International Conference on Frontiers in Life and Earth Science
© 2018 IJSRST | Volume 5 | Issue 1 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X

Synthesis of Natural Clay Supported Silver Nanoparticles and Its Application in Synthesis of Xanthenes

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ABSTRACT

Synthesis of Natural clay supported silver nanoparticle has been carried out by reduction method. The Natural clay supported nanoparticles were characterized by UV, FE-SEM, EDS and XRD analysis. The catalytic activity of nanoparticle for synthesis of Xanthenes were studied and Progress of reaction was monitored by TLC, products were characterized by ^{1}H-NMR spectroscopy. It was observed that a nanoparticle shows good catalytic activity and good yield of the reaction.

Keywords : Natural Clay, Silver Nanoparticles, Xanthenes, Reduction

I. INTRODUCTION

Xanthenes are important biologically active heterocyclic compounds with anti-bacterial,[1] anti-viral,[2]and anti-inflammatoryactivity.[3]Those compounds are also shows applications in dyes,[4]Laser Technology[5] and pH-sensitive fluorescent materials for visualizationof biomolecules.[6]Several methods have been reported for the synthesis of benzoxanthenes, such as the cyclocondensation reaction of 2-hydroxyaromatic aldehydes and 2-tetralone,[7] the reaction of benzaldehyde and acetophenone[8] and the condensation of β-naphthol with alkyl or aryl aldehydes[9] in acidic condition.

The synthesis of xanthene by use of silver nanoparticle as a catalyst by the condensation of β-naphthol with aryl aldehydes are also reported.[10-11]M. Dabiri et al. gave synthesis of aryl-14H-dibenzo[a,j]xanthene and 1,8-dioxo-octahydroxanthene derivativesusing montmorillonite K10 as reusable eco-friendly catalyst under solvent-free conditions.[12]

There are many methods for preparation of silver nanoparticles are known such asChemical Reduction,[13] reverse micelles process,[14] microwave dielectric heating reduction,[15] ultrasonic irradiation,[16] radiolysis,[17]solvothermal synthesis,[18] electrochemical synthesis,[19] plant mediated synthesis[20-22] etc.

In this report we have synthesized Natural Clay supported Ag Nanoparticles by reduction method and are subjected as a catalyst for the synthesis of Xanthenes from β-naphthol and aryl aldehydes.

II. METHODS AND MATERIAL

Silver nitrate ($AgNO_3$), Sodium borohydride, Aryl Haide, β-naphthol were supplied by Loba Chem. All chemicals were used as received without any further purification.Double-distilled deionised water was used.Melting points were uncorrected and determined in an open capillary tube.^{1}H NMR spectra were recorded in$DMSO\text{-}d_6$ on a BrukerAvance-III 400 MHz spectrometer using TMS as an internal standard.The residual solvent signals were used as references and

the chemical shifts converted to the TMS scale (DMSO-d_6: δ_H = 2.49 ppm).

A. Preparation of Natural Clay supported Ag Nanoparticles.

Natural clay supported Ag nanoparticle catalyst was prepared by stirring 3 gm. of activated clay with Silver Nitrate (0.01mol) in 50 ml water then the 10 ml 0.1M aq. solution of $NaBH_4$ was added drop wise to above mixture and stirred for overnight then filtered and dried at 150^{0}C for 1 hr. in hot air oven followed by grinding in morter.

The prepared nanoparticles are characterized by UV spectroscopy, FE-SEM, EDS and XRD.

The UV spectrum(Figure 1) shows the absorption maximum between 400 to 500 nm. The average Particle size from FE-SEM images (Figure 2)is 56.32 nm. EDS spectra (Figure 3) shows the presence of silver and from powder XRD (Figure 4) planes 111, 200, 220 and 311 at38.5°, 44.48°, 64.69° and 77.62° confirm the formation of silver nanoparticles.All the diffraction peaks are well corresponding with the standard diffraction data of JCPDS file No. 04-0783 for face-centered cubic Ag.

