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Research Article

N-butyl Pyridinium Bromide Ionic Liquid Assisted Preparation of Cobalt Oxide: An Efficient Nanocatalyst for the Synthesis of Tetrahydrobenzo[a]xanthen-11-one Derivatives

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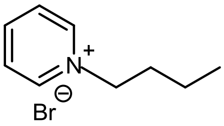
ABSTRACT

An efficient and green protocol for the synthesis of tetrahydrobenzo[a]-xanthen-11-one derivatives by one-pot, three-component coupling reaction of aromatic aldehydes, dimedone, and 2-naphthol at 100 °C under solvent-free conditions in the presence of Co3O4 nanocatalyst is described. Cobalt oxide nanocatalyst was synthesized using a simple reflux method in an aqueous medium using a pyridinium-based ionic liquid, N-butyl pyridinium bromide. Morphology, structure, and particle size of Co3O4 nanocatalyst are characterized by FE-SEM, FT-IR, and XRD spectroscopy. The present methodology offers several advantages such as high yields, short reaction times, and simple workup.

Keywords: Xanthene, Cobalt oxide; N- butyl pyridinium bromide; Ionic liquid; Nanocatalyst.

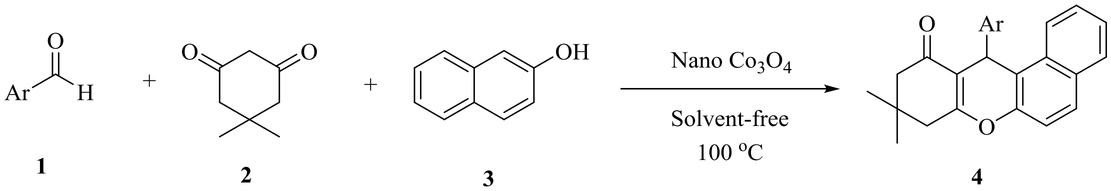
Introduction

Xanthenes derivatives have been investigated for the broad spectrum of their biological and pharmaceutical properties such as anti-inflammatory antiviral and antibacterial [1]. Thus, the development of new methods for the synthesis of xanthene and benzoxanthene derivatives is an important area of synthetic research. The conventional protocol involves a three-component condensation of aldehydes, dimedone, and 2-naphthol [2]. Transition metal oxides have many applications of interesting properties arising due to their variable oxidation state [3]. Cobalt oxide Co_3O_4 is an important transition metal oxide because of its application in various fields of research and industry including pigments, gas sensors, magnetic materials, catalysts, anode materials for rechargeable Li batteries, electrochromic devices, electrochemical systems, and high-temperature solar selective absorbers [4]. The difference in oxygen defect, oxygen holes, and oxygen adsorbed in a different state of cobalt in Co_3O_4 (a mixed valance material that is formally Co^{II} Co^{III} O_4) is thought to be the reason for the high activity and selectivity of these metal oxide catalysts [5]. Therefore, due to the effect of particle shape and size on the properties of materials, the need to try new methods to produce cobalt oxide nanocrystals with controllable size and morphology for researchers. There are many fabrication methods including thermal decomposition, wet chemical method, electrochemical precipitation, and sol-gel for the preparation of cobalt oxide nanoparticles [6], [7]. However, some reported methods face drawbacks such as relatively high temperatures, the use of special tools, or low product yields. Among the different methods, the co-precipitation method is a cost-effective and convenient method due to its ease of execution, no need for equipped devices, no need for expensive raw materials, and the ability to do it in any laboratory. Ionic liquids (ILs) can act as solvents for reactants and also the morphology templates for the products at the same time. This behavior makes it possible to synthesize inorganic materials with novel or improved properties.[8],[9]. For this reason, in this paper, for the first time, pyridinium-based ionic liquid (N-butyl pyridinium bromide [BuPy]Br) (Scheme 1). is used to synthesize Co_3O_4 nanostructures by co-precipitation method and the effect of NaOH concentration as a precipitating agent on the shape, size, and properties of the nanoparticles were investigated. Then the nanocatalyst was applied in a multicomponent reaction for the synthesis of tetrahydrobenzo[a]-xanthen-11-one derivatives under solvent-free conditions (Scheme 2).



