

SYNTHESIS OF OXIMES WITH THE DOPED POTASSIUM FLUORIDE ANIMAL BONE MEAL AS A CATALYST

M. Ait Taleb^{1,2*}, R. Mamouni^{1*}, N. Saffaj¹, M. Ait Benomar¹,
A. Bakka¹, A. Mouna², A. Benlhachemi³, B. Bakiz³, S. Lazar⁴

¹*Equipe de Matériaux, Catalyse & Valorisation des Ressources Naturelles,*

²*Equipe de Chimie Bio-Organique Appliquée, ³Laboratoire de Matériaux
& Environnement, Université Ibn Zohr, BP 8106, 80000 Agadir, Morocco*

⁴*Laboratoire de Biochimie, Environnement & Agroalimentaire, URAC 36,
Université Hassan II-Casablanca, BP 146, 20650 Mohammedia, Morocco*

*Corresponding authors: r.mamouni@uiz.ac.ma / mohamedaitaleb004@gmail.com

Received: December, 11, 2016

Accepted: November, 29, 2017

Abstract: The potassium fluoride doped Animal Bone Meal (KF/ABM) was prepared and characterized using several techniques to identify the structural properties. After, it has been used as a new and eco-friendly catalyst for the preparation of from aldehydes and ketones oximes under solvent-free conditions. It is clearly shown that this reaction (using this catalyst) can lead to the corresponding oximes in good yields (80 %) to excellent yields (96 %). In the case of dissymmetric aldehydes and ketones, this catalyst can lead to a mixture of *Z*- and *E*- isomers (*Z/E* = 86/14–90/10). The remarkable advantages of this catalyst are high conversion, short reaction times, cleaner reaction profiles, reusability up to 8 times without significant loss of activity, and reduction in catalyst toxicity.

Keywords: *animal bone meal, catalyst, eco-friendly, oximes, reusable catalyst*

INTRODUCTION

The transformation of aromatic aldehydes and ketones to their corresponding oximes is one of the most ubiquitous reactions in organic chemistry. It has been extensively studied in view of the importance of the synthesized oximes as intermediates in organic synthesis [1 – 3]. Thus, this reaction continues to attract the attention of researchers for its importance in organic synthesis and temptation to find the mild and easy reaction conditions.

Consequently, a large number of researchers were interested in the synthesis of oximes. Classically, they were prepared by the condensation reaction of aldehydes and ketones with hydroxylamine hydrochloride [4]. Currently, several procedures for the preparation of oximes are described in the literature such as the use of formic acid [5], pyridine-chloroform [6], CaO [7], ethanol-pyridine [8], Al₂O₃ [9], TiO₂/SO₄²⁻ [10], ZnO [11], NaOH [12 – 15], Na₂SO₄ under ultrasound irradiation [16], ethylenediamine and oxone [17], hyamine [18], Bi₂O₃ [19], Cu-SiO₂ [20], DOWEX(R)50WX4 [21], Na₂CaP₂O₇ [22], Fe₃O₄ [23], K₂CO₃ [24], animal bone meal [25] and chemically treated eggshell wastes as a heterogeneous and eco-friendly catalyst [26].

However, there are a number of limitations to use of these methods, related to the difficulty of reuse, the use of expensive reagents, the generation of a large amount of toxic waste, long reactions times, and drastic reaction conditions. Therefore, it is necessary to develop new methods for the preparation of oximes under mild and eco-friendly conditions in order to minimize adverse effects both on human health and the environment. This can be done by reducing or eliminating the use and generation of hazardous substances such as toxic by-products or wastes and toxic catalysts. Recently, the use of solid supported reagents (heterogeneous catalysts) in this reaction have an important role due to its stability and reusability, ease of handling, clean reaction profiles, high selectivity, short reaction time, and non-toxicity. Among these catalysts, Animal Bone Meal (ABM) and sodium nitrate doped ABM (NaNO₃/ABM) [25]. In continuation of our research program to explore the effectiveness of ABM and its analogs doped catalysts, we wish to develop in this paper a practical approach for the synthesis of some oximes using the potassium fluoride doped ABM (KF/ABM) as reusable, cost-effective and eco-friendly catalyst under solvent-free conditions. This catalyst has recently been developed and used as a new eco-friendly catalyst for preparation of chalcones and aza-Michael adducts [27].

