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Efficient hydration of nitriles to amides catalysed by sodium nitrate modified fluorapatite

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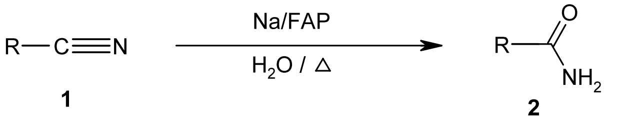
Abstract—The selective hydration of several nitriles to amides have been carried out in water without organic solvent in presence of sodium nitrate modified synthetic fluorapatite in heterogeneous media. The yields obtained are generally high. © 2003 Elsevier Science Ltd. All rights reserved.

Nitriles hydration is an important method to synthesise amides. Commonly this reaction is carried out using a strong acid or base. However under these conditions the carboxylic acid is formed as a by-product. To enhance the selectivity of the amides synthesis, several catalysts or reagents have been used as cobalt,[1] palladium,[2] rhodium,[3] sodium percarbonate,[4] hydrogen peroxide,[5] sodium perborate,[6] chloromethylsilane,[7] potassium trimethylsilanolate[8] and others.[9] Biotransformations[10] were also used in this synthesis. More interestingly, the use of a heterogeneous process enhances the selectivity in this reaction. The advantage of this methodology is well known as the environmentally friendly chemistry. Few examples of heterogeneous catalysts have been used in the nitriles hydration as KF/Al_2O_3,[11] resines,[12] amberlyst,[13] MnO_2/SiO_2,[14] and KF/natural phosphate.[15] On the other hand, we have demonstrated that the synthetic fluorapatite (FAP) can be used as a new heterogeneous catalyst in organic synthesis in the the liquid phase.[16] FAP modified with sodium nitrate has been also used as a catalyst for Knoevenagel condensation.[17]

In this work, we wish to describe an efficient selective hydration of nitriles by Na/FAP catalyst in heterogeneous media in water (Scheme 1).



Scheme 1.

The fluorapatites have been prepared by reaction between diammonium phosphate, calcium nitrate and ammonium fluoride in presence of ammonia (Scheme 2) as described previously.[16] The FAP obtained was calcined at 900°C before use. The structure of this catalyst was confirmed by X-ray diffraction, infrared spectra and chemical analysis. The surface area of calcined FAP was determined by the BET method and found to be $S = 15.4\ m^2\ g^{-1}$. The total pore volume was calculated by the BJH method ($V_T = 0.058\ cm^3\ g^{-1}$).

The modified FAP has been prepared by impregnation of the FAP with a solution of sodium nitrate ($NaNO_3$/FAP = 1/2 w/w) followed by calcination at 900°C. The surface area of the new catalyst Na/FAP was deter-

$$6\ (NH_4)_2HPO_4 + 10\ Ca(NO_3)_2 + 2\ NH_4F + 6\ NH_4OH \longrightarrow Ca_{10}(PO_4)_6F_2 + 20\ NH_4(NO_3) + 6\ H_2O$$

Fluorapatite

Scheme 2.

Keywords: nitriles hydration; amides synthesis; reaction in water; heterogeneous catalysis; fluorapatite; sodium nitrate.

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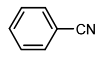
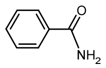
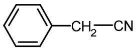
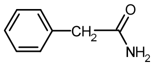
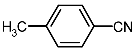
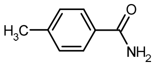
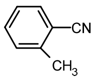
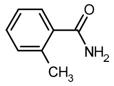
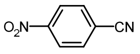
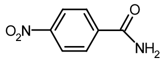
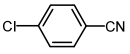
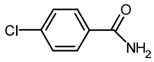
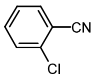
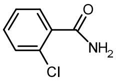
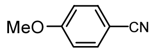
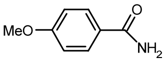
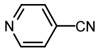
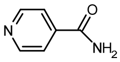
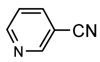
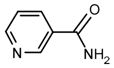
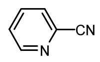
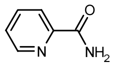
Table 1. Hydration of nitriles to amides catalysed by FAP and Na/FAP

