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Research Article

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A Novel Clay catalyst: N-Acetylation of Aniline

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ABSTRACT

N-Acetylation of aniline by using clay as catalyst gives good yield acetic anhydride is commonly used as reagent for acylation of aniline but use of acetic anhydride is banned in Countries due to its utility in narcotics business. In the present investigation, we used acetic acid and novel clay

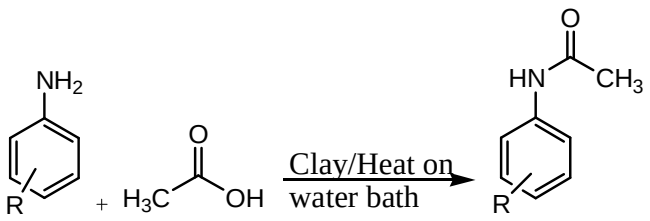
Key words: clay, acetylation, aniline, nanomaterial.

INTRODUCTION

N-acetylation of anilines is a common important chemical reaction in organic synthesis. Various catalyst are reported for N-acetylation which includes heteropolybion based ionic liquids [1]., Acetic anhydride in commonly used as reagent for acetylation of anilines but use of acetic anhydride is banned in some Countries due to its utility in narcotics business thus development new methodology for acetylation of aniline in greener way by using clay. Inspired by the researchers from our City , who [2-8] reported different catalysts for various other organic synthesis, we decided to use clay as a catalyst. Clays have a long history of use as a catalyst in organic synthesis. Clays are easily available and ecofriendly low cost chemical substance. Clays have been used in acid & base catalyzed reaction. Hence in continuation of the work earlier carried, we decided to use clay as catalyst. The clay is characterized by XRD and FESEM. The acylation of anilines and its derivatives has been carried the product is identified from melting point and spectral data. The yield is found to be 80-95%.

Preparation of catalyst: This clay is collected from rockey part of Bashir farm At Jatadevale Tq Pathardi Dist Ahmednagar of Maharashtra State India**:** Crush the clay in fine powder in mortar and pestle wash with distilled water and 0.1 M H_2SO_4 to remove organic particles soak. This mixture with 24 hour then filters with whatman filter paper. Wash the catalyst with distilled water to remove adsorbed acid. Dry it at 110^0Cin oven then cool then it is ready to use catalyst in several reactions this catalyst is characterized by using XRD and FESEM technique.

Reaction Scheme:



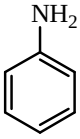
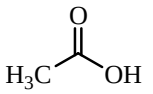
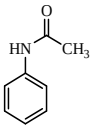
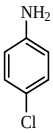
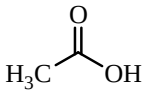
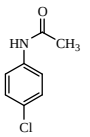
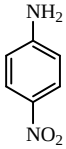
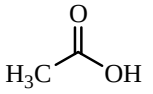
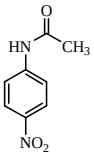
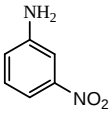
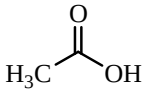
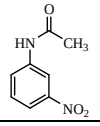
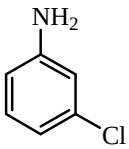
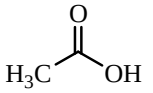
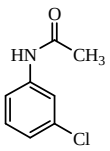
EXPERIMENTAL SECTION

All chemicals were obtained from sigma Aldrich Company and used as received. The milting points were determined by open capillary methods and are uncorrected. The reaction is monitored by checking TLC. In all the cases the distances travelled by the sample was found to be different that the parent compound started. The catalyst is characterized by using X-Ray powder diffraction (XRD), Energy-dispersive X-Ray Spectroscopy(EDS), Field Emission Scanning Electron Microscope (FESEM) Nova Nano SEM450 UOP from Central Instrumentation Facility Savitribai Phule Pune University. The products were purified by repeated crystallization from hot water. Infrared spectra were recorded on FTIR using KBr, NMR spectra were recorded on 500 MHZ (Bruker)in $CDCl_3$ from Central Instrumentation Facility Savitribai Phule Pune University.

XRD= powder crystal X-Ray diffraction.
FESEM = Field Emission Scanning Electron Microscope.
EDS= Energy Diffraction X-Ray Spectroscopy.

General procedure for the synthesis of N-acetylation of`Aniline and Substituted Aniline.
A mixture of aniline and clay (0.10) gm in acetic acid (3) ml in 100ml & round bottom Flask was heated over gentle flame using water condenser. Heating was continue for 1 Hour the reaction mixture was the carefully filtered in crushed ice 20ml in 100 ml beaker with stirring. the shining white crystals of products were separated slowly. Filter the product on were separated slowly. Filter the product on Buchner funnel. Recrystallize from hot water.

