

## Synthesis of functionalized alkenes via Knoevenagel condensation using Marine Fish Scales as a new efficient and eco-friendly catalyst

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### Abstract

The preparation of Marine Fish Scales (MFS) and its analog doped with NaNO<sub>3</sub> (NaNO<sub>3</sub>/MFS) as new catalysts was discussed in this work. Then, these materials were characterized by TGA/TDA, X-ray diffraction, SEM, EDX, and IR spectrophotometer. The MFS and NaNO<sub>3</sub>/MFS can be used as eco-friendly catalysts for the Knoevenagel condensation and led to the functionalized alkenes in high yields with short reaction time. The tests show that 100 mg is the optimum mass, as well as the suitable solvent, is ethanol for the condensation of Knoevenagel. These parameters led to excellent yields (between 9% and 97% using NaNO<sub>3</sub>/MFS). These catalysts can be also reused for several times.

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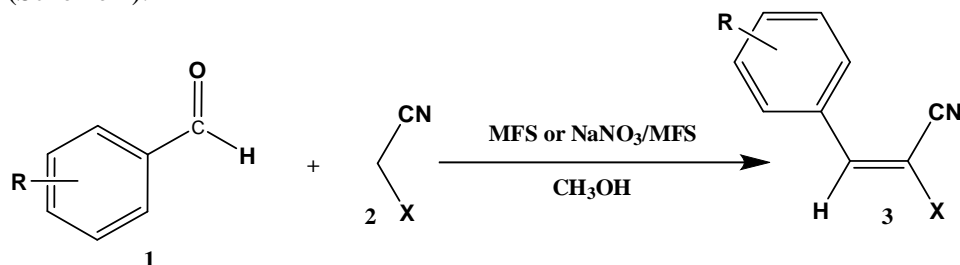
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## 1. Introduction

The Knoevenagel condensation is a very important reaction in organic synthesis and mainly favors the formation of carbon-carbon bonds ( $sp^2$ - $sp^2$ ). It is a reaction that produces substituted alkenes with high biological activity [1]. These products involved in the synthesis of cosmetic and pharmaceutical products [2]. This reaction was discovered in 1894 by Emil Knoevenagel in the presence of diethylamine as a catalyst [3]. In this reaction, a carbonyl compounds react with one equivalent of carbanion to produce a  $\alpha,\beta$ -unsaturated carbonyl compounds (Scheme 1). It catalyzed by solid catalysts which are easy to remove at the end of the reaction (heterogeneous catalysts), namely dimethylamino [4], potassium fluoride [5], surfactants [6], ionic liquids [7-11], modified silica [12-14], the anionic resins [15], the alkaline earth oxides [16], the calcined hydrotalcites [17], the aluminophosphates oxynitrides [18], the nanoparticles of Ni [19],  $ZrO_2$  [20], and modified SBA-1 [21]. The others heterogeneous catalysts have been used in this condensation such as: zeolites [22], oxides  $La_2O_3$  and  $MgO$  [23], lithium hydroxide  $LiOH$  [24], sepiolites [25], aluminophosphate oxynitrides ALPON) [26], Lewis acids such as  $LaCl_3$  [27],  $ZnCl_2$  [28],  $CuCl_2$  [29], triphenylphosphane [30], fluorapatite [31], diphosphate  $Na_2CaP_2O_7$  [32], hydroxyapatite [33], and natural phosphate [34]. However, most of these catalysts involve the use of expensive reagents, harsh and drastic reaction conditions, extended reaction times, difficulty of reuse for several times, and the generation of a large amount of toxic waste. Thus, it is necessary to develop new methods for the Knoevenagel condensation under mild and eco-friendly conditions. In this work we develop new heterogeneous catalysts which are eco-friendly in order to minimize the risks to the environment and human health. This catalyst consists mainly of chemically treated Marine Fish Scales (MFS) and its analog modified with  $NaNO_3$  ( $NaNO_3$ /MFS) in order to improve their catalytic performances in the Knoevenagel condensation reaction (Scheme 1).



**Scheme 1.** Reaction of Knoevenagel.

## 2. Materials and methods

### 2. 1. Chemical products

All chemicals products and solvents used in this work are pure and purchased from Sigma-Aldrich. The fish scales were collected from the port of Agadir city.

