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ARTICLE TYPE

The preparation and characterization of Boehmite nanoparticles-TAPC: A tailored and reusable nanocatalyst for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones

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A one-pot multi-component, green, and highly efficient protocol has been described for the synthesis of a wide range of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-ones using TAPC supported on boehmite nanoparticles (BNPs-TAPC) as an eco-friendly and recyclable nanocatalyst in excellent yields under solvent-free conditions. Short reaction time, easy and quick isolation of the products, use of inexpensive heterogeneous nanocatalyst, solvent-free process and excellent chemoselectivity are other remarkable features of this environmentally benign protocol. The BNP-TAPC was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and FT-IR methods.

Introduction

Heterogeneous catalysts provide numerous opportunities for recovering and recycling catalysts from reaction environments. These features can lead to improved processing steps, better process economics, and environmentally friendly industrial manufacturing. However, further efforts are necessary in the design of new heterogeneous catalysts to reach activity and selectivity values competitive with homogeneous ones.

Homogeneous catalysts are known for high activity and selectivity but the major disadvantage of the homogeneous catalysts is the need to separate off the reaction products and recover the catalyst. This can be both complex and expensive. Other disadvantages are that these catalysts are relatively easily decomposed so temperatures must be well controlled, and that they can be deactivated if poisonous by-products are formed. Heterogeneous catalysts are not soluble like homogeneous and hence can be recovered and even reused but lacks the activity and selectivity of homogeneous catalysts. If a homogeneous catalyst is anchored on to a solid support, its activity and selectivity can be retained and it can be rendered suitable for recovery and reuse.[1]

Functionalization of nanoparticles with organic components is currently an area of intense scientific interest for a wide variety of goals.[2] The good dispersability in organic media of such surface modified nanoparticles by organic molecules offers many possibilities in important areas of chemistry such as catalysis, analytical chemistry and medical research.[3]

In recent years, boehmite with nanoscale dimensions and morphological specificity has attracted enormous interest from both fundamental and practical viewpoints.[4]

Moreover, boehmite (Fig. 1), which is an aluminum oxyhydroxide (AlO(OH)), contains terminal groups that render high reactivity to the surface and provide a hydrophilic environment improving the homogeneity of the medium being for all these reasons a promising support.[5]

On the other hand as a typical oxyhydroxy compound, boehmite is also extensively used as an absorbents,[6] catalysts,[7] filler in membrane,[8] optical materials,[9] coatings,[10] composite reinforcement material in ceramics.[11]

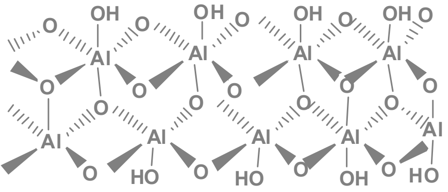

Fig. 1 Boehmite Structure.

Organic syntheses involving greener process and under solvent-free conditions have been investigated world wide due to stringent environment and economic regulations.[12]

Xanthenes and benzoxanthenes are important classes of biologically active heterocyclic compounds that are known to possess great biological activities such as antiplasmodial,[13] anti-inflammatory,[14] antiviral,[15] antibacterial[16] and also have been used as antagonists for drug-resistant leukemia lines.[17]

A number of xanthene based compounds are also available from natural sources.[18] Santalin pigments, as they are popularlyknown, have been isolated from a number of plant species.[18]

Various literature procedures are available to synthesize

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xanthenes and benzoxanthenes, including silica supported $NaHSO_4.SiO_2$,[19] strontium triflate[20] p-toluenesulfonic acid(*p*TSA)/ionic liquid([bmim]BF_4),[21] $InCl_3/P_2O_5$,[22] iodine,[23] tetra(n-butyl)ammonium fluoride[24] and proline triflate.[25] Even though various procedures are reported, disadvantages including low yields, prolonged reaction times, use of an excess of reagents/catalysts and use of toxic organic solvents necessitate the development of an alternative route for the synthesis of xanthene derivatives.

Multicomponent reactions (MCRs) have attracted considerable attention due to significant advantages such as simplicity of operation, reduction of isolation and purification steps, and minimization of costs, time and waste production[26] (Fig. 2). Thus, MCRs are accepted as green chemical processes.