Table: 1 N- Acetylation of aniline by using clay as catalyst

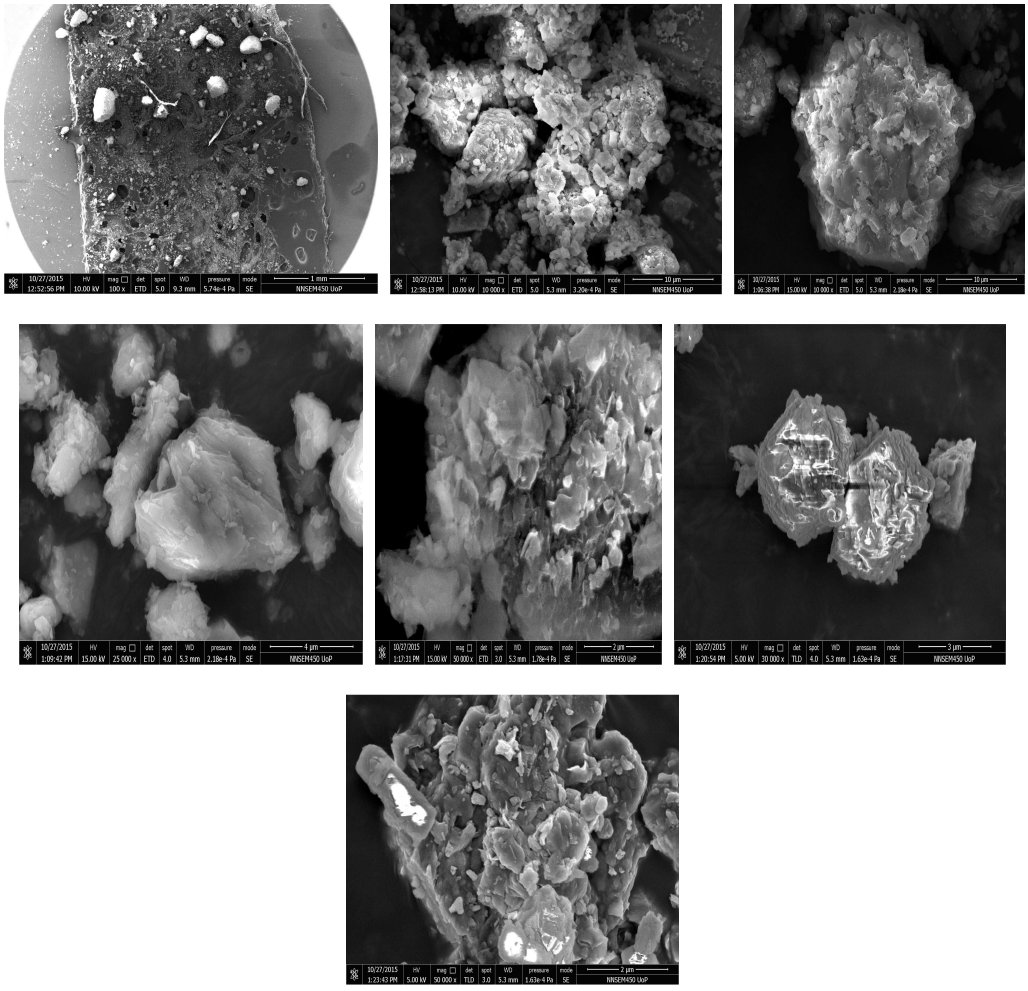
Entry	Aniline	Acetic Acid	Product	Yield	Meltin Point
A				95	115
B				95	172
C				80	215
D				80	126
E				90	78

RESULTS AND DISCUSSION

Spectral data:
a) IR (KBr): 3310, 3250, 3181, 3125, 3069, 2990, 2857, 2796, 1664, 1599, 1510, 1484, 1391, 825 cm^{-1}; PMR (CDCl3): 2.19(S, 3H), 7.31(d, 2H), 7.1(m, 3H), 7.9(S, 1H).
b) IR (KBr): 3300, 3260, 3191, 3125, 3069, 2990, 2857, 2796, 1664, 1599, 1535, 1484, 1391, 825 cm^{-1}; PMR (CDCl3): 2.19(S, 3H), 7.28(d, 2H), 7.3(m, 2H), 7.4(S, 1H).

c)IR (KBr): 3200, 3260, 3191, 3125, 3059, 2991, 2857, 2797, 1664, 1598, 1534, 1485, 1390, 825 cm^{-1}; PMR (CDCl3): 2.10(S, 3H), 7.18(d, 2H), 7.33(m, 2H), 7.41(S, 1H).
d) IR (KBr): 3894, 3625, 3413, 3113, 3059, 2620, 2665, 2497, 1987, 1614, 1520, 731 cm^{-1}; PMR (CDCl3): 2.2(S, 3H), 7.4(m, 1H), 7.5(m, 1H), 7.8(d,1H), 7.9(d, 1H), 8.0(S, 1H).
e) IR (KBr): 3295, 3253, 3184, 3119, 3078, 3019, 2928, 2846, 2797, 2680, 2560, 2327, 2183, 1590, 1470, 777 cm^{-1}; PMR (CDCl3): 2.19(S, 3H), 7.0(d,1H), 7.2(m,1H), 7.3(d, 1H), 7.6(S,1H), 7.8(S, 1H).