### 2. 2. Instrumentation

TGA (Thermogravimetric Analysis) and TDA (Thermodifferential Analysis) were carried out on a TGA SHIMADZU DTG-60 Thermogravimetric in an alumina crucible, at a heating rate of  $10\text{ }^{\circ}C/min$  under atmospheric pressure. The XRD patterns were recorded on a Panalytical diffractometer, equipped with a copper X-ray (wavelength  $\lambda = 1.54 \cdot 10^{-10}$  m, tension  $V = 45\text{ kV}$ , intensity  $I = 35\text{ mA}$ ), and with a monochromator eliminating  $K\beta$  radiation. The scanning electron microscope (SEM) was carried out on a Supra 40 VP COLUMN GEMINI ZEISS coupled to an analyzer (Oxford Instruments X-Max  $20\text{ mm}^2$ ) with EDXS detector (Energy Dispersive X-rays Spectroscopy) instrument. The IR spectra were recorded by JASCO FT/IR 4000 spectrophotometer (spectrum from  $4000$  to  $500\text{ cm}^{-1}$  at resolution  $4\text{ cm}^{-1}$ , ATR mode). NMR data were recorded on Bruker ARX 300 spectrometers.  $^1H$  NMR and  $^{13}C$  NMR spectra were

recorded in the deuterated solvent ( $\text{CDCl}_3$ ). All NMR data were acquired and processed using either TopSpin 3.5 software (Bruker).

### 2. 3. Preparation of supports MFS and $\text{NaNO}_3/\text{MFS}$

The collected fish scales were thoroughly cleaned, washed several times with distilled water at room temperature to eliminate the attached fats and dirty, and left in the open air to eliminate bad odors. Then, they were treated with NaOH as described the literature [35, 36]. The resulting material was named MFS. A portion of this material (MFS) was doped with an aqueous solution of sodium nitrate ( $\text{NaNO}_3$ ) with a proportion of  $\text{NaNO}_3/\text{MFS} = 1/2$ . This mixture was stirred vigorously at room temperature, evaporated to dryness, dried, and calcined at  $800^\circ\text{C}$  for 2 hours [37-40]. The resulting material was named  $\text{NaNO}_3/\text{MFS}$ .

### 2. 4. The general study of the reaction of Knoevenagel

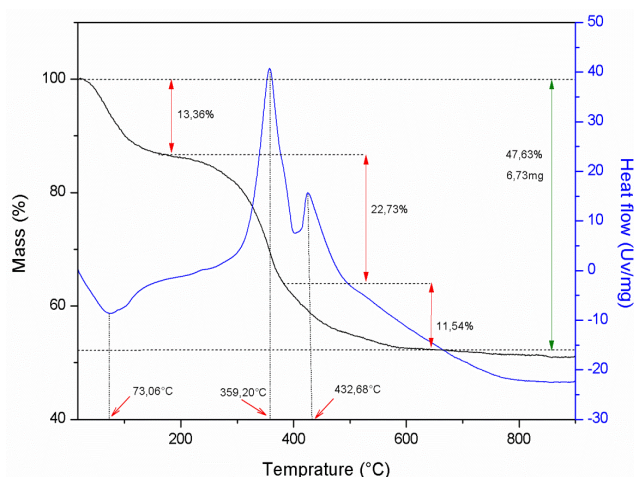
1 mmol of an activated methylene derivatives **1** (malononitrile, ethyl cyanoacetate) and 1 mmol of an aromatic aldehyde **2** were condensed in the presence of 100 mg of the catalyst (MFS or  $\text{NaNO}_3/\text{MFS}$ ) and 5 ml of methanol. The mixture was heated at  $60^\circ\text{C}$ . At the end of the reaction, the mixture was washed with dichloromethane and the catalyst was removed by simple filtration.