MATERIALS AND METHODS

Catalyst preparation

The modified bones KF/ABM was prepared by impregnating the bones with an aqueous solution of potassium fluoride. The weight ratio used was KF/bones = 1/2. The mixture was stirred vigorously at room temperature for 4 h, evaporated, dried and calcined at 800 °C for 2 h as described in the literature [26]. The catalyst obtained was characterized by X-ray diffraction, scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDS).

Characterization methods

All chemical reagents and solvents were of analytical grade, were purchased from Sigma-Aldrich, and were used without further purification. The animal bone has been collected from restaurants in Agadir city.

The XRD patterns of were recorded on a Panalytical diffractometer, equipped with a copper X-ray (wavelength $\lambda = 1.54 \cdot 10^{-10}$ m, tension $V = 45$ kV, intensity $I = 35$ mA), and with a monochromator eliminating K β radiation. The SEM pictures were recorded on Supra 40 VP COLUMN GEMINI ZEISS coupled to an analyzer (Oxford Instruments X-Max 20 mm²) with EDXS instrument. NMR spectra were recorded on a Bruker AVANCE 300 instrument (¹H-NMR, 300 MHz; ¹³C-NMR, 75.5 MHz), both with tetramethylsilane as an internal standard. Deuterated chloroform (CDCl₃) and deuterated methanol (CD₃OD) are used as solvents. All NMR data were acquired and processed using either TopSpin 3.5 software (Bruker). The IR spectra were recorded by JASCO FT/IR-4000 spectrophotometer (spectrum from 4000 to 500 cm⁻¹ at resolution 4 cm⁻¹, ATR mode).

General procedure of oximes preparation

1 mmol of aldehyde or ketone **1** were mixed with 1.5 mmol of hydroxylamine hydrochloride **2** in the presence of 100 mg of KF/ABM as a heterogeneous catalyst at 80 °C under solvent-free conditions (Figure 1). After completion of the reaction (monitored by TLC), the reaction mixture was dissolved in 20 mL of dichloromethane. Then, the catalyst was separated by simple filtration using a glass Buchner funnel fitted with a sintered glass disc. The obtained filtrate was concentrated under reduced pressure to obtain the desired products (oximes) [25]. These products were purified by recrystallization from an ethanol or by chromatography on silica gel column (hexane/ethyl acetate: 2/10). The products were analyzed by ¹H NMR, ¹³C NMR, IR and melting points.

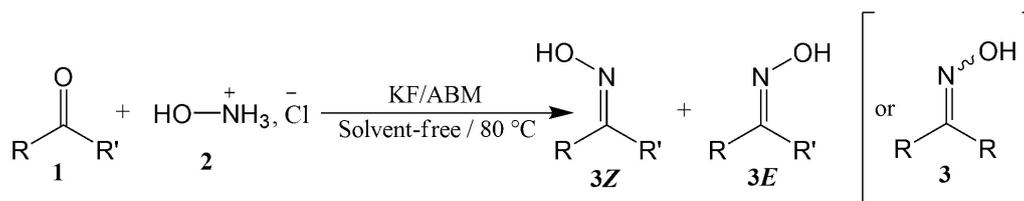


Figure 1. Synthesis of oximes using KF/ABM catalyst

RESULTS AND DISCUSSION

Characterization of catalyst

The XRD pattern of KF/ABM shows presence of 3 phases: potassium calcium hydrogen phosphate (K₃CaH(PO₄)₂), fluorapatite (Ca₅(PO₄)₃F), and potassium calcium fluoride (KCaF₃) (Figure 2).

The K₃CaH(PO₄)₂ was compared with the JCPDS Card N° 00-035-0808. This identification was confirmed by the comparison with the approximate parameters of

monoclinic: $a=9.8826 \text{ \AA}$, $b=5.7352 \text{ \AA}$, $c=7.4307 \text{ \AA}$, $\alpha=\gamma=90.000^\circ$ and $\beta=94.1240^\circ$ (characterized with C2/m space group (N° 12)).

The $\text{Ca}_5(\text{PO}_4)_3\text{F}$ was confirmed by comparison with the standards JCPDS data N° 01-073-1727. This system crystallizes in hexagonal system with a space group P63/m. The lattice parameters of this phase were in excellent agreement with standard data: $a=b=9.3700 \text{ \AA}$, $c=6.8800 \text{ \AA}$, $\alpha=\beta=90.000^\circ$ and $\gamma=120.000^\circ$.