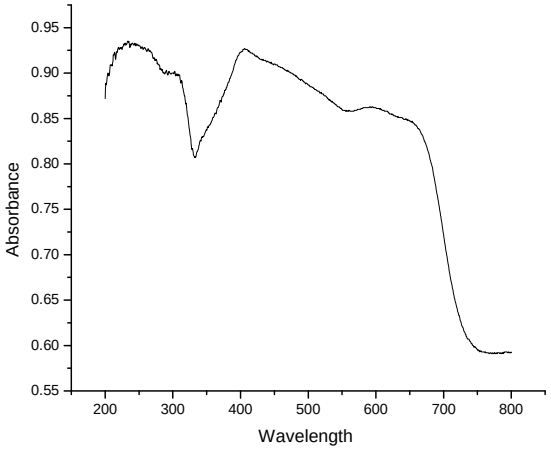


Figure 1. UV Spectrum of Natural Clay – Ag Nanoparticles

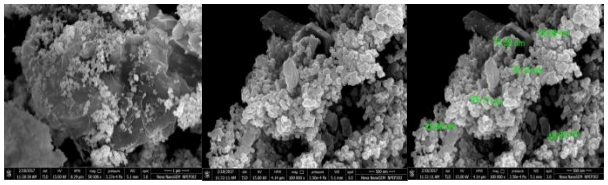


Figure 2.FE-SEM images of Natural Clay – Ag Nanoparticles

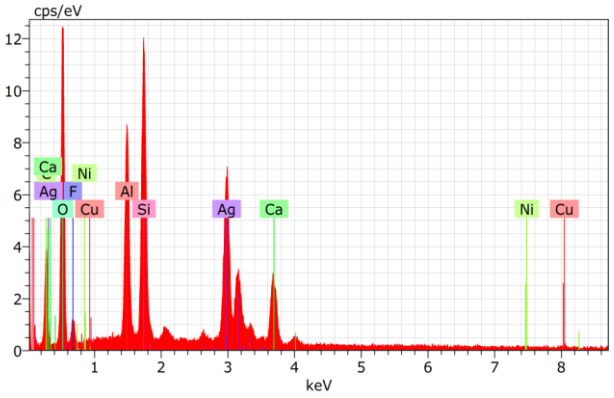


Figure 3. EDS Spectra of Natural Clay – Ag Nanoparticles

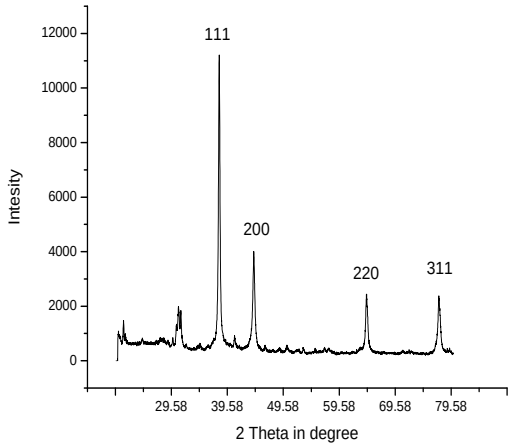
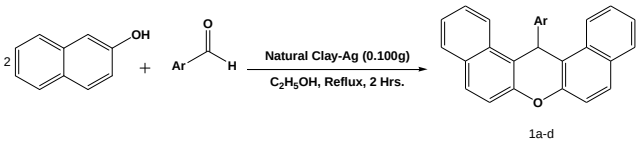


Figure 4. XRD Spectrum of Natural Clay – Ag Nanoparticles

B. General Procedure for Synthesis of Xanthene

A mixture of 2-naphthol (2 mmol), aryl aldehyde (1 mmol) and catalyst (0.100 g) was refluxed in ethanol. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was filtered and washed with diethyl ether (5 mL) to isolate of catalyst. The solvent was evaporated under reduced pressure and the crude product obtained was purified by recrystallization from ethanol.



Scheme 1. Synthesis of Xanthene

The product**1a**was isolated as a white solid **Yield :M.P.:**182-184°C; **^{1}H NMR (500 MHz, DMSO) δ** 8.71 (d, *J* = 8.6 Hz, 2H), 7.93 (dd, *J* = 8.4, 3.5 Hz, 4H), 7.71 – 7.61 (m, 4H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.15 (t, *J* = 7.7 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.74 (s, 1H).

The product **1b** was isolated as a white solid **Yield :M.P.:** 288°C;**^{1}H NMR (500 MHz, DMSO) δ** 8.67 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 4H), 7.64 (t, *J* = 8.9 Hz, 4H), 7.57 (d, *J* = 8.9 Hz, 2H), 7.48 (t, *J* = 7.1 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.76 (s, 1H).

The product **1c** was isolated as a yellow solid **Yield :M.P.:** 206°C;**^{1}H NMR (500 MHz, DMSO) δ** 8.66 (d, *J* = 8.5 Hz, 2H), 7.96 – 7.89 (m, 4H), 7.62 (t, *J* = 8.1 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.71 – 6.65 (m, 3H), 3.54 (s, 3H).