N-butylpyridinium bromide [BPy][Br]

Scheme 1. Chemical structures of ionic liquid.



1 2 3 4

Scheme 2. Synthesis of tetrahydrobenzo[a]-xanthen-11-one derivatives 4a-f.

2. Experimental

2.1. Synthesis of Co_3O_4 nanostructures

In a round-bottomed flask, 0.5 mmol of ionic liquids and 0.5 mmol of $Co(NO_3)_2 \cdot 6H_2O$ were added to a solution of sodium hydroxide in 10 mL of distilled water under vigorous stirring at room temperature to form a homogeneous suspension (1, 2, and 3 mmol of NaOH added that the molar ratio of NaOH to $Co(NO_3)_2 \cdot 6H_2O$ was 2:1, 4:1 and 6:1 respectively). Then, this solution was refluxed for 24 h. After cooling to room temperature, this precipitate was centrifuged and washed with distilled water and ethanol (96%) several times. The Co_3O_4 nanostructures as a black powder were finally obtained by calcination in the electric oven at 400°C for 3 h. A blank sample was also synthesized without any template and labeled as NO IL.

2.2. General procedure for the synthesis of tetrahydrobenzo[a]xanthen-11-ones

A mixture of 2-naphthol (1 mmol), aldehyde (1 mmol), dimedone (1 mmol), and catalyst (0.05 g) was stirred at 100 °C under solvent-free conditions for the appropriate time indicated in Table 3. The progress of reactions was monitored by TLC (ethyl acetate/n-hexane=1/3). After completion of the reaction, dichloromethane (10 ml) was added and then filtered. A solid was obtained which was purified by recrystallization from hot ethanol to afford pure products.

3. Result and discussion

3.1. Catalyst characterization

The FT-IR spectra of all samples are shown in Figure 1. In all samples, there are two characteristic absorption bands at about 572 and 667 cm^{-1} due to the stretching vibration mode of (Co-O), which provides clear evidence for the presence of the crystalline Co_3O_4 The first peak at 572 cm^{-1} belongs to the stretching vibration mode of (Co^{3+} - O) bond in the octahedral hole. The second band at about 667 cm-1 is attributed to the (Co^{2+} - O) bond where Co $^{2+}$ is in the tetrahedral hole [10]. Broadband at about 3427 cm^{-1} and a small band at 1018 cm$^{-\ 1}$ corresponding to the stretching and bending modes of (O-H) of the water molecules absorbed by the samples or KBr.

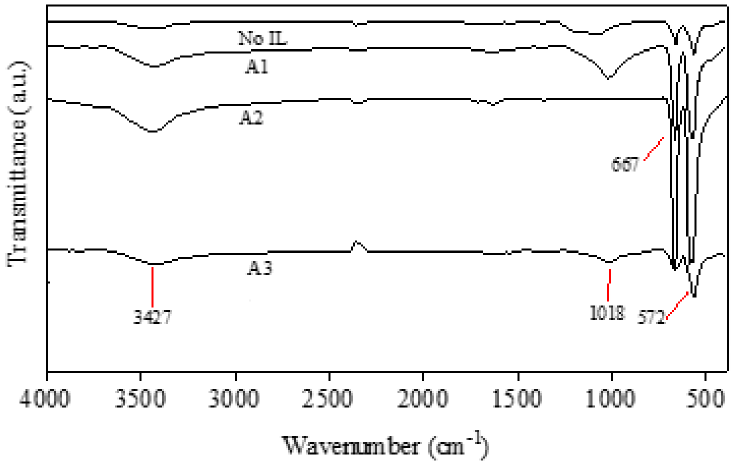


Fig 1. FT-IR spectrum of Co_3O_4 nanocatalyst.

Figure 2 showed the XRD pattern of the final products. The XRD patterns indicate the monophasic fcc Co_3O_4 phase. As shown in figure 2 almost all of peaks intensities of (111), (220), (311), (222), (400), (422), (511), (440), can be perfectly indexed to a pure cubic phase (space group: Fd3m of Co_3O_4 (a=8.0840A) reported in the literature (JCPDS 74-2120) [11]. The particle size of the investigated Co_3O_4 solids was calculated from the line broadening analysis of some diffraction line of metal oxide phases using Scherer equation: D = k. λ / β1/2. Cos (θ) where k is the Scherer's constant (0.89), D the mean crystalline diameter (nm), λ the X-Ray wavelength, β1/2 is the full width half maximum (FWHM) of the metal oxide diffraction peaks and θ is the diffraction angle.