## 3. Results and discussions

### 3. 1. Support characterization

#### 3. 1. 1. TGA/TDA analysis

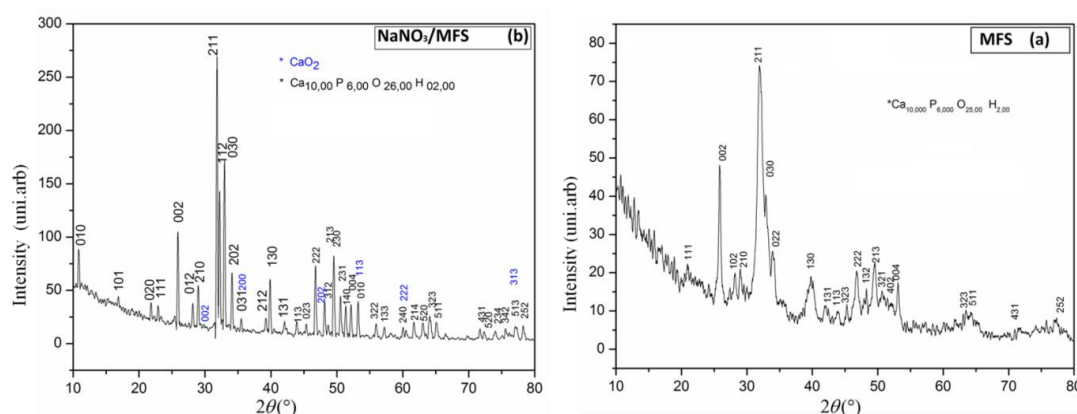
The thermal analysis TGA coupled with TDA of our support gives us an idea about the effect of temperature on fish scales. This characterization is done on scraps of 14.142 mg of the crude scales from  $17.37^\circ\text{C}$  to  $900^\circ\text{C}$ . Figure 1 illustrates the results of this analysis. Three losses are observed in the TGA spectrum. The first loss is equal to 13.36% (mass %). It is located between  $18^\circ\text{C}$  and  $150^\circ\text{C}$  which corresponds to the loss of surface and structural water. The second is equal to 22.73% and located between  $150^\circ\text{C}$  and  $385^\circ\text{C}$  which corresponds to the loss of organic matter. The last loss is equal to 11.54% located between  $385^\circ\text{C}$  and  $606^\circ\text{C}$  corresponds to the loss of the rest of the organic matter. The TDA spectrum showed an endothermic peak at  $73.06^\circ\text{C}$  corresponding to the loss of water. Two exothermic peaks with a maximum of around  $348.46^\circ\text{C}$  and  $432.68^\circ\text{C}$  which correspond to the loss of organic matter in two stages.



**Figure 1.** The results of TGA and TDA of the raw scales.

### 3. 1. 2. XRD analysis

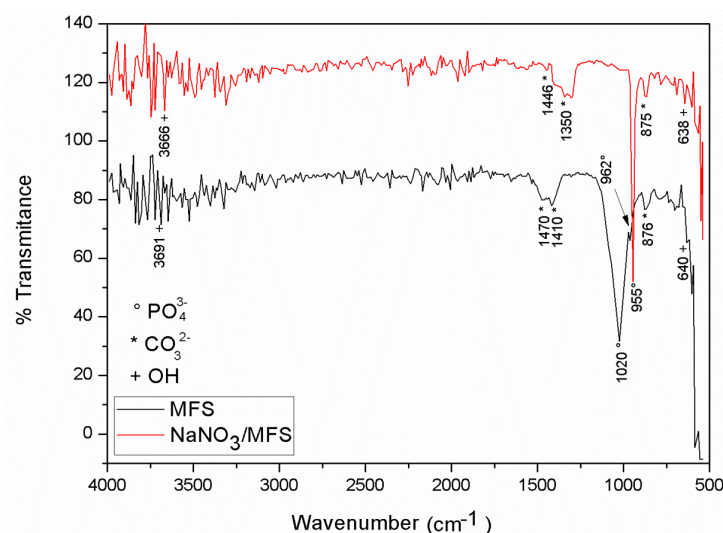
The X-ray diffraction patterns of MFS and NaNO<sub>3</sub>/MFS is present in figure 2. The diagram a shows the presence of a major phase called hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> which was confirmed by the JCPDS data standard (96-900-2214). The identification allowed us to assign the Miller indices (hkl) to the Bragg peaks following the approximate hexagonal parameters  $a = b = 9.4080 \text{ \AA}$ ,  $c = 6.8890 \text{ \AA}$ ,  $\alpha = \beta = 90.00^\circ$ , and  $\gamma = 120.00^\circ$  which is characterized by a P63/m space group. According to the diagram b, it is observed that the NaNO<sub>3</sub>/MFS support is well crystallized since the peaks are fines. This is due to the elimination of organic matter during calcination. Two phases Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> and CaO<sub>2</sub> were observed. The first phase is hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> which was justified by comparison with file JCPDS number 96-101-1243. This structure is crystallized in the hexagonal system characterized by the following parameters:  $a = b = 9.4000 \text{ \AA}$ ,  $c = 6.930 \text{ \AA}$ ,  $\alpha = \beta = 90.00^\circ$  and  $\gamma = 120.00^\circ$  with space group P63/m. The second phase is in agreement with that of CaO<sub>2</sub> (JCPDS number 01-085-0514). It is characterized by parameters following  $a = b = 5.0100 \text{ \AA}$ ,  $c = 5.9200 \text{ \AA}$ ,  $\alpha = \beta = 90.00^\circ$ , and  $\gamma = 90.00^\circ$  and under the tetragonal crystal system with a space group is F4/mmm.