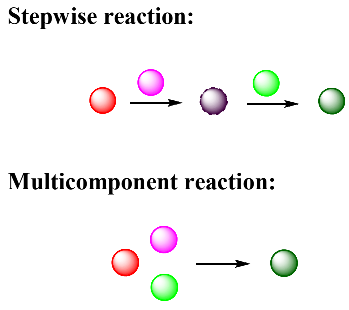
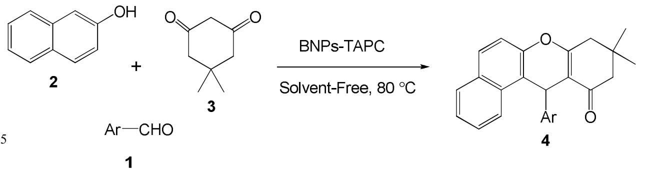


Fig. 2 Stepwise reaction versus multicomponent reaction.

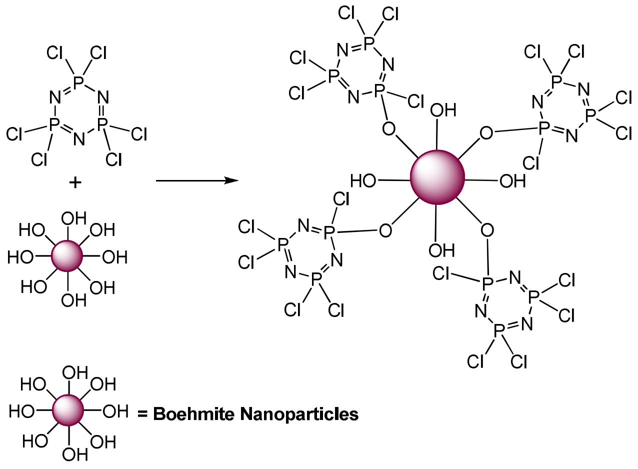
Due to our interest in the multicomponent syntheses[27] and in continuation of our work on the development of new synthetic methodologies,[28] in the present work we report the preparation, characterization and investigation of catalytic activity of TAPC supported on boehmite nanoparticles (BNPs-TAPC) for the preparation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives (Scheme 1). As far as we know, our report constitutes the first example of boehmite nanoparticles as support for hexachlorocyclotriphosphazene (TAPC) in heterogeneous catalysis.



Scheme 1 The condensation reaction of β-naphthol, a variety of aldehydes, and dimedone.

Results and discussion

1,3,5-Triazo-2,4,6-triphosphorine-2,2,4,4,6,6-hexachloride (TAPC), usually called hexachlorocyclotriphosphazene or trimeric phosphonitrilic chloride were widely used in organic synthesis,[29] but one major problem, which has been associated with this homogeneous catalyst, is the recovery of catalyst from reaction medium, therefore, one way to overcome this problem is to immobilize it on solid supports. In other words, the reusability of a supported catalyst is of great importance from economical and synthetic points of view.



Scheme 2 The route for the preparation of BNPs-TAPC.

The route for the preparation of BNPs-TAPC is shown in Scheme 2. This Catalyst was synthesized by the reaction of boehmite nanoparticle with 1,3,5-triazo-2,4,6-triphosphorine-2,2,4,4,6,6-hexachloride (TAPC) due to the inherent affinity of phosphorus toward oxygen and the presence of hydroxyl groups in boehmite structure. The BNP-TAPC was characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and FT-IR methods.