The KCaF_3 was confirmed by comparison with the standard JCPDS N° 00-003-0567. The Miller indices (hkl) were in conformity with approximate parameters of a cubic ($a=b=c=8.7500 \text{ \AA}$ and $\alpha=\beta=\gamma=90^\circ$).

Scanning Electron Microscopy (SEM) of KF/ABM is shown in Figure 3. The SEM images of KF/ABM sample clearly showed large agglomerates with dimensions of from 5 to 10 μm . These agglomerates are formed by the agglomeration of small particles having regular (between 0.2 and 1.2 μm) (Figure 3b). These particles contain some active cavities that would be very interesting for catalysis.

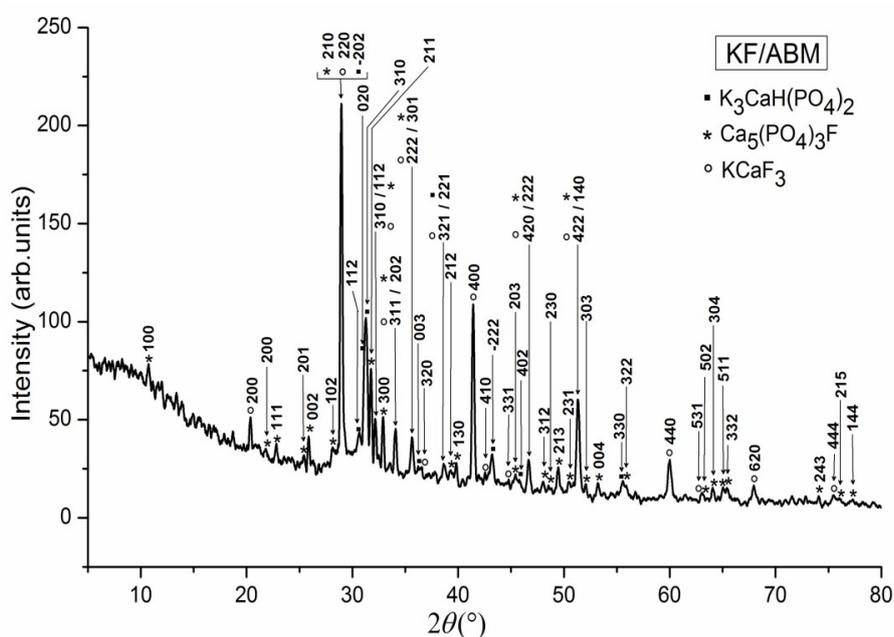


Figure 2. X-ray diffraction patterns of the KF/ABM catalyst

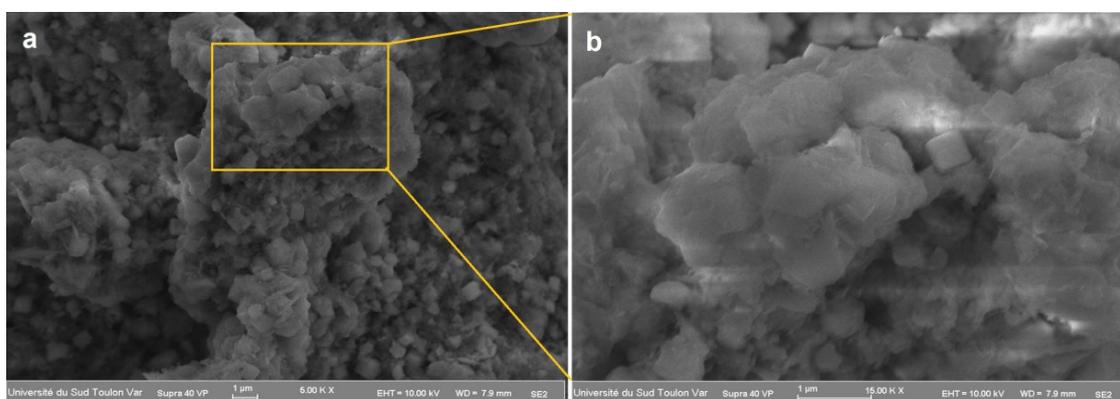


Figure 3. SEM micrographs of KF/ABM catalyst (a) 5.00 KX and (b) 15.00 KX

EDX analysis of KF/ABM was conducted on the external surface which contains various particles sizes. From Figure 4, the EDX micrograph shows clearly that the average fractions of atoms were: 39.81 % (K), 32.04 % (F), 16.87 % (Ca) and 8.75 % (P). In addition, a small amount of Si (1.66 %), Na (0.45 %), Mg (0.41 %), and Br (0.01 %) have been revealed. These analyses confirm those of XRD (presence of $K_3CaH(PO_4)_2$, $Ca_5(PO_4)_3F$, and $KCaF_3$).

