



## NOTE

### Hydrolysis of Nitrile in Presence of Different Zeolite Catalysts Under Microwave IR-Radiation

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The hydrolysis of nitriles in presence of different zeolite catalysts under microwave irradiations gives corresponding amide in high yield in few minutes.

**Key Words:** Microwave, Amide, Nitrile, Zeolite-A, X, Y catalysts.

Development of the simple and general synthetic routes for widely used organic compounds from the readily reagents is one of the major challenges in organic synthesis. Zeolites have found many important industrial, agricultural applications due to their- high activity levels, regenerability, molecular shape selectivity<sup>1-6</sup>. Zeolites are effective catalysts in organic chemistry and they have great utility in industry<sup>7</sup> in alkylation reaction, polymerization, cyclization<sup>8</sup>, photoreduction<sup>9</sup> or preparation of nitroalkenes<sup>10</sup>, occur in gas phase or with reactants sorbed within zeolite in inert solvent. Zeolites has been used as catalyst for number of organic reactions and offer several advantages over other classical catalysts *i.e.*, non-corrosive properties, cheapness, mild reactions, high yields, high selectivity, ease of setting and work up. In the last few years a growing interest in the use of microwave irradiation in organic synthesis<sup>11,12</sup>. The hydrolysis of nitriles under conventional heating methods is reported in literature<sup>13</sup>. But this method requires longer reaction time and tedious work up. So, we have the need of alternative technique for the hydrolysis of nitriles.

**Zeolite-A [Gel AM :** 3.7 Na<sub>2</sub>O: 1.6 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>:106.4 H<sub>2</sub>O and Gel AF : 1.5 Na<sub>2</sub>O: 1 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>: 96.4 H<sub>2</sub>O]<sup>17</sup>; Zeolite-X [Gel XM: 3.7 Na<sub>2</sub>O: 2.7 SiO<sub>2</sub>:1 Al<sub>2</sub>O<sub>3</sub>: 128.8 H<sub>2</sub>O, Gel XC, ratio 1: 5.7 Na<sub>2</sub>O: 4.7 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>: 114.5 H<sub>2</sub>O, Gel XC, ratio 2: 5.4 Na<sub>2</sub>O: 6.5 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>: 104.6 H<sub>2</sub>O and Gel XF: 5.7 Na<sub>2</sub>O: 3.2 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>: 100 H<sub>2</sub>O]<sup>14</sup>; Zeolite-Y [Gel YM: 12.4, Gel YF: 4Na<sub>2</sub>O: 10 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>: 235 H<sub>2</sub>O Na<sub>2</sub>O: 11.4 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>: 410 H<sub>2</sub>O, Gel YC: 10 Na<sub>2</sub>O: 20 SiO<sub>2</sub>: 1 Al<sub>2</sub>O<sub>3</sub>: 408 H<sub>2</sub>O and Gel YF, High sodium: 10 Na<sub>2</sub>O: 10 SiO<sub>2</sub>: 1Al<sub>2</sub>O<sub>3</sub>: 250 H<sub>2</sub>O ].

The suspension of a nitrile (200 mg) in water (5 mL) in presence of zeolite (800 mg) as catalyst is taken in the open Erlenmeyer flask. The flask was subjected to 70 % irradiation

level (560 W) in the kenstar OM-9925 (800 W) unmodified domestic microwave oven operating at 2450 MHz for 5-7 min. The contents were allowed to cool and poured into water (30 mL). The solid separated was filtered off and washed with ethanol (3 mL) and recrystallized (from DMF).

**2-Pyridylacetamide:** m.p. 120-122 °C, (colourless needles, water). IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3377, 3188, 3112, 3017, 1678, 1646, 1597, 1570, 1439, 1402. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 200 MHz): 8.51-8.43 [m, 1H, H-C(6)], 7.78 [td, *J* = 7.8, 1.8, H-C(4)], 7.40 [d, *J* = 8.0, H-C(3)], 7.30 [ddd, *J* = 8, 5, 1, H-C(5)], 3.75 [s, 2H-C(2)]. <sup>13</sup>C NMR (CD<sub>3</sub>OD, 50 MHz): 174.97 (C1), 156.82 (C2'), 149.86 (C6'), 138.76 (C4'), 125.69 (C3'), 123.59 (C5'), 45.12 (C2). Anal. calc. for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O (m.w. 136.06): C 61.75, H 5.92, N 20.57, found: C 62.08, H 5.57, N 20.83.

**3-Cyanopropanamide:** m.p. 86-88 °C (colourless amorphous solid). IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3414, 3225, 2293, 2248, 1681, 1619, 1421. <sup>1</sup>H NMR (D<sub>2</sub>O, 200 MHz): 2.80-2.65 [m, 4H, 2H-C(2), 2H-C(3)]. <sup>13</sup>C NMR (D<sub>2</sub>O, 50 MHz) : 177.90 (C1), 123.04 (C4), 32.38 (C2), 15.12 (C3). MS (CI, isobutane): 197 (2 M<sup>+</sup>+1). Anal. calc. for C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>O (m.w. 98.11): C 48.97, H 6.16, found: C 49.34, H 6.08.