Substrate		Product		Yield (%) (time (h))[a]	
				With FAP	With $NaNO_3$/FAP
1a		**2a**		6 (24)	95 (3)
1b		**2b**		7 (24)	90 (16)
1c		**2c**		12 (24)	85 (12)
1d		**2d**		8 (24)	81 (24)
1e		**2e**		41 (24)	90 (24)
1f		**2f**		4 (24)	94 (24)
1g		**2g**		8 (24)	68 (24)
1h		**2h**		3 (24)	60 (24)
1i		**2i**		51 (24)	94 (2)
1j		**2j**		48 (24)	91 (2)
1k		**2k**		45 (24)	98 (2)

[a] Yields in products isolated and identified by ^1H NMR, ^{13}C NMR and IR spectroscopy.

mined by the BET method as 5.4 m^2 g^{-1} and the total pore volume obtained by the BJH method is 0.0032 cm^3 g^{-1}. The infrared spectra are run at 150°C under vacuum. The spectrum of dried FAP doped with sodium nitrate seems to be a simple combination of nitrate and phosphates bands. It is worth noting that in spectra of both FAP and doped, no hydroxyls bands are observed in the range of 3000–4000 cm^{-1}. The calcined material has a very interesting set of peaks for OH groups at high frequency (3710 and 3639 cm^{-1}) and a broad peak at around 1460 cm^{-1}. All these peaks are in the spectrum of $Ca(OH)_2$ when heated to 300°C to remove some water. Therefore, it seems that the active species in CaOH type unit, maybe formed by reaction of NaO species with Ca centres. The XPS indicates a very small amount of carbon in both dried and calcined materials, so we can rule out a significant amount of $CaCO_3$ in the samples. The XRD patterns of calcined Na/FAP showed the apparition of new phases, so the CaO phase ($2\theta = 32.2$; 37.5 and 54.0) is clearly identified. Two new phases are probably $CaNaPO_4$ and $Na_2Ca_4(PO_4)_3F$ obtained by an exchange of sodium with calcium. No crystalline phases of Na_2O and CaF_2 were observed. The basic properties of FAP and Na/FAP have been estimated by the adsorption of phenol at 0.44 and 0.57 mmol g^{-1} (2 h), respectively, using GC analysis.

The hydration of nitriles **1** to amides **2** was carried out in water at 100°C using 2.5 mmol of nitrile and 0.1 g of the catalyst. The work-up included the addition of ethanol, filtration to separate the catalyst and evaporation. The products obtained were purified by washing with hexane and identified by ^1H, ^{13}C NMR and IR spectroscopy. First of all, we have tested the activity of the FAP alone in this reaction. The yields of amides **2** after 24 h of reaction time are moderate for **2e** and **2i**–**k** and poor for the others amides. In this reaction the nitriles derivatives of pyridine ring are more reactive than those of benzene. Thereafter we have used the modified phosphate Na/FAP to carried out the hydration of nitriles. Firstly we have used various quantities of water to optimise the synthetic conditions. Thus the yields of isolated amide **2a** were 42, 95, 89, 68 and 58% using 1, 5, 10, 15 and 20 ml of water respectively. The best conditions for this reaction were found to be 2.5 mmol of substrate, 0.1 g of Na/FAP and 5 ml of water, which have been applied to synthesis several amides **2** as can be seen in Table 1. The yields obtained are generally high. The nitriles with the pyridine ring **3i–k** are also more active than the benzene derivatives when we use Na/FAP as catalyst. The nitrile **1h**, with the electron-donating methoxy group gave the lowest yield of amide. IR and ^{13}C NMR spectra were utilised, in addition to ^{1}H NMR to confirm that, in this case, some carboxylic acid is formed as a side product. However, none of the other products showed any contamination with acid.

In conclusion, we have prepared the sodium nitrate modified synthetic fluorapatite and used it as an excellent catalyst for the selective hydration of nitriles to amides. This transformation has been applied to the synthesis of several amides with good yields in environmentally friendly water. Na/FAP can be used as a good and versatile new catalyst for the selective hydration of nitriles to amides.

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