The product **1d** was isolated as a White solid **Yield :M.P.:** 188-190°C;**^{1}H NMR (500 MHz, DMSO) δ** 8.65 (d, *J* = 8.5 Hz, 2H), 7.90 (dd, *J* = 13.5, 8.4 Hz, 4H), 7.62 (dd, *J* = 11.8, 4.6 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 1H), 6.43 (d, *J* = 8.9 Hz, 2H), 2.62 (s, 6H).

III. RESULTS AND DISCUSSION

The reaction conditions were optimized on the basis of the catalysts,solvents and different temperatures for carbon-carbonand carbon-oxygen bond formations. Thus the model reaction was carried out using benzaldehyde and 2-naphtholas shown in table 1.

Table 1. Optimization of reaction conditions

Entry	Catalyst (gm)	Solvent	Temp.°C	Time	Yield (%)[a]
1	None	none	R. T.	2 Hrs.	00
2	None	EtOH	R. T.	2 Hrs.	00
3	0.100	EtOH	R. T.	2 Hrs.	00
4	0.100	CH_2Cl_2	R. T.	2 Hrs.	00
5	0.100	DMF	R. T.	2 Hrs.	00
6	None	none	Reflux	2 Hrs.	<10
7	0.100	EtOH	Reflux	2 Hrs.	90
8	0.100	CH_2Cl_2	Reflux	2 Hrs.	50
9	0.100	DMF	Reflux	2 Hrs.	55

[a]Isolated Yield

As an outcome of these experiments we found that no conversion was found at room temperature with catalyst entry 3 in table 1. Whereas very less conversion on heating in absence of solvent entry 6 in table 1.Good conversion in presence of DCM and DMF entry 8 and 9 in table 1.Natural Clay supported Ag nanoparticles is the most active catalyst for this cyclization reaction in presence of ethanol as a solvent at reflux temperature entry 7 in table 1.

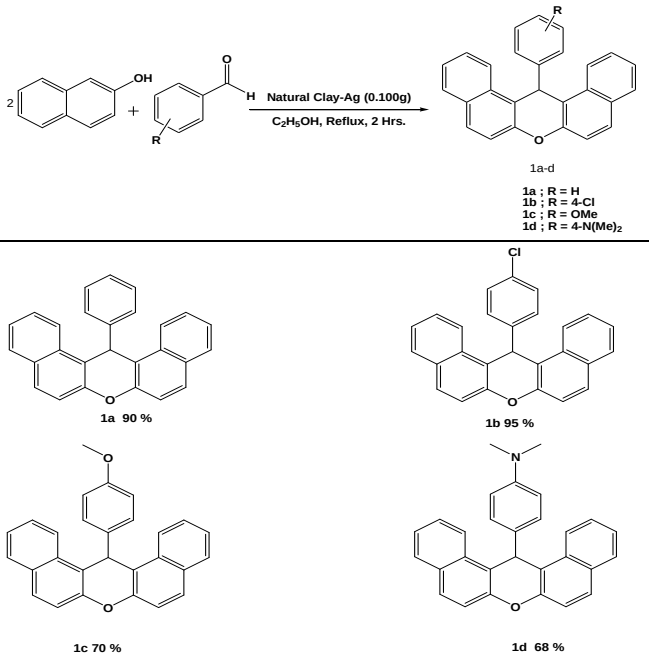
The activity of catalyst was tested for some different aldehydessuch as p-chlorobenzaldehyde, Anisaldehyde and 4-N,N,- dimethyl Benzaldehyde entry 2, 3and 4 in table 2 with 2-naphthol. The isolated products were characterized by ^{1}H-NMR spectroscopy.

Table 2.synthesis of xanthenes by using Natural Clay Ag nanoparticles

Entry	Aldehydes	Xanthene	Yield (%)[a]
1	Benzaldehyde	1a	90
2	p-Chlorobenzaldehyde	1b	95
3	Anisaldehyde	1c	70
4	Para-N,N-dimethyl Benzaldehyde	1d	68

Reaction condition: Aldehyde (1mmol), 2-naphthol (2 mmol), Natural Clay Ag Nanoparticles (0.100 gm), EtOH, reflux, 2 Hrs.

Table 3. Scope of Cyclisation between different Aryl Aldehydes and 2- naphthol



Reaction condition: Aldehyde (1mmol), 2-naphthol (2 mmol), Natural Clay Ag Nanoparticles (0.100 gm), EtOH, reflux, 2 Hrs.

IV.CONCLUSION

In summary, we have developed a mild, highly efficient method for synthesis of biologically active xanthenes in the presence of natural clay supported AgNPs as catalyst. The method requires a simple work-up, is inexpensive, short reaction times and gives good yields.

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