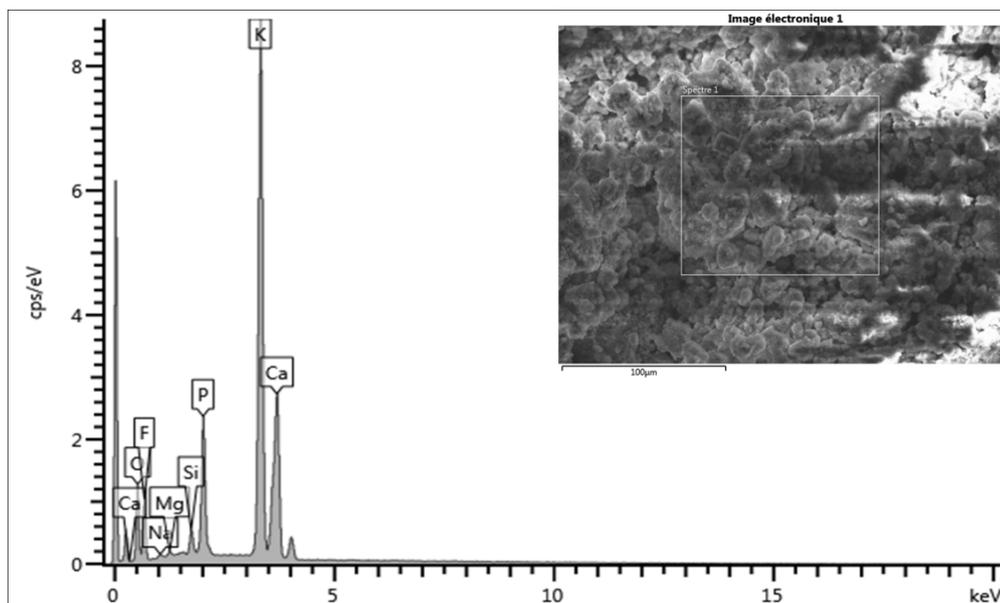


Figure 4. EDX spectrum of KF/ABM catalyst

Determination of optimal conditions

The synthesis of oximes was optimized using 1 mmol of benzaldehyde **1a** and 1.5 mmol of hydroxylamine hydrochloride **2** in the presence of KF/ABM as a catalyst at 80 °C (Figure 5).

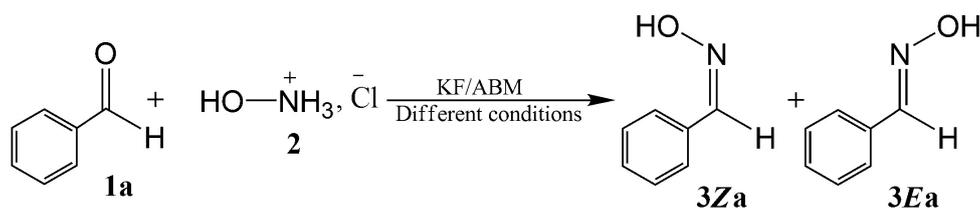


Figure 5. Optimization of oximation using benzaldehyde **1a**

It is preferable to test the effectiveness of the KF/ABM catalyst in the synthesis of oximes. For this purpose, we used different amounts of KF/ABM (0 to 250 mg) in solvent-free conditions. Table 1 illustrates the results of this study.

Without catalyst, the oximation of benzaldehyde **1a** with hydroxylamine hydrochloride **2** was carried out. The oximes **3Za** and **3Ea** were obtained in very low yield (5 %) even after one hour (Entry 1, Table 1). However, in the presence of different quantities of KF/ABM catalyst (from 0 mg to 250 mg), the reaction between **1a** and **2** provided the desired oximes **3Za** and **3Ea** in good (82 % yield, **3Za/3Ea**: 85/15) (Entry 2, Table 1) to excellent yields (98 % yield, **3Za/3Ea**: 88/12) (Entries 5 and 6, Table 1) after only 5

min. These results reveal that the 100 mg of KF/ABM is the optimal amount which can provides numerous advantages in terms of economy of catalyst cost and the purity of the obtained products.

