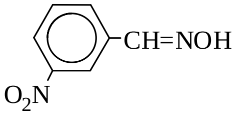
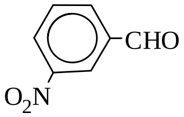
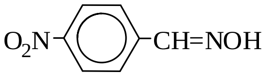
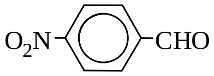
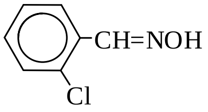
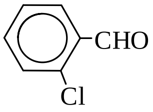
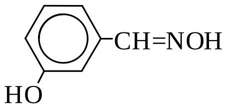
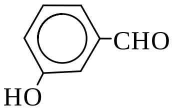
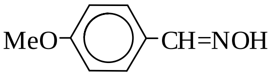
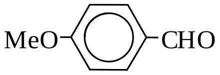
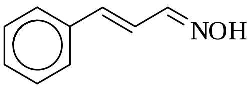
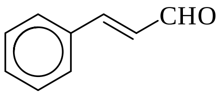
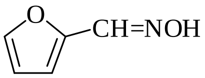
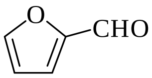
[b] Temperature of oil bath was 70-80 $^{o}$C and irradiation with microwave (MW) was carried out under 600W power amplitude.

obtain the optimum reaction conditions and showing the influence of the reaction components, we performed benzaldehyde oxime as a model compound with nano $SiO_2$-$H_2SO_4$ system under different reaction conditions (Table 1). As the result shown, the solely $H_2SO_4$ or nano $SiO_2$ or bulk $SiO_2$ did not show any efficiency even at the prolonged reaction time (entries 1 and 2). However, by the combination of nano $SiO_2$ with $H_2SO_4$ in a molar ratio of 3:1.5, respectively, deoximation of 1 mmol benzaldehyde oxime was carried out perfectly under microwave irradiation (600 W) within 50 sec (entry 9). Versatility of this synthetic protocol for deoximation of various aldoximes was also studied (Tables 2). The results show that all types of aldoximes were deoximated successfully by nano $SiO_2/H_2SO_4$ system within 40-120 sec to afford the corresponding aldehydes in moderate to excellent yields (54-95%). Furfural oxime and Cinnamaldehyde oxime produced moderate yields of the corresponding products. Further increasing of the reaction time and changing in the molar ratios gave no significant improvement in the yields but rather decomposition occurred (Table 2, entry 7, 8). In continuation of this research program, we found that with nano $SiO_2/H_2SO_4$ under microwave irradiation (600 W) various ketoximes were converted to secondary amides (Table 3). As it was shown in Table 3, good to excellent yields were obtained for the Beckmann rearrangement of entries 1-8 without any by-product or parent ketone formation. Based on the qualitative analysis by GC–MS, it could be found that their main by-product is the corresponding ketone and only trace amounts of dimericoxime was observed (0.1%). Much better results could be obtained if aryl ketoximes were used. Beckmann rearrangement of benzophenone oxime, a symmetrical oxime, reached to 100% and no by-product was detected after reaction (Table 3, entry 6). A plausible mechanism for the nano $SiO_2$-$H_2SO_4$ catalyzed Beckmann rearrangement was illustrated in Scheme 3. The nano $SiO_2$-$H_2SO_4$ facilitates the rearrangement process through co-ordination of its O–H with – OH of oximes, followed by the transfer of R group.



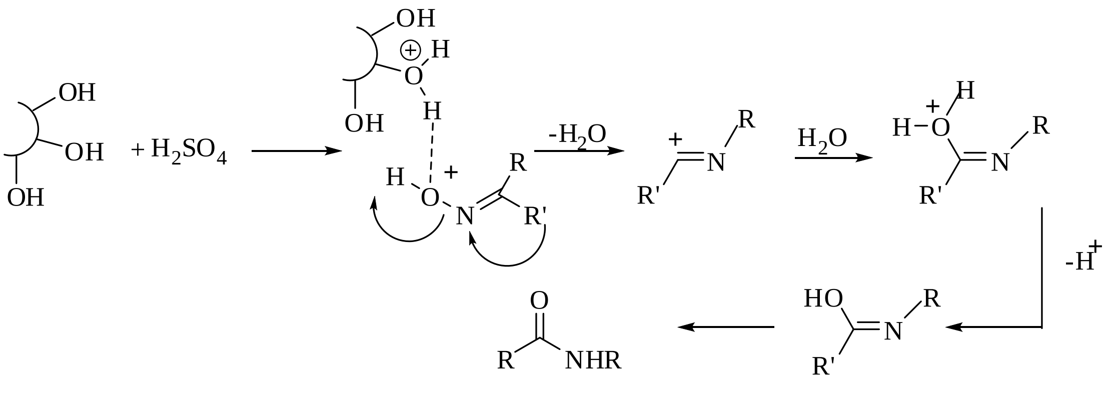
**Scheme 2.**

**Table 2.** Deoximation of aldoximes with nano $SiO_2/H_2SO_4$ system[a].

| Entry | Substrate | Product | Time (s) | Yield (%)[b] | m.p. ($^oC$) | |
|---|---|---|---|---|---|---|
| | | | | | Obs. | Lit.[d] |
| 1 |  |  | 50 | 94 | - | - |
| 2 |  |  | 50 | 93 | 58 | 55-56 |
| 3 |  |  | 40 | 92 | 108 | 106 |
| 4 |  |  | 50 | 95 | - | - |
| 5 |  |  | 60 | 93 | 99 | 100-103 |
| 6 |  |  | 50 | 95 | - | - |
| 7 |  |  | 120 | 68 | - | - |
| 8 |  |  | 90 | 54 | - | - |