**Figure 2.** X-ray diffraction patterns of the MFS (a) and NaNO<sub>3</sub>/MFS (b).

### 3. 1. 3. IR analysis

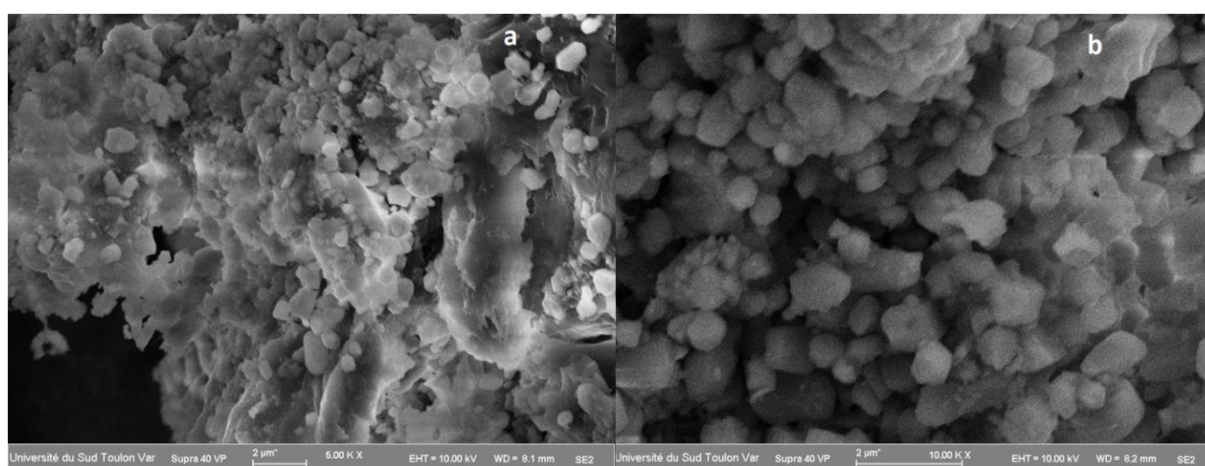
The IR spectrum of our supports shows the presence of the characteristic bands of hydroxyapatite which confer the results of RDX (Figure 3). Broadband at 3691 cm<sup>-1</sup> and 640 cm<sup>-1</sup> corresponds to OH<sup>-</sup>. The bands 1020 cm<sup>-1</sup>, 962 cm<sup>-1</sup>, and 955cm<sup>-1</sup> are attributed to PO<sub>4</sub><sup>3-</sup>. The bands 1470 cm<sup>-1</sup>, 1410 cm<sup>-1</sup>, and 876 cm<sup>-1</sup> are derived from carbonate groups CO<sub>3</sub><sup>2-</sup>.