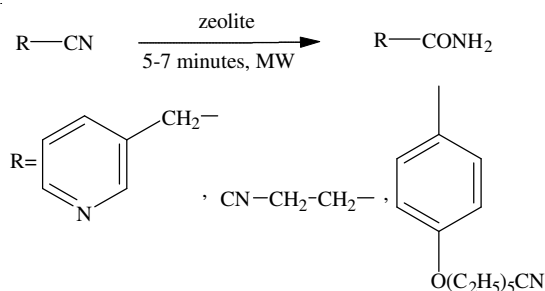
**4-(5-Cyanopentoxy)benzamide:** Colourless solid m.p. 97-101°C. IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3466, 2140, 1614, 1566, 1401. <sup>1</sup>H NMR (CD<sub>3</sub>OD, 200 MHz): 7.84 [AA'BB', *J* = 6.8, 2, H-C(2), H-C(6)], 6.98 [AA'BB', *J* = 6.8, 2, H-C(3), H-C(5)], 4.06 [t, *J* = 6.2, 2H-C(1')], 2.49 [t, *J* = 6.8, 2H-C(5')], 1.90-1.57 (m, 6H). MS (EI, 70 eV): 232 (M<sup>+</sup>, 25), 137 (33), 121 (100), 96 (14), 55 (8), 41(5). Anal. calc. for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (m.w. 232.12): C 67.22, H 6.94, N 12.06, found: C 67.54, H 6.90, N 12.

We have explored our work for the hydrolysis of different nitriles into corresponding amides using Zeolite-A, X, Y catalysts in presence of microwave irradiations (**Scheme-I**) in a few

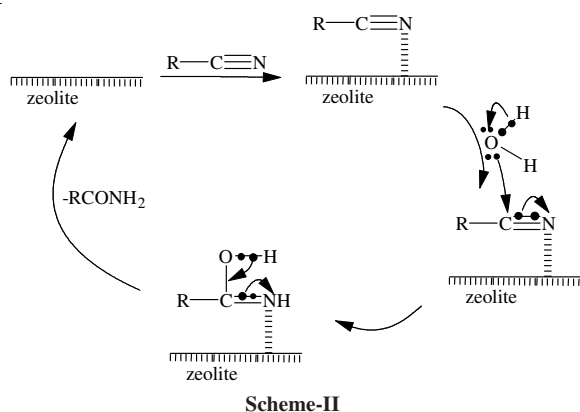
TABLE-1  
HYDROLYSIS OF NITRILES INTO AMIDES IN PRESENCE OF DIFFERENT CATALYSTS

Nitrile	Amide	With zeolite-A		With zeolite-X		With zeolite-Y		m.p. (%)
		Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	
		7	74	7	65	7	70	120-122
		5	79	5	71	5	74	86-88
		7	73	7	63	7	68	97-101

minutes, which results in an increase in the purity of the products besides enhancing the chemical yields (Table-1). The product was identified on the basis of their IR, <sup>1</sup>H NMR and by comparison of their R<sub>f</sub> values with those of the authentic samples prepared by standard routes.



The hydrolysis of cyanides to corresponding amides involves the coordination of cyanides to metal cations of Zeolite-A, X, Y catalysts through the nitrogen atom which become susceptible to nucleophilic attack at the carbon atom and thus results in enhancement of the rate of nucleophilic attack on nitriles co-ordinated to a metal ion is generally in the range 106 to 108 (Scheme-II). The amide needs to be expelled from the co-ordination sphere and be replaced by a new nitrile molecule in order to make a more favourable catalytic system.



## Conclusion

In conclusion, we have shown that the hydrolysis of nitriles into corresponding amides in presence of Zeolite-A, X, Y catalysts occurs in a few minutes with improved yield under microwave irradiation.

## REFERENCES

1. D.W. Breck, *Zeolite Molecular Sieves*, John Wiley & Sons Inc., (1974).
2. L. Smart and E. Moore, *Solid State Chemistry: An Introduction*, 1st Edition, Chapman and Hall (1992).
3. I.E. Maxwell, *Catal. Today*, **1**, 385 (1987).
4. R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge and J. Rousell, *Tetrahedron Lett.*, **27**, 279 (1986).
5. R.J. Giguere, T.L. Bray, S.M. Duncan and G.M. Ajetich, *Tetrahedron Lett.*, **27**, 4945 (1986).
6. A. Loupy, L. Perrex, M. Liagre, K. Burle and M. Moneuse, *Pure Appl. Chem.*, **73**, (2001).
7. W. Hölderich, M. Hesse and F. Naumann, *Angew. Chem. Int. Ed. Engl.*, **27**, 226 (1988).
8. S.E. Sen, Y.Z. Zhang and S.L. Roach, *J. Org. Chem.*, **61**, 9534 (1996).
9. J.V. Rao, S.R. Uppili, D.R. Corbin, S. Schwarz, S.R. Lustig and V. Ramamurthy, *J. Am. Chem. Soc.*, **120**, 2480 (1998).
10. R. Sreekumar, S.R. Padmakumar and P. Rugmini, *Tetrahedron Lett.*, **39**, 5151 (1998).
11. (a) S. Caddick, *Tetrahedron*, **51**, 10403 (1995); (b) P. Lidstrom, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, **57**, 9225 (2001).
12. (a) A.K. Bose, M.S. Manhas, S.N. Ganguly, A.H. Sharma and B.K. Banik, *Synthesis*, 1578 (2002); (b) A. Loupy, A. Petit, J. Hamelin, F. Texier-Boullet, P. Jacquault and D. Mathe, *Synthesis*, 1213 (1998).
13. D.R. Milic, D.M. Opsenica, B. Adnadevic and B.A. Solaja, *Molecule*, **5**, 118 (2000).
14. P.M. Slangen, J.C. Jansen and H. van Bekkum, *Microporous Mater.*, **9**, 259 (1997).