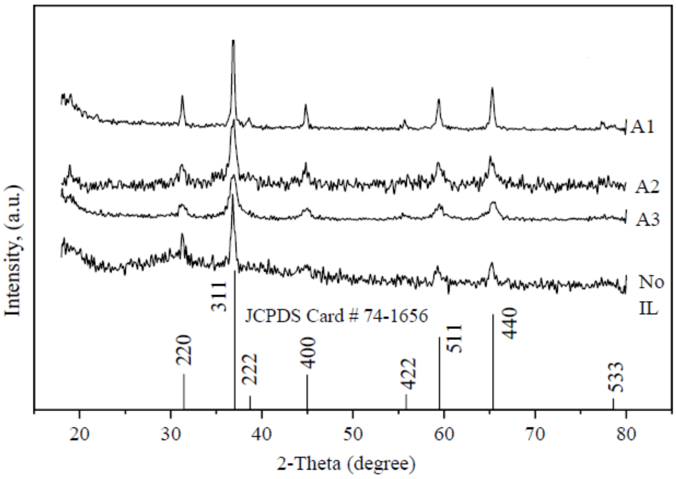


Fig 2. XRD spectrum of Co_3O_4 nanocatalyst

The morphology of the products was characterized by scanning electron microscopy (SEM). Figure 3 shows the FE-SEM images of samples A1, A2, A3, and NO IL. As shown in Table 1, the change in NaOH concentration affected the morphology and particle size, so with increasing concentration, the average size of the crystals decreased. The reason for these changes can be stated that the increase in sodium hydroxide causes sudden temperature changes in the system, which increases the speed of the nucleation process and ultimately leads to the formation of smaller particles [12]. Variation in morphology and the average size of cobalt oxide nanostructures is a result of template effects. The results of cobalt nano-oxide synthesis based on ionic liquid under reflux conditions and different amounts of sodium hydroxide with morphological information and crystal size are given in Table 1.

Table 1. Effect of the template and the amount of base on morphology and crystallite particle size of Co_3O_4 nanostructures

Sample	IL	NaOH/ $Co(NO_3)_2 \cdot 6H_2O$	Size (nm)	Morphology
NO IL	-	2:1	17	Nanosheet
A1	1	2:1	28	nanoparticle
A2	1	4:1	17	nanosheet
A3	1	6:1	12	Nanosheet–nanoparticle