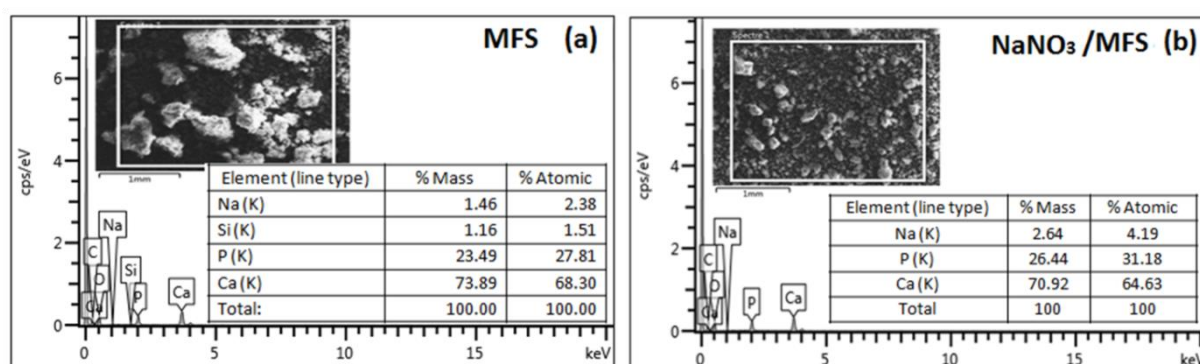
**Figure 3.** The FT-IR spectra of MFS and NaNO<sub>3</sub>/MFS.

### 3. 1. 4. SEM/EDX analysis

The SEM analysis of MFS indicates that this powder is characterized by the formation of the particles whose dimension is between 1 and 5  $\mu\text{m}$  (Figure 4a). The assembly of these particles formed the agglomerates with mean sizes of 20  $\mu\text{m}$ . For the second support ( $\text{NaNO}_3/\text{MFS}$ ), the SEM images show homogeneous particles whose mean size is between 1 and 4  $\mu\text{m}$  (Figure 4b). To characterize our catalysts, we have also carried out the EDX analysis which gave us the results presented in figure 5. We have observed that the MFS support (Figure 5a) consists mainly of calcium and phosphorus with 68.30% and 27.81% molar percentages respectively, which confirms the XRD analysis with a Ca/P ratio = 2.45 which is greater than 1.67 characterizes the stoichiometric hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . The XRD analysis of  $\text{NaNO}_3/\text{MFS}$  support in (Figure 5b) shows the presence of two phases, which is confirmed by EDX which clearly shows the high molar percentages of calcium and phosphorus (%Ca = 64.63%, %P = 31.18%) Ca/P = 2.07 greater than that which characterizes stoichiometric hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (1.67) and a there phase  $\text{CaO}_2$ .



**Figure 4.** SEM micrographs of MFS (a) and  $\text{NaNO}_3/\text{MFS}$  (b).



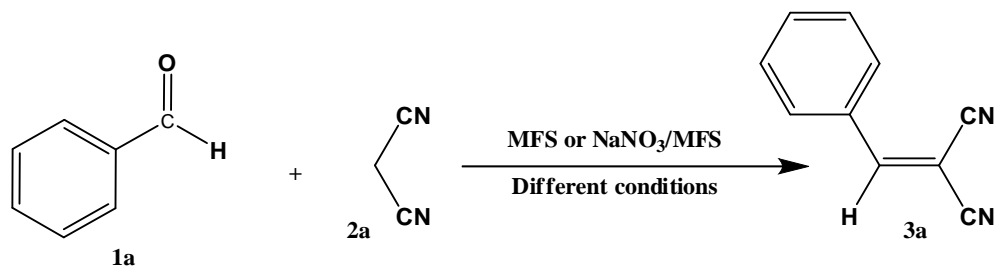
**Figure 5.** EDX spectrum of MFS (a) and  $\text{NaNO}_3/\text{MFS}$  (b).