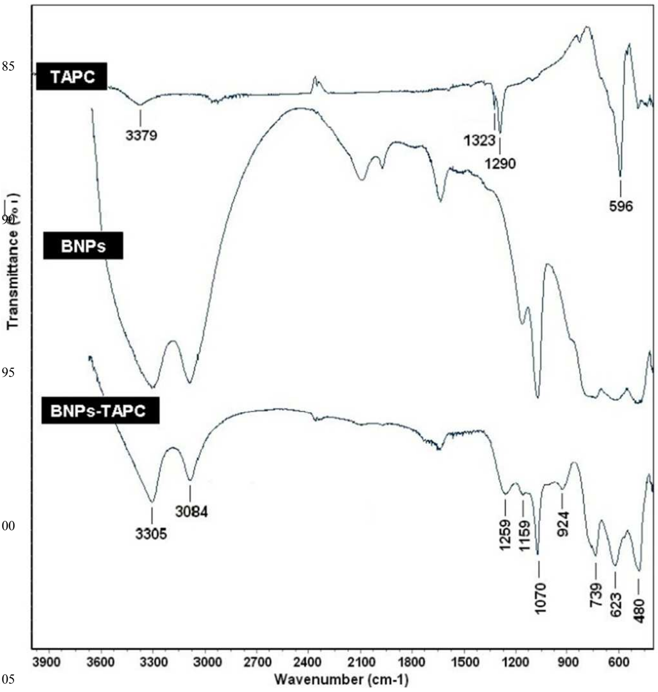


Fig. 3 FT-IR spectra (KBr disk) of TAPC, BNPs, and BNPs-TAPC.

The most informative evidence, which confirmed the anchoring of TAPC on the boehmite nanoparticles was obtained by comparison of the FT-IR spectra of TAPC, boehmite nanoparticles (BNPs) and BNPs-TAPC (Fig. 3). In the BNPs-TAPC spectrum, the stretching vibration of (P-O) due to

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attachment of the TAPC to the boehmite nanoparticles was observed at ~924 cm^{-1} and also the (P=N) stretching band of TAPC at ~1290 cm^{-1}, was appeared at ~1259 cm^{-1} in the BNPs-TAPC. In addition to, the reduced intensity of Al-OH groups at ~3084, 3305 cm^{-1} was observed in the BNPs-TAPC. These observations clearly confirmed the formation of the BNPs-TAPC catalyst.

The XRD patterns of BNPs and BNPs-TAPC are shown in Fig. 4. In Fig. 4a, all the XRD peaks can be identified clearly as boehmite with an cubic orthorhombic unit cell (a=2.859 Å, b=12.24, Å c=3.691 Å, space group symmetry Cmcm (63), JCPDS PDF No. 074-1895) and Fig. 4b, can be indexed on the basis of boehmite nanoparticles structure with supporting TAPC and very sharp peaks appeared at 32.17º, 56.48º 2θ can be associated with the presence of phosphorus in boehmite (a=18.8 Å, space group symmetry I -, JCPDS PDF No. 025-0608). These peaks confirmed that TAPC has been supported on boehmite nanoparticles.

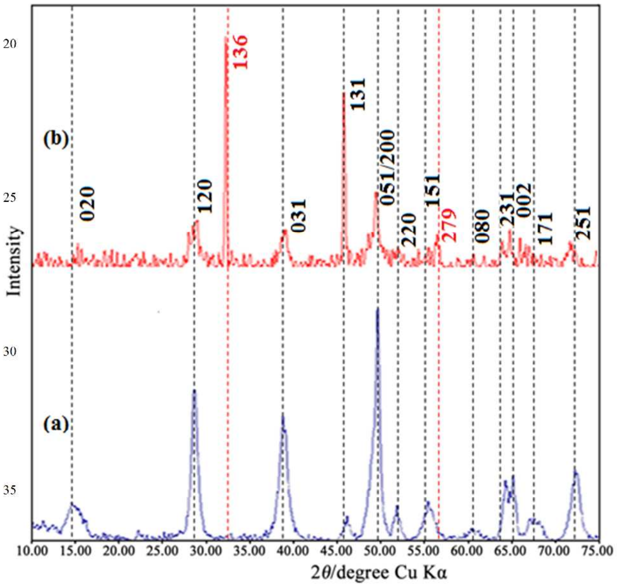

Fig. 4 XRD pattern of (a) BNPs, (b) BNPs-TAPC.

The morphology of BNPs and BNPs-TAPC was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The TEM image of boehmite nanoparticles showed that cubic orthorhombic structures for the unit cells of boehmite with average size of ~20–30 nm (Fig. 5a), on the other hand, core-shell structures of BNPs-TAPC from the Fig. 5b, clearly indicates that TAPC has been supported on the boehmite with the preservation of the nanosize structure. In addition, the SEM image of supported catalyst (Fig. 6d) showed that particles have regular geometric shape in comparison with boehmite nanoparticles (Fig. 6c).