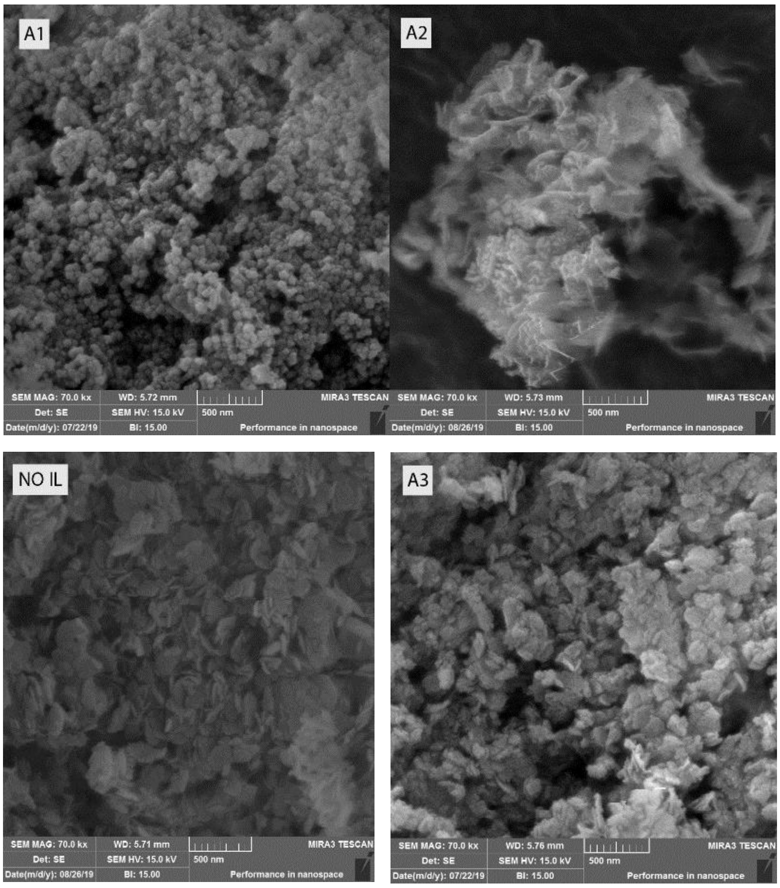


Fig 3. FE-SEM images of Co_3O_4 nanocatalyst

To evaluate the catalytic activity of Co_3O_4 nanostructures in the preparation of the tetrahydrobenzo[a]-xanthen-11-one derivatives, various reaction conditions were examined to determine the optimum conditions for the reaction. The results are summarized in Table 2. In an initial study, to examine the catalytic activity of the catalyst and the amount of catalyst in this reaction, equimolar amount of benzaldehyde, dimedone, and 2-naphthol in solvent-free conditions at 80 °C for 100 min. was examined. The best results were obtained using 0/05 g of Co_3O_4 NPs (Entry 3). Using lower amounts of catalyst resulted in lower yields. While higher amounts of catalyst did not affect the reaction times and yields and in the absence of catalyst nearly no product could be detected (Table 2). We next investigated the effect of temperature on the formation of the product. Increasing temperature to 100 °C affected the reaction condition and increased the yield to 90% (Entry 6).

In the next step, the reaction of benzaldehyde with 2-naphtol and dimedone in different for 100 min. in reflux, conditions were examined in the presence of Co_3O_4 NPs (0/05 gr). The highest yield (90%) was obtained under solvent-free conditions. The studies on the effect of common organic solvents on the course of the reaction as delineated in (Table 2) revealed that the use of solvent is not beneficial to improve the yield of the desired product. The generality and synthetic scope of this protocol were demonstrated by synthesizing a series of xanthen-11-one derivatives (Table 3). A wide range of aromatic aldehydes was well tolerated under the optimized reaction conditions.

Table 2: The effect of catalyst, temperature, and solvent on the synthesis of tetrahydrobenzo[a]-xanthen-11-one derivatives.

Entry	Catalyst (g)	Temperature (°C)	Solvent (5 ml)	Yield (%)
1	–	80	-	10
2	0.04	80	-	70
3	0.05	80	-	80
4	0.06	80	-	80
5	0.05	r.t.	-	35
6	0.05	100	-	90
7	0.05	110	-	90
8	0.05	reflux	H_2O	20
9	0.05	reflux	EtOH	25
10	0.05	reflux	EtOAc	40
11	0.05	100	-	90

Reaction conditions: Benzaldehyde (1 mmol), 2-naphthol (1 mmol), and dimedone (1mmol)

Table 3: Synthesis of tetrahydrobenzo[a]-xanthen-11-one derivatives in the presence of Co3O4 NPs under solvent-free conditions at 100 °C.

Entry	Ar	Product	Time (min)	Yield (%)
1	C_6H_6	4a	100	90
2	$4\text{-}NO_{2\text{-}}C_6H_4$	4b	90	95
3	$4\text{-Me-}C_4H_4$	4c	100	85
4	$2,4\text{-Di Cl-}C_6H_3$	4d	90	85
5	$4\text{-}ClC_6H_4$	4e	90	92
6	$4\text{-}FC_6H_4$	4f	90	95

4. Conclusion

In summary, the spinel phase of Co_3O_4 nanostructures has been successfully synthesized by the reflux method. In this study, ionic liquid (N-butyl pyridinium bromide) was used as a template and the effect of NaOH concentration as a precipitating agent on the size and morphology of nanostructures was investigated. Then Co_3O_4 NPs as a heterogeneous solid acid catalyst were used for the synthesis of xanthen-11-one derivatives. The method offers several advantages including high yields, application of an inexpensive catalyst, easy workup, and performing reaction under solvent-free conditions that are considered to be relatively environmentally benign.

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