

Microwave assisted synthesis of some Schiff bases on NaY zeolite: A green chemical approach

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ABSTRACT: An efficient, extremely fast and ecofriendly method for the synthesis of some Schiff bases of p-aminobenzoic acid over NaY zeolite under microwave irradiation has been reported. A considerable increase in the reaction rate has been observed with reasonable good yield. Zeolite acts as a solid support as well as catalyst for the synthesis of Schiff bases.

Key Words: NaY zeolite, Schiff bases, p-aminobenzoic acid, microwave.

INTRODUCTION

Zeolites are micro porous, crystalline aluminosilicates made up of corner-sharing SiO₄ and AlO₄ tetrahedra. By virtue of their structure, crystalline and variable stoichiometry, zeolite catalysts have well defined pore size distribution, high and adjustable acidity, very high surface area and good thermal stability¹. Due to presence of high surface area, thermal stability and tunable acidity²⁻⁵, zeolites can potentially replace solvents and conventional corrosive liquid acids in many of their applications⁶⁻¹¹. The utility of zeolites as selective adsorbents and as catalysts for petrochemical processes has also been reported¹²⁻¹³.

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields e.g., biological, inorganic and analytical chemistry¹⁴⁻¹⁸. In recent years, the acceleration of a wide range of chemical reactions using microwave dielectric heating has been reported¹⁹. The solvent free conditions under microwave irradiation offer several advantages.

For example; it avoids use of expensive and toxic solvents which are hazardous and causes severe health problems. On the other hand, solvent free conditions offer green chemical route for synthesis of organic compounds. This paper describes the synthesis of some Schiff bases of p-aminobenzoic acid using NaY zeolite as a solid support and an efficient acid catalyst under microwave irradiation. The work is solvent free and therefore, environment benign and operationally simple method for synthesis.

EXPERIMENTAL

General Procedure:

All the reactions were carried out in a domestic microwave oven (Kenstar, Model No. OM-26 E 60, Power-1200 W). Melting points were determined in open capillaries and are uncorrected. Reactions were monitored by thin layer chromatography using silica gel-G as adsorbent. TLC plates were prepared by spreading method. These were dried in the air and then activated by heating in hot air oven at 110°C for 30 min. Iodine vapours were used for visualization of TLC plates. IR spectra (KBr pellets) were recorded on perkin-Elmer 1800 (FTIR) Spectrometer. ¹HNMR spectra were recorded on Jeol JNM FX 100 FTNMR Spectrometer (chemical shifts in δ) in DMSO-d₆ using TMS as internal reference. Mass spectra were recorded on a Jeol SX-102/DA 6000 mass spectrometer.