### 3. 2. Optimization of the Knoevenagel

MFS and its analog  $\text{NaNO}_3/\text{MFS}$  once prepared, their efficiency must be tested in the Knoevenagel condensation. Thus, the reaction parameters were optimized using benzaldehyde **1a** and malononitrile **2a** in the presence of MFS or  $\text{NaNO}_3/\text{MFS}$  (Scheme 2). First, we have examined the effect of the reaction time using the previous reactants in the presence of methanol and the MFS or  $\text{NaNO}_3/\text{MFS}$  as catalysts at 60  $^{\circ}\text{C}$  in various times. From the results obtained, it is showed that the yield of this reaction is a maximum in the presence of  $\text{NaNO}_3/\text{MFS}$  which reaches 95% only in 5



min with complete disappearance of the starting reagents. In the case of MFS, the yield is 79% for 20 min. In this case, it should be mentioned that the reaction was carried out with high yields at low times and that the starting reagents are still present in the reaction mixture.



**Scheme 2.** Optimization of Knoevenagel condensation.

We have assumed that the NaNO<sub>3</sub>/MFS support gives better yields, we have evaluated different factors of this doping such as 1/8, 1/4, 1/2, 2/3. We performed well with factors greater than 1/2 (96% at 5 min with 1/2 and 96% at 5 min with 2/3) Different quantities of MFS or NaNO<sub>3</sub>/MFS catalysts (0-200 mg) were also evaluated and 95% was isolated in only 5 min with a mass greater than 100 mg using NaNO<sub>3</sub>/MFS and 42% at 20 min with the same mass of MFS. Various temperatures were tested such as 20, 40, 60, and 80 °C. The optimum yields were obtained at 60 °C. Indeed, we obtained 95% at 5 min with NaNO<sub>3</sub>/MFS and 79% at 20 min with MFS. Finally, the solvent effect was examined in the condensation of benzaldehyde **1a** with malononitrile **2a** in the presence of MFS or NaNO<sub>3</sub>/MFS as a catalyst at 60 °C. In various solvents, such as H<sub>2</sub>O, EtOH, CH<sub>3</sub>OH, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and C<sub>3</sub>H<sub>6</sub>O, we have found that CH<sub>3</sub>OH is the best solvent which can lead to a high yield of 79% after 20 min with MFS and 95% with NaNO<sub>3</sub>/MFS even after 5 min at 60 °C. It can be concluded that the operating conditions for achieving better yields for Knoevenagel condensation are: 100 mg of MFS or NaNO<sub>3</sub>/MFS with a doping factor of 1/2 in a CH<sub>3</sub>OH as solvent at 60 °C. Consequently, we adopted these parameters for the follow-up of this study.

### 3. 3. Knoevenagel condensation of the various aldehydes

MFS and its analog NaNO<sub>3</sub>/MFS once prepared, their efficiency must be tested in the Knoevenagel condensation. Thus, the reaction To evaluate the catalytic activity of our catalysts MFS and NaNO<sub>3</sub>/MFS, we have carried out the condensation of the various aldehydes with malononitrile or ethyl cyanoacetate. Table 1 shows the results of this study. It is clearly shown that all the condensations finished after 5 min to 20 min with yields between 74% and 97%. From table 1, we observed that the Knoevenagel condensation corresponds to the electronic effects and the nature of the substituent in the aromatic aldehydes. Indeed, it can be seen that the malononitrile is the most active methylene compound, which explains the partially-yields (Entries 1-6) compared to those of ethyl cyanoacetate (Entries 7-12). On the other hand, the presence of attractant groups NO<sub>2</sub> on the aromatic aldehydes (4-nitrobenzaldehyde and 3-nitrobenzaldehyde) increases the reaction rate and yields (Entries 5, 6, 11, and 12). Comparing with the aldehydes which carry donor groups (CH<sub>3</sub>, OCH<sub>3</sub>, and Cl) which produce **3b**, **3c**, **3d**, **3h**, **3i**, and **3j** (Entries 2, 3, 4, 8, 9, and 10). This can be explained by a high electron density of the substituents. Concerning the benzaldehyde which has a medium reactivity with malononitrile and ethyl cyanoacetate, the corresponding yields of alkenes **3a** and **3g** were relatively good. Finally, the expected products of the Knoevenagel condensation were obtained with high regioselectivity and can be isolated with excellent yields by simple recrystallization.