Table 1. Study of the effect of the amount of KF/ABM in the **3Za** and **3Ea** synthesis

Entry	Reagent	ABM [mg]	Yield [%]/Time [min]	3Za/3Ea [%]
1	1a	0	5/60	– ^a
2	1a	50	82/5	85/15
3	1a	100	96/5	86/14
4	1a	150	97/5	87/13
5	1a	200	98/5	88/12
6	1a	250	98/5	88/12

Reactions conditions: Benzaldehyde **1a** (1 mmol), hydroxylamine hydrochloride **2** (1.5 mmol), different amounts of KF/ABM (0-250 mg) at 80 °C under solvent-free conditions.

^aDifficult to separate.

Thereafter, solvent effects were examined under the same conditions as mentioned above (1 mmol of **1a** and 1.5 mmol of **2**). All assays were performed in the presence of KF/ABM (100 mg) in different solvents (Table 2).

After each essay (5 min), the reaction was not completed with water, methanol, dichloromethane, chloroform, and acetone. In this case, the reaction mixture obtained at the end contains both starting materials and product (**3Za** + **3Ea**) (Entries 1, 2, 4, 5 and 6, Table 2). The results in Table 2 show clearly that the best solvents were aliphatic alcohols such as methanol and ethanol (76 % and 90 % yields, **3Za/3Ea**: 83/17 and 85/15, respectively) (Entries 2 and 3, Table 2). However, it should be noted that this reaction gives the corresponding oximes **3Za** and **3Ea** in very good yields under solvent-free conditions (96 % yield, **3Za/3Ea**: 86/14) (Entry 7, Table 2). Thus, we chose the solvent-free conditions process to synthesize the others oximes.

Table 2. Synthesis of **3Za** and **3Ea** using KF/ABM in different solvents

Entry	Reagent	Solvent	Yield [%]/Time [min]	3Za/3Ea [%]
1	1a	Water	64/5	84/16
2	1a	Methanol	76/5	83/17
3	1a	Ethanol	90/5	85/15
4	1a	Dichloromethane	67/5	84/16
5	1a	Chloroform	66/5	84/16
6	1a	Acetone	56/5	83/17
7	1a	Without solvent	96/5	86/14

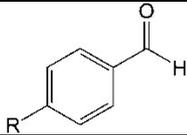
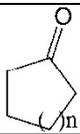
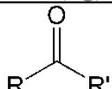
Reactions conditions: Solvent (1 mL), benzaldehyde **1a** (1 mmol), hydroxylamine hydrochloride **2** (1.5 mmol), and KF/ABM (100 mg) at 80 °C.

In the same conditions as those mentioned above, various aldehydes and ketones **1a-i** (1 mmol) were condensed with hydroxylamine hydrochloride **2** (1.5 mmol) at 80 °C in the presence of KF/ABM catalyst (100 mg) under solvent-free conditions (Table 3).

The progress of the reaction was monitored by TLC. The isolated compounds were purified by chromatography on silica gel column (hexane/ethyl acetate: 2/10) or by recrystallization from ethanol to obtain the desired oximes **3a-i**. In the case of dissymmetric aromatics aldehydes and acetophenone (Entries 1-5 and 8, Table3), two isomeric oximes **3Z** and **3E** are generated (the **3Z** (Z-isomers) are obtained in excellent yields). While, in the case of symmetric ketones, one oxime **3** was obtained (Entries 6, 7

and 9, Table 3). The physical and spectral data (IR, Mp, ^1H NMR, and ^{13}C NMR) of the synthesized products are in good agreement with those reported in the literature.

Table 3. Synthesis of the various oximes using KF/ABM

Entry	Aldehyde or ketone	Yield [%] ^a / Time [min]	3Z/3E [or 3] [%] ^b	Mp 3Z/3E [or 3] [°C] [lit.]
				