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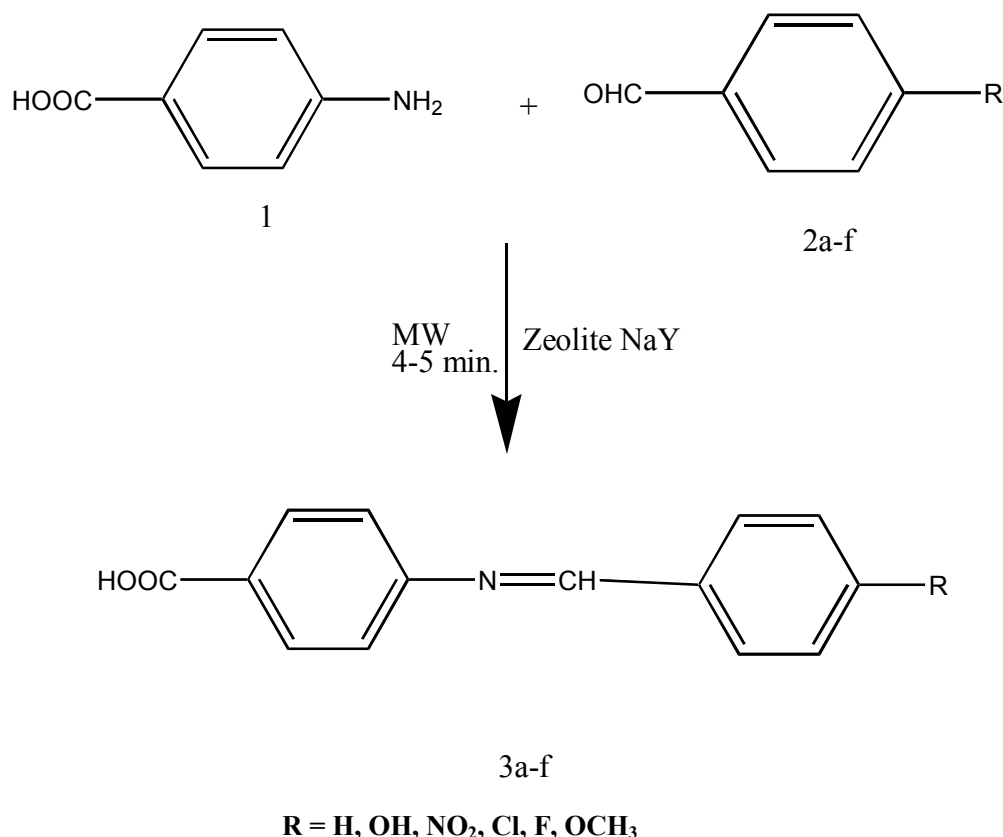
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Typical procedure for the synthesis of Schiff bases: Benzaldehyde (0.01mol) and 4.0g zeolite NaY were mixed together using a pastel and mortar. Then p-aminobenzoic acid (0.01mol) was added and transferred in an Erlenmeyer flask with a funnel as loose top and irradiated under microwave irradiation for 5 minutes. After irradiation product was separated from zeolite using ethanol by stirring for 15 minutes on magnetic stirrer. Then the reaction mixture was filtered and product was obtained by evaporating the filtrate. The resulting solid was recrystallized from ethanol. Catalyst was reused after washing with ethanol, drying in air overnight. Similarly, other compounds (3b-f) were also synthesized.

RESULTS AND DISCUSSION

Conventional method for the synthesis of these compounds requires 10-15 hours reflux and suitable solvents with catalytic amount of acetic acid. Thus, conventional method is time taking and therefore, these are not ecofriendly. However, when the same reaction was carried out in microwave (without using NaY

zeolite), the reaction time is reduced, but still solvent and acetic acid have to be used, which are expensive, toxic and create the problem of waste disposal of solvent. However, present work making the use of NaY zeolite, both the acetic acid and solvent have been avoided and reaction time has also been found to be reduced as compared to conventional and microwave (without using NaY zeolite) methods. The yield of products was also increased. Therefore, the present work may be regarded as a green approach under solvent free conditions. The reaction has been carried out by grinding appropriate reactants with zeolite NaY and then exposing the reaction mixture under microwave irradiation. The progress of reaction was monitored by thin layer chromatography. Structures of compounds were characterized by IR, NMR and mass spectral data (Table - 3). A comparison of time required for synthesis and yield of products in conventional and microwave method (with and without use of zeolite NaY) has been reported in Table-1. Zeolite catalyst can be reused by simple washing it with ethanol and drying in air overnight.