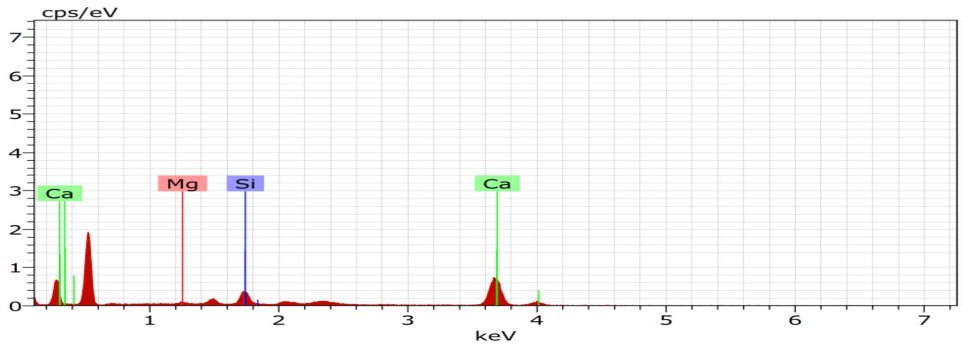
a. Characterization of the clay by using Field emission scanning electron microscope (FESEM) by using Novananosem 450 instruments



First image is subjected high voltage at 10.00 kV with magnification of 100 X, detector used is ETD, Spot 5.0 gives information about area covered by beam on detector, working difference is 9.3 mm, pressure apply on sample is negative pressure means vacuum pressure is applied on sample it is 5.74e-4 pa, mode of action is secondary electron Second image is subjected high voltage at 10.00 kV with magnification of 10000 X (pixel), detector used is ETD, Spot 5.0 gives information about area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample is negative pressure is applied on sample it is 3.20e-4 pa, mode of action is secondary electron. Third image is subjected high voltage at 15.00 kV with magnification of 10000 X, detector used is ETD, Spot 5.0 gives information about area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample is negative pressure is applied on sample it is 2.18e-4 pa, mode of action is secondary electron. Fourth image which is subjected high voltage at 15.00 kV with magnification of 25000 X, detector used is ETD, Spot 4.0 gives information about area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample is negative pressure is applied on sample it is 2.18e-4 pa, mode of action is secondary electron. Fifth image which is subjected

high voltage at 15.00 kV with magnification of 50000 X, detector used is ETD, Spot 3.0 gives information about area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample vacuum pressure is applied on sample it is 1.78e-4 pa, mode of action is secondary electron. Sixth image which is subjected high voltage at 5.00 kV with magnification of 30000 X, detector used is TLD, Spot 4.0 gives information about area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample is negative pressure is applied on sample it is 1.63e-4 pa, mode of action is secondary electron. Seventh image which is subjected high voltage at 5.00 kV with magnification of 50000 X, detector used is TLD, Spot 3.0 gives information about area covered by beam on detector, working difference is 5.3 mm, pressure apply on sample is negative pressure means vacuum pressure 1.63e-4 pa, mode of action is secondary electron.

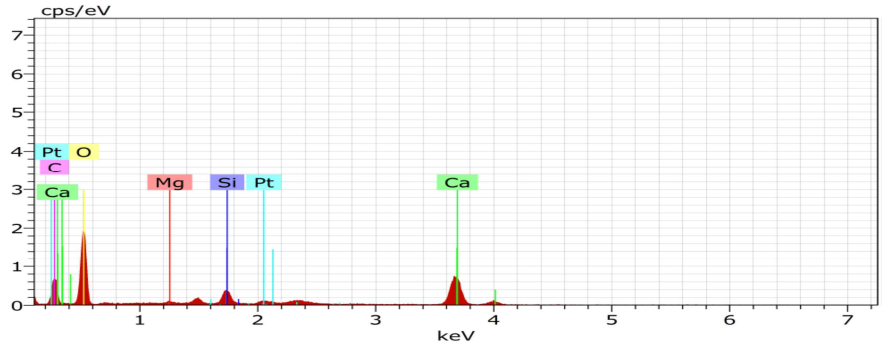
b. Characterization of clay by using Energy dispersive X-ray spectroscopy (EDS)



Spectrum: BN2 403
El AN Series unn. C norm. C Atom. C Error (1 Sigma)
[wt.%] [wt.%] [at.%] [wt.%]

Ca 20 K-series 44.79 86.66 81.82 1.59
Si 14 K-series 6.39 12.36 16.65 0.32
Mg 12 K-series 0.51 0.99 1.54 0.07

Total: 51.69 100.00 100.00



Spectrum: BN2 403
El AN Series unn. C norm. C Atom. C Error (1 Sigma)
[wt.%] [wt.%] [at.%] [wt.%]

O 8 K-series 46.03 50.50 62.25 6.09
Ca 20 K-series 30.65 33.63 16.55 1.09
C 6 K-series 9.71 10.66 17.50 1.57
Si 14 K-series 4.40 4.83 3.39 0.23
Mg 12 K-series 0.35 0.39 0.32 0.05
Pt 78 M-series 0.00 0.00 0.00 0.00

Total: 91.14 100.00 100.00

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