1	R= -H (1a)	96/5	86/14	(129/35) [10]
2	R= -OCH ₃ (1b)	96/5	88/12	(133/45) [10]
3	R= -CH ₃ (1c)	95/5	86/14	(106/80) [10]
4	R= -Cl (1d)	94/5	87/13	(146/110) [10]
5	R= -NO ₂ (1e)	96/5	87/13	(132/182) [10]
				
6	n=1 (1f)	80/5	80	(58) [19]
7	n=2 (1g)	81/5	81	(86) [16, 19, 24]
				
8	R= -C ₆ H ₅ and R'= -CH ₃ (1h)	85/5	90/10	(77/55) [24]
9	R=R'= -C ₆ H ₅ (1i)	93/5	93	(143) [10]

Reactions conditions: Different aldehydes or ketones **1** (1 mmol), hydroxylamine hydrochloride **2** (1.5 mmol), and KF/ABM (100 mg) at 80 °C under solvent-free conditions. ^aIsolated Yield. ^bSeparated by column chromatography.

These results show clearly that the use of KF/ABM catalyst can lead to the oximes in good yield (80 % yield) (Entry 6, Table 3) to excellent yield (96 % yield) (Entries 1, 2 and 5, Table 3). In the case of substituted benzaldehyde (**1a-e**), the use of electron donating groups (*p*-OCH₃ and *p*-CH₃) or electron withdrawing groups (*p*-NO₂ and *p*-Cl) has no effect on the yield of the reaction. Indeed, these four substrates (**1b-e**) and benzaldehyde give almost the same yields to the corresponding oximes (Entries 1-5, Table 3).

In order to demonstrate the effectiveness of KF/ABM catalyst, we made a comparison between this catalyst and the NaNO₃/ABM catalyst [25].

The yields obtained using these catalysts (KF/ABM and NaNO₃/ABM) for all the substrates were almost similar. Indeed, in each entry, KF/ABM and NaNO₃/ABM gave the corresponding oximes in higher yields than using ABM alone under the same experimental conditions (80-96 % for KF/ABM and 78-96 % for NaNO₃/ABM). Concerning the reaction time, all the reactions were carried out in only 5 min using both catalysts (KF/ABM or NaNO₃/ABM). This shows that they are effective compared to the ABM alone.

The difference between the two catalysts (KF/ABM and NaNO₃/ABM) is in the selectivity. Indeed, the use of NaNO₃/ABM catalyst gives only the *E*-isomer for all the substrates (dissymmetric substrates) in very high yields (between 78 % and 96 %) and high purity. However, the use of KF/ABM catalyst gives rise to the two isolable and

identifiable *Z*- and *E*-isomers for the dissymmetric substrates in very high yields (between 85 % and 96 % as mixture of *Z* and *E* with ratio *Z/E* is between 86/14 and 90/10). Thus, the advantage of KF/ABM catalyst is that it can be used to synthesis *Z*-isomers and *E*-isomers from dissymmetric substrates. However, the NaNO₃/ABM always gives *E*-isomer in high purity. This is probably due to the difference in structure and phases of KF/ABM and NaNO₃/ABM catalysts.

The reuse of KF/ABM was studied in order to demonstrate the effectiveness of catalyst recycling (Figure 6). For this purpose, the KF/ABM catalyst was washed with acetone after each use, recovered quantitatively by simple filtration. Then, it was regenerated by calcination at 500 °C for 2 h for each new reuse.

It was observed that the recovered KF/ABM catalyst leads to a product **3a** (**3Za** + **3Ea**) in good yields even after eight successive catalytic cycles (5 min). Indeed, the yield decreased by 10 % after eighth rounds. The loss of efficiency of the catalyst is due to the reduction of a number of active centers.