**Table 1. Results obtained by the reaction of Knoevenagel catalyzed by MFS and NaNO<sub>3</sub>/MFS**

Entry	X	R	Product <sup>a</sup>	Yield (%) <sup>b</sup> /Time (min)	
				MFS	NaNO <sub>3</sub> /MFS
1	CN	C <sub>6</sub> H <sub>5</sub>	<b>3a</b>	79/ 20	95/5
2		4-MeOC <sub>6</sub> H <sub>4</sub>	<b>3b</b>	77/20	93/5
3		4-MeC <sub>6</sub> H <sub>4</sub>	<b>3c</b>	76/20	93/5
4		4-ClC <sub>6</sub> H <sub>4</sub>	<b>3d</b>	78/20	96/5
5		4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>3</b>	81/20	97/5
6		3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>3f</b>	80/20	96/5
7	CO <sub>2</sub> Et	C <sub>6</sub> H <sub>5</sub>	<b>3g</b>	77/20	93/5
8		4-MeOC <sub>6</sub> H <sub>4</sub>	<b>3h</b>	74/20	91/5
9		4-MeC <sub>6</sub> H <sub>4</sub>	<b>3i</b>	75/20	92/5
10		4-ClC <sub>6</sub> H <sub>4</sub>	<b>3j</b>	76/20	94/5
11		4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>3k</b>	79/20	94/5
12		3-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<b>3l</b>	78/20	94/5

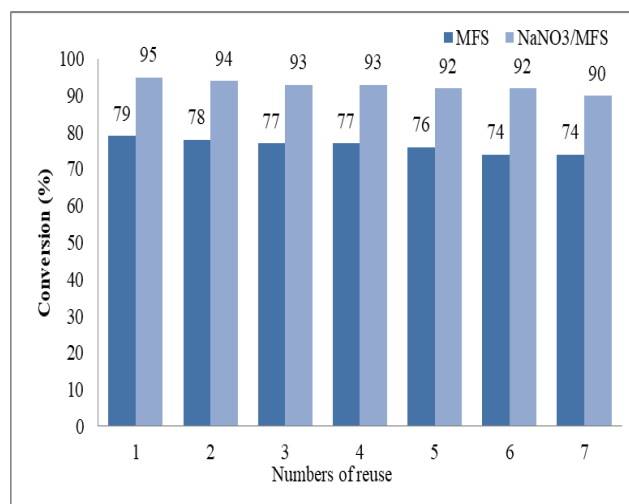
Reactions carried out with various aromatic aldehydes (2 mmol) and the activated methylene derivatives in the presence of 100 mg of the catalyst (MFS or NaNO<sub>3</sub>/MFS) in 5 ml of methanol at 60 °C.

<sup>a</sup>All the products were characterized by 1 H-NMR, 13 C-NMR, and comparison with authentic samples prepared according to the methods of the literature.

<sup>b</sup>Yields of pure isolated products after purification by simple recrystallization from EtOH.

### 3. 4. The reuse of MFS and NaNO<sub>3</sub>/MFS

In order to evaluate the recyclability of our catalysts MFS and NaNO<sub>3</sub>/MFS, we have reused them several times. Each reaction was carried out under the same conditions optimized above, using 2 mmol of benzaldehyde **1a** to obtain product **3a**. After completion of the reaction, the MFS and NaNO<sub>3</sub>/MFS supports were separated and washed with acetone and then regenerated by calcination for 2 h at 500 °C for each reuse. Figure 6 shows the results of this study. The benzaldehyde conversion decreased from 95% to 90% using NaNO<sub>3</sub>/MFS and from 79% to 74% using MFS after 7 rounds of reuse. This decrease can be justified probably by the loss of active sites after each reaction.

**Figure 6.** Reusability of MFS and NaNO<sub>3</sub>/MFS in the Knoevenagel condensation.

## 4. Conclusion

In this study, we have developed the new procedure in the organic synthesis using a new materials MFS and its analog  $\text{NaNO}_3/\text{MFS}$  as heterogeneous and eco-friendly catalysts in the Knoevenagel condensation between malononitrile (or ethyl cyanoacetate) with various aromatic aldehydes. This procedure can assure some advantages such as higher yields, milder conditions, short reaction times, the possibility to reuse the seventh time, and reduction of environmental problems.

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