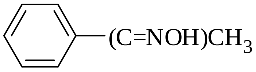
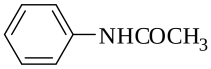
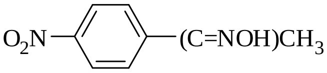
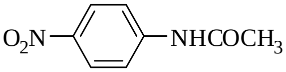
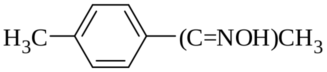
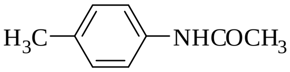
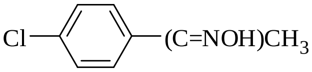
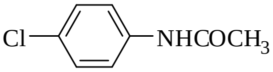
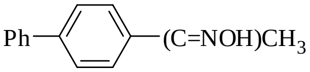
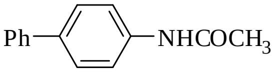
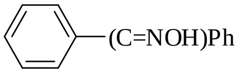
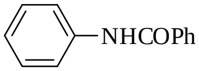
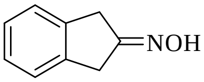
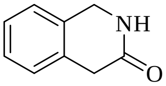
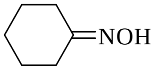
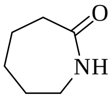
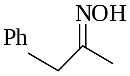
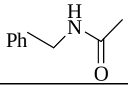
[a] All reactions were carried out with the molar ratio of Subs./nano $SiO_2/H_2SO_4$ (1:3:1.5) under microwave irradiation (600 W).
[b] Yields refer to isolated pure products.
[c] Reactions were carried out under microwave irradiation (500 W).
[d] Lit. m.p. obtained from ref. 31.

In order to show the efficiency of this deoximation system, we compared our results with those of reported in the literature for Sulfamic acid [23], PTSA-Lewis acid [24], PEG-$SO_3H$ [25], $H_3PO_4$ [26], $(EtO)_2POCl$ [27], $AlCl_3$-$ZnCl_2$/ $SiO_2$ [28], $P_2O_5/SiO_2$ [29] and Propylphosphonicanhydride ($T_3P$) [30]. As shown in Table 4 nano $SiO_2/H_2SO_4$ method seems to be convenient with respect to other existing reports and can be used as an alternative, which will avoid tedious purifications or the use of toxic or expensive reagents and has advantages of high conversion, high selectivity and simple work-up procedure.



**Scheme 3.**

**Table 3**. Beakmann rearangment of ketoximes with nano $SiO_2/H_2SO_4$ system.[a]

| Entry | Substrate | Product | Time (s) | Conversion (%) | Yield (%)[b] | m.p. (°C) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Obs. | Lit.[c] |
| 1 |  |  | 50 | ~98 | 95 | 115 | 114-15 |
| 2 |  |  | 90 | ~98 | 95 | 213 | 215 |
| 3 |  |  | 90 | ~98 | 93 | 151 | 148.5 |
| 4 |  |  | 90 | ~98 | 93 | 176-77 | 177-79 |
| 5 |  |  | 90 | ~98 | 95 | 168 | 172 |
| 6 |  |  | 50 | 100 | 93 | 161 | 163 |
| 7 |  |  | 60 | ~98 | 93 | 98-99 | 102 |
| 8 |  |  | 50 | ~98 | 96 | 68-70 | 71 |
| 9 |  |  | 50 | ~98 | 87 | 59 | 61 |

[a] All reactions were carried out under microwave irradiation (600 W) with the molar ratio of Subs./nano $SiO_2/H_2SO_4$ (1:5:2).
[b] Yields refer to isolated pure products.
[c] Lit. m.p. obtained from ref. 31-35.

**Table 4.** Comparison of nano $SiO_2/H_2SO_4$ with other reported reaction systems.

| Entry | System [Ref] | Condition | Time (min) /Yield (%) | | |
|---|---|---|---|---|---|
| | | | Acetophenone oxime | Cyclohexanone oxime | Benzophenone oxime |
| 1 | Sulfamic acid [23] | $CH_3CN$ | 360/96 | 360/40 | 480/88 |
| 2 | PTSA-Lewis acid [24] | $CH_3CN$ | 300/97 | 300/40 | - |
| 3 | PEG-$SO_3H$ [25] | $CH_3CN$ | 300/87 | 360/85 | 300/90 |
| 4 | $H_3PO_4$ [26] | M.W | 1/74 | 1.2/73 | 3/78 |
| 5 | $(EtO)_2POCl$ [27] | Toluene | 30/91 | - | 20/91 |
| 6 | $AlCl_3$ -$ZnCl_2$/ $SiO_2$ [28] | M.W | 11.5/87 | - | 7/82 |
| 7 | $P_2O_5/SiO_2$ [29] | M.W | 3/80 | 3/85 | 3/95 |
| 8 | Propylphosphonic anhydride ($T_3P$) [30] | THF | 120/98 | 90/89 | 90/93 |
| 9 | Nano $SiO_2/H_2SO_4$ | M.W | 0.5/95 | 0.5/96 | 0.5/93 |

## 4. Conclusion

In this paper, we have shown the combination system of nano $SiO_2$ and $H_2SO_4$ efficiently catalyzed deoximation of various oximes to the corresponding carbonyl compounds and ketoximes to amides in high yields under solvent-free conditions. Simplicity, excellent yields, mildness and eco-friendly aspects of this synthetic protocol are the advantages which make nano $SiO_2$/ $H_2SO_4$ system a effective way to the present methodologies in this area.

## Acknowledgments

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