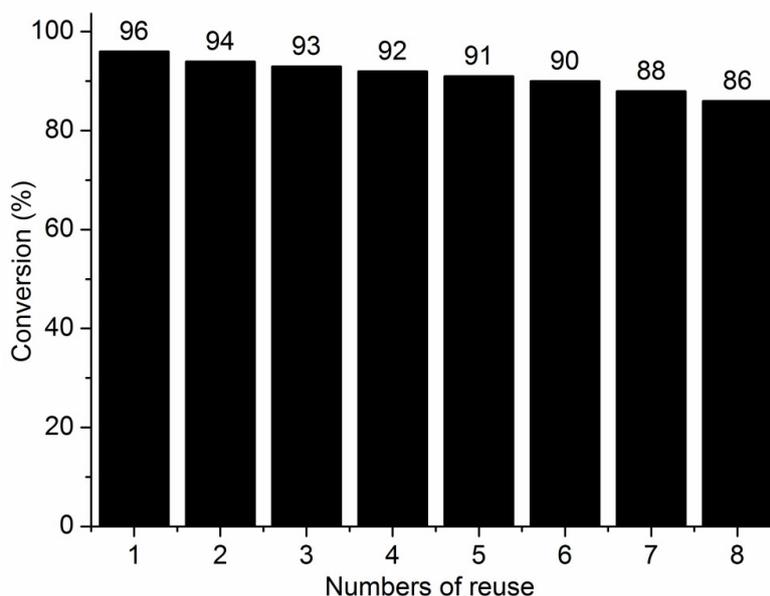


Figure 6. Reusability of KF/ABM catalyst

CONCLUSIONS

In conclusion, we developed a simple and effective method of oximes synthesis using KF/ABM under mild conditions. The specificity of the KF/ABM catalyst is that it can give a mixture of the two geometrical isomers (*Z*- and *E*-oximes) in the case of dissymmetric aldehydes and ketones with *Z/E* ratios ranging from 84/14 to 90/10. Compared to the conventional methods, the main advantages of this procedure are milder conditions, higher yields, short reaction times, possibility to reuse or recycling, and reduction of environmental problems.

ACKNOWLEDGMENTS

We would like to thank Mr Abdellatif Lanknifli, the Dean of the Polydisciplinary Faculty of Taroudant for giving us the solvents and acids, and Professors Abdelhay Khallaayoun for recording FTIR spectra.

We also thank the CNRST for its financial support of PPR2/2016/21 project.

REFERENCES

1. Jin, J., Li, Y., Wang, Z.J., Qian, W.-X., Bao, W.L.: A Concise, Metal-Free Approach to the Synthesis of Oxime Ethers from Cross-Dehydrogenative-Coupling of sp^3 C–H Bonds with Oximes, *European Journal of Organic Chemistry*, **2010**, 2010 (7), 1235-1238;
2. Flick, A.C., Caballero, M.J.A., Lee, H.I., Padwa, A.: 2,3-Bis(phenylsulfonyl)-1,3-butadiene as a Reagent for the Synthesis of the Azatricyclic Core of (\pm)-Halichlorine, *Journal of Organic Chemistry*, **2010**, 75 (6), 1992-1996;
3. Ghiaci, M., Aghaei, H., Oroojeni, M., Aghabarari, B., Rives, V., Vicente, M.A., Sobrados, I., Sanz, J.: Synthesis of paracetamol by liquid phase Beckmann rearrangement of 4-hydroxyacetophenone oxime over H_3PO_4/Al -MCM-41, *Catalysis Communications*, **2009**, 10 (11), 1486-1492;
4. Hajipour, A.R., Mahboubghah, N.: 1-Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane Periodate: a Mild and Efficient Oxidant for the Cleavage of Oxime Double Bonds under Anhydrous Conditions, *Journal of Chemical Research, Synopses*, **1998**, 122-123;
5. Olah, G.A., Keumi, T.: Synthetic Methods and Reactions; 60¹ Improved One-Step Conversion of Aldehydes into Nitriles with Hydroxylamine in Formic Acid Solution, *Synthesis*, **1979**, 112-113;
6. Sosnovsky, G., Krogh, J.A., Umhoefer, S.G.: A One-Flask Conversion of Aldehydes to Nitriles Using Hydroxylamine Hydrochloride and Selenium Dioxide, *Synthesis*, **1979**, 1979 (9), 722-724;
7. Sharghi, H., Sarvari, M.H.: A mild and versatile method for the preparation of oximes by use of calcium oxide, *Journal of Chemical Research (S)*, **2000**, 24-25;
8. Miller, P., Kaufman, D.H.: Mild and Efficient Dehydration of Oximes to Nitriles Mediated by the Burgess Reagent, *Synlett*, **2000**, 1169-1171;
9. Kad, G.L., Bhandari, M., Kaur, J., Rathee, R., Singh, J.: Solventless preparation of oximes in the solid state and via microwave irradiation, *Green Chemistry*, **2001**, 3 (6), 275-277;
10. Guo, J.-J., Jin, T.-S., Zhang, S.-L., Li, T.-S.: TiO_2/SO_4^{2-} : an efficient and convenient catalyst for preparation of aromatic oximes, *Green Chemistry*, **2001**, 3, 193-195;
11. Sharghi, H., Hosseini, M.: Solvent-Free and One-Step Beckmann rearrangement of ketones and aldehydes by zinc oxide, *Synthesis*, **2002**, 8, 1057-1060;
12. Osadchenko, I.M., Tomilov, A.P.: Phase-Transfer Catalysis in Synthesis of Oximes, *Russian Journal of Applied Chemistry*, **2002**, 75 (3), 511-512;
13. Abele, E., Abele, R., Dzenitis, O., Lukevics, E.: Indole and Isatin Oximes: Synthesis, Reactions, and Biological Activity. (Review), *Chemistry of Heterocyclic Compounds - A Series of Monographs*, **2003**, 39, 3-35;
14. Damljanovic, I., Vukicevic, M., Vukicevic, R.D.: A Simple Synthesis of Oximes, *Monatshefte fur Chemie*, **2006**, 137 (3), 301-305;
15. Ramon, R.S., Bosson, J., Diez-Gonzalez, S., Marion, N., Nolan, S.P.: Au/Ag-Cocatalyzed Aldoximes to Amides Rearrangement under Solvent- and Acid-Free Conditions, *Journal of Organic Chemistry*, **2010**, 75 (4), 1197-1202;
16. Li, J.-T., Li, X.-L., Li, T.-S.: Synthesis of oximes under ultrasound irradiation, *Ultrasonics Sonochemistry*, **2006**, 13, 200-202;
17. Xia, J.-J., Wang, G.-W.: Efficient preparation of aldoximes from arylaldehydes, ethylenediamine and oxone in Water, *Molecules*, **2007**, 12, 231-236;
18. Lad, U.P., Kulkarni, M.A., Patil, R.S.: Synthesis of oximes in aqueous medium using Hyamine as an ecofriendly catalyst at ambient temperature, *RASAYAN Journal of Chemistry*, **2010**, 3 (3), 425-428;