Table-1 Physical data of synthesized compounds

Comp. No.	R	M. P.	Yield (%) & [Time] (Conventional)	Yield (%) & [Time] (MW Solvent)	Yield (%) [Time] (NaY zeolite)	Mol. Weight	Mol. Formula
3a	H	178 °C	75 (6 hr.)	85 [9 min]	90 [5 min]	225	C ₁₄ H ₁₁ NO ₂
3b	OH	190 °C	65 (6 hr.)	72 [9 min]	80 [5 min]	241	C ₁₄ H ₁₁ NO ₃
3c	NO ₂	167 °C	80 (5 hr.)	88 [8 min]	95 [4 min]	270	C ₁₄ H ₁₀ N ₂ O ₄
3d	Cl	185 °C	77 (6 hr.)	88 [9 min]	92 [5 min]	259	C ₁₄ H ₁₀ ClNO ₂
3e	F	155 °C	77 (5 hr.)	90 [8 min]	95 [4 min]	243	C ₁₄ H ₁₀ FNO ₂
3f	OCH ₃	198 °C	75 (6 hr.)	86 [9 min.]	92 [5 min]	255	C ₁₅ H ₁₃ NO ₃

Table 2: Elemental Analysis of Synthesized Compounds

Compd. No.	Calculated /Found (%)		
	C	H	N
3a	74.65/74.62	4.92/4.88	6.22/6.15
3b	69.70/69.67	4.60/4.58	5.81/5.77
3c	62.22/62.20	3.73/3.70	10.37/10.38
3d	64.75/64.69	3.88/3.82	5.39/5.36
3e	69.13/69.11	4.14/4.11	5.76/5.73
3f	70.58/70.57	5.13/5.11	5.49/5.45

Table 3: Spectral data of synthesized compounds

Comp. No.	Spectral Data	
3a	IR (cm ⁻¹):	3450 (-OH str., COOH), 1690 (C=O str.), 1631 (C=N str.), 3020 (Ar-H str.)
	¹ H NMR (δ):	10.22 (s, 1H, OH), 8.31 (s, 1H, CH=N), 7.0-8.0 (m, 4H, Ar-H)
	MS(m/z):	225 (M ⁺), 148, 135, 104
3b	IR (cm ⁻¹):	3456 (-OH str.), 1698 (C=O str.), 1625 (C=N str.), 3025 (Ar-H str.)
	¹ H NMR (δ):	10.22 (s, 1H, OH), 8.30 (s, 1H, CH=N), 7.0-8.1 (m, 4H, Ar-H)
	MS(m/z):	241 (M ⁺), 148, 135, 120
3c	IR (cm ⁻¹):	3440 (-OH str., COOH), 1685 (C=O str.), 1640 (C=N str.), 3030 (Ar-H str.), 1550, 1390 (-NO ₂ symm. and asymm. Str.)
	¹ H NMR (δ):	10.22 (s, 1H, OH), 8.32 (s, 1H, CH=N), 6.9-8.0 (m, 4H, Ar-H)
	MS(m/z):	270(M ⁺), 148, 135, 149
3d	IR (cm ⁻¹):	3444 (-OH str., COOH), 1694 (C=O str.), 1635 (C=N str.), 3025 (Ar-H str.), 742 (C-Cl str.)
	¹ H NMR (δ):	10.22 (s, 1H, OH), 8.28 (s, 1H, CH=N), 7.1-8.1 (m, 4H, Ar-H)
	MS(m/z):	260 (M +1), 259 (M ⁺), 148, 135, 138
3e	IR (cm ⁻¹):	3445 (-OH str., COOH), 1691 (C=O str.), 1625 (C=N str.), 3015 (Ar-H str.), 1095 (C-F str.)
	¹ H NMR (δ):	10.22 (s, 1H, OH), 8.30 (s, 1H, CH=N), 7.2-8.0 (m, 4H, Ar-H)
	MS(m/z):	243(M ⁺), 148, 135, 118
3f	IR (cm ⁻¹):	3454 (-OH str., COOH), 1696 (C=O str.), 1628 (C=N str.), 3025 (Ar-H str.), 1181 (C-O-CH ₃ str.)
	¹ H NMR (δ):	10.22 (s, 1H, OH), 8.30 (s, 1H, CH=N), 7.0-8.1 (m, 4H, Ar-H), 3.74 (-OCH ₃)
	MS(m/z):	255 (M ⁺), 148, 135, 143.

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