To optimize the reaction conditions, the condensation reaction of β-naphthol (1 mmol), benzaldehyde (1 mmol), and 5,5-dimethylcyclohexane-1,3-dione (dimedone) (1 mmol) using different catalysts under solvent-free conditios at 80 °C was selected as a model in the presence of different amounts of BNP-TAPC. The best results were obtained when the reaction was carried out with 10 mg of BNP-TAPC (Table 1, entry 6). In addit

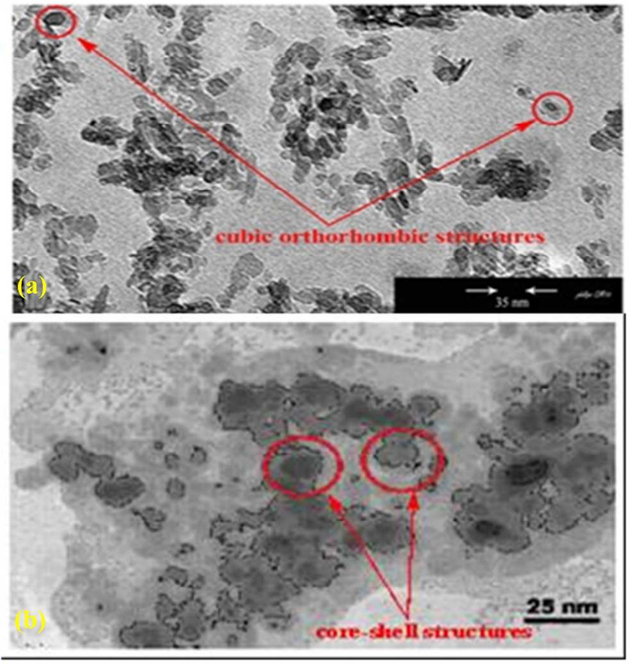

Fig. 5 TEM image of (a) BNPs and (b) BNPs-TAPC.

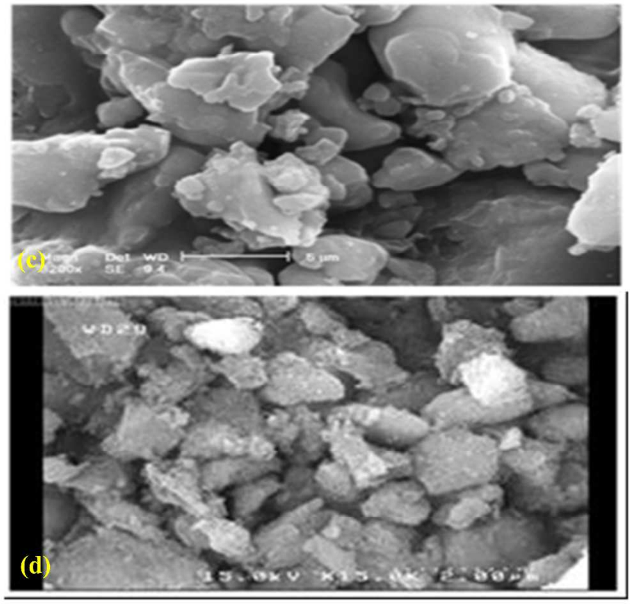

Fig. 6 SEM image of (c) BNPs and (d) BNPs-TAPC.

addition, no product was detected in the absence of the catalyst (Table 1, entry 5). The less amount of catalyst gave a low yield even after a prolonged reaction time, and the more amount of it could not cause the obvious increase for the yield of product but could shorten the reaction time (Table 1, entries 7 and 8).

To study the generality of the procedure, a series of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives having different electronic properties were synthesized using the optimized conditions. The results are presented in Table 2. As can be seen, electronic effects and the nature of substituents on the

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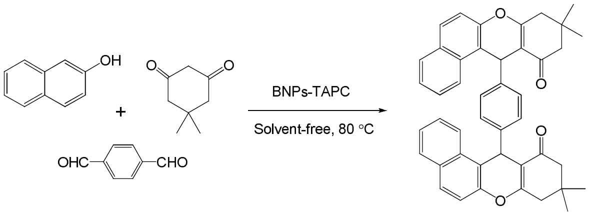
Table 1 The condensation reaction of benzaldehyde, *β*-naphthol and 5,5-dimethylcyclohexane-1,3-dione under different conditions

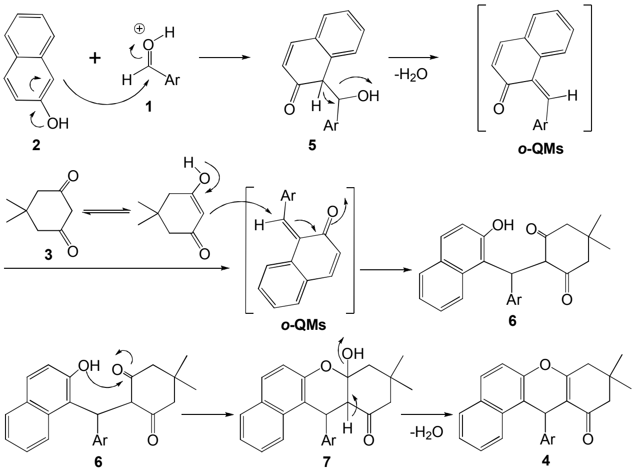
Entry	Conditions/Amount of catalyst^{ref}.	Time	Yield^{a} (%)
1	TCT,solvent-free, 80 ºC^{30}/ 5 mol%	50 min	90
2	$Sr(OTf)_2$, $ClCH_2CH_2Cl$, 80 ºC^{20}/10 mol%	5 h	85
3	Proline Triflate, H_2O, reflux^{25}/10 mol%	5 h	79
4	$HClO_4$-SiO_2, solvent-free, 80 ºC^{32}/	1.2 h	89
5	BNPs-TAPC, solvent-free, 80 ºC/ 0 g	1 h	0
6	BNPs-TAPC, solvent-free, 80 ºC/0.01 g	10 min	93
7	BNPs-TAPC, solvent-free, 80 ºC/0.02 g	5 min	92
8	BNPs-TAPC, solvent-free, 80 ºC/0.03 g	2 min	95

[a] Isolated yields.

aromatic ring did not show strongly obvious effects in terms of yields under the reaction conditions. The three-component cyclocondensation reaction proceeded smoothly under solvent-free conditios and was completed in 8-15 min. Benzaldehyde and other aromatic aldehydes containing electron-withdrawing groups or electron-donating were employed and reacted well to give the desired products in excellent yields with high purity. It is noteworthy that the reaction proceeded without the protection of acidic hydroxyl substituents (Table 2, entries 5-7). This reaction is also compatible with other functional groups such as halo, nitro, and ether (Table 2). This reaction was further explored for the synthesis of bis-benzo[*a*]xanthen-11-one compound (Table 2, entry 12) in excellent yields by the reaction of terephthalaldehyde with 2 equiv. *β*-naphthol and 5,5-dimethyl-1,3-cyclohexanedione under similar conditions (Scheme 3).



Scheme 3 The condensation reaction of *β*-naphthol, terephthalaldehyde, and dimedone.



Scheme 4 Tentative mechanism for the formation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives.

A possible mechanism for the formation of product **4** is shown in Scheme 4. Adventitious entry of moisture leads to the release of HCl. The *in situ* generated HCl acts as a protic acid to activate the carbonyl oxygen. The reaction proceeds through the intermediate ortho-quinone methides (*o*-QMs), which is formed by the nucleophilic addition of *β*-naphthol **2** to aldehyde **1** catalyzed by H^+. Subsequent Michael-type addition of the enolic form of dimedone **3** to the *o*-QMs gives the intermediate **6**, followed by cyclization to afford the corresponding product **4**, accompanied by loss of H_2O.

Table 2 Boehmite-TAPC Catalyzed Synthesis of 12-Aryl-8,9,10,12- tetrahydrobenzo[*a*]xanthen-11-ones^{a}

Entry	Aldehyde/(Product)	Yield (%)^{b} /Time (min)	Mp (mp)^{ref}
1	C_6H_5CHO (**4a**)	93 (10)	150-152 (151-153)^{22}
2	$4\text{-}MeC_6H_4CHO$ (**4b**)	99 (8)	173-176 (175-176)^{30}
3	$4\text{-}MeOC_6H_4CHO$ (**4c**)	99 (10)	206-208 (207-208)^{30}
4	$3,4\text{-}(MeO)_2C_6H_3CHO$ (**4d**)	99 (10)	199-202 (201-204)^{31}
5	$4\text{-}HOC_6H_4CHO$ (**4e**)	95 (10)	222-224 (223-225)^{22}
6	$3\text{-}HOC_6H_4CHO$ (**4f**)	95 (15)	238-240 (240-241)^{22}
7	$2\text{-}HOC_6H_4CHO$ (**4g**)	99 (10)	230-232 (227-228)^{32}
8	$4\text{-}ClC_6H_4CHO$ (**4h**)	99 (10)	180-182 (180-182)^{22}
9	$2,4\text{-}Cl_2C_6H_3CHO$ (**4i**)	95 (8)	174-178 (178-180)^{22}
10	$2\text{-}O_2NC_6H_5CHO$ (**4j**)	99 (12)	223-225 (223-225)^{22}
11	$3\text{-}NOC_6H_5\text{-}CHO$ (**4k**)	95 (12)	179-180 (168-170)^{22}
12	$4\text{-}OHCC_6H_5CHO$ (**4l**)	95 (12)	307-310 (310-311)^{30}

[a] The purified products were characterized by mp and ^{1}H and ^{13}C NMR spectroscopy. [b] Yield refers to pure isolated product.

Leaching of active species was not observed and the catalyst was recovered by decantation leaving the solid with hot ethanol. The reaction was repeated five times without significant loss of activity or selectivity. Thus, after the first run, which gave the corresponding product in 99% yield, after recovery the catalyst was subjected to a second reaction from which it gave the desired

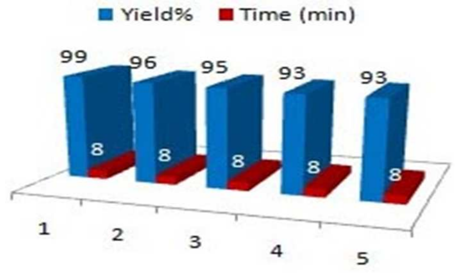


Fig. 7 Recyclability of BNP-TAPC for the preparation of 9,9-dimethyl-12-*p*-tolyl-9,10-dihydro-8*H*-benzo[*a*]xanthen-11(12*H*)-one.

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product in 96% yield; the average chemical yield for 5 consecutive runs was 95%, which clearly demonstrates the practical recyclability of the BNPs-TAPC nanocatalyst (Fig. 7).

FT-IR spectra of BNP-TAPC nanocatalyst after 1 and 5 catalytic cycles are presented in Fig. 8. These spectra look quite similar and this definitely indicates that the active component catalyst did not loss from the solid catalyst.

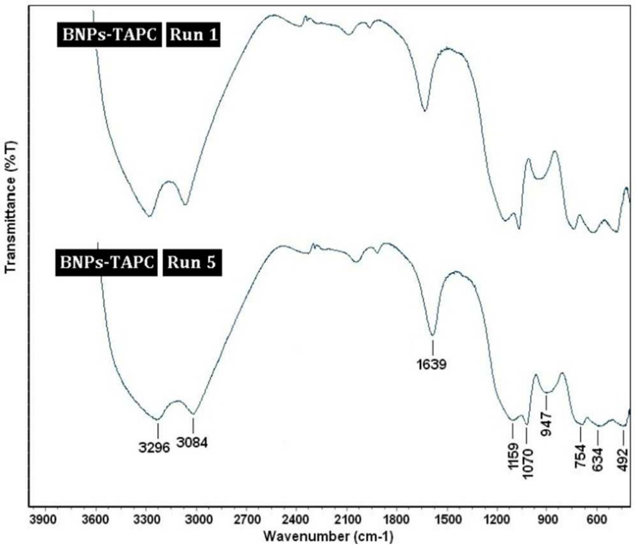

Fig. 8 The comparative FT-IR spectra for BNPs-TAPC after 1 and 5 catalytic cycles.

Experimental

General procedure for the preparation of BNPs-TAPC

In a 100 ml round-bottom flask equipped and a magnetic stirrer bar, boehmite naoparticles (50 mg), TAPC (50 mg) and CH_2Cl_2 (20 mL) were mixed and sonicated for 1 h at 30° C and then the reaction mixture was refluxed at 40 °C for 12 h. Then, the solids were collected by filtration, washed thoroughly with CH_2Cl_2 and dried at room temperature to afford a cream powder as the product.

General procedure for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-one derivatives with BNPs-TAPC

To a mixture of aldehyde (1.0 mmol), β-naphthol (1 mmol, 0.144 g), and 5,5-dimethylcyclohexane-1,3-dione (1.0 mmol), was added BNPs-TAPC (10 mg) and heated at 80 ºC for an appropriate time (Table 3). The reaction was monitored by TLC. After completion of the reaction, ethanol was added the reaction mixture, and it was stirred for 5 min at 25 ºC. The reaction mixture was filtered to remove the catalyst and the filtrate was poured into cold water. The solid was suction filtered, washed with cold water (20 mL × 2) to afford pure product. The spectral and physical properties of known products were compared with those reported in the literature. In every case excellent agreement was obtained.

Conclusions

In this study, we have described an eco-friendly and novel methodology for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives using BNPs-TAPC as an environmentally benign and recoverable nanocatalyst under solvent-free conditions. The novel heterogeneous nanocatalyst was efficiently applicable to a wide variety of aromatic aldehydes bearing different types of substituents, affording the desired products in excellent yields. This catalyst can be reused five times without significant loss in catalytic activity. This methodology also overcomes the formation of unwanted by-products, slow reaction times and hazardous solvents. thus, we believe this will find significant application in the field of organic synthesis and could be an important addition to the existing methodologies.

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Notes and references

1 Z. M. Michalska, *Platinum Metals Rev*., 1974, **18**, 65.
2 K. G. Thomas and P. V. Kamat, *Acc. Chem. Res*., 2003, **36**, 888.
3 M. Qhobosheane, S. Santra, P. Zhang and W. H. Tan, *Analyst*, 2001, **126**, 1274.
4 (a) E. Delgado-Pinar, J. C. Frias, L. J. Jimenez-Borreguero, M. T. Albelda, J. Alarcon and E. Garcia-Espana, *Chem. Commun*., 2007, 3392; (b) R. Aucejo, J. Alarcon, C. Soriano, M. C. Guillem, E. Garcia-Espana and F. Torres, *J. Mater. Chem*., 2005, **15**, 2920; (c) R. Aucejo, P. Diaz, E. Garcia-Espana, J. Alarcon, E. Delgado-Pinar, F. Torres, C. Soriano and M. C. Guillem, *New J. Chem*., 2007, **31**, 44; (d) H. C. Lee, H. J. Kim, S. H. Chung, K. H. Lee, H. C. Lee and J. S. Lee, *J. Am.Chem. Soc*., 2003, **125**, 2882; (e) H. R. Zargar, M. R. Bayati, H. R. Rezaie, F. Golestani-Fard, R. Molaei, S. Zanganeh and A. Kajbafvala, *J. Alloys Compd*., 2010, **507**, 443.
5 E. Carbonell, E. Delgado-Pinar, J. Pitarch-Jarque, J. Alarcon and E. García-Espana, *J. Phys. Chem. C*, 2013, **117**, 14325.
6 (a) V. S. Burkat, V. S. Dudorova, V. S. Smola, and T. S. Chagina, Physicochemical properties of alumina used for removing fluorides in the dry cleaning systems, in Light Metals, TMS, Warrendale, Pa, USA, (1985), pp. 1443; (b) C. Nedez, J. P. Boitiaux, C. J. Cameron and B. Didillon, *Langmuir*. 1996, **12**, 3927.
7 (a) J.-L. Le Loarer, H. Nussbaum, and D. Bortzmeyer, Alumina extrudates, methods for preparing and use as catalysts or catalyst supports, WO 9856499, December (1998); (b) H. Liu, J. Deng and W. Li, *Catal. Lett*., 2010, **137**, 261.
8 V. Vatanpour, S. S. Madaeni, L. Rajabi, S. Zinadini and A. A. Derakhshan, *J. Membr. Sci*., 2012, **401**, 132.
9 D. Mishra, S. Anand, R. K. Panda and R. P. Das, *Mater. Lett*., 2000, **42**, 38.
10 D. Mishra, S. Anand, R. K. Panda and R. P. Das, *Hydrometallurgy*, 2000, **58**, 169.
11 K. Prabhakaran, S. Ananthakumar and C. Pavithran, *J