19. Saikia, L., Baruah, J.M., Thakur, A.J.: A rapid, convenient, solventless green approach for the synthesis of oximes using grindstone chemistry, *Organic and Medicinal Chemistry Letters*, **2011**, 1 (12), 1-6;
20. Ramanjaneyulu, K., Seshagiri Rao, P., Rambabu, T., Jayarao, K., Sundari Devi, Ch.B.T., Venkateswara Rao, B.: Cupper supported silica promoted one-pot synthesis of aromatic oxime derivatives, *Der Pharma Chemica*, **2012**, 4 (1), 473-478;
21. Setamdideh, D., Khezri, B., Esmaeilzadeh, S.: Synthesis of Oximes with NH₂OH.HCl/DOWEX(R)50WX4 System, *Journal of the Chinese Chemical Society*, **2012**, 59, 1119-1124;
22. Elmakssoudi, A., Abdelouahdi, K., Zahouily, M., Clark, J., Solhy, A.: Efficient conversion of aldehydes and ketones into oximes using a nanostructured pyrophosphate catalyst in a solvent-free process, *Catalysis Communications*, **2012**, 29, 53-57;
23. Zeynizadeh, B., Karimkoshteh, M.: Magnetic Fe₃O₄ nanoparticles as recovery catalyst for preparation of oximes under solvent-free condition, *Journal of Nanostructure in Chemistry*, **2013**, 3 (57), 1-6;
24. Kim, B.R., Sung, G.H., Kim, J-J., Yoon, Y-J., A Development of rapid, practical and selective process for preparation of Z-Oximes, *Journal of the Korean Chemical Society*, **2013**, 57 (2), 295-299;
25. Ait Taleb, M., Mamouni, R., Saffaj, N., Mouna, A., Taha, M.L., Benlhachemi, A., Bakiz, B., Ezahri, M., Villain, S.: Animal Bone Meal as new recyclable and ecological catalyst for the oximes Synthesis in solvent-Free Conditions, *Journal of Materials and Environmental Science*, **2016**, 7 (12), 4580-4588;
26. Ait Taleb, M., Mamouni, R., Ait Benomar, M., Bakka, A., Mouna, A., Taha, M.L., Benlhachemi, A., Bakiz, B., Villain, S.: Chemically treated eggshell wastes as a heterogeneous and eco-friendly catalyst for oximes preparation, *Journal of Environmental Chemical Engineering*, **2017**, 5 (2), 1341-1348;
27. Riadi, Y., Abrouki, Y., Mamouni, R., El Haddad, M., Routier, S., Guillaumet, G., Lazar, S.: New eco-friendly animal bone meal catalysts for preparation of chalcones and aza-Michael adduct, *Chemistry Central Journal*, **2012**, 6 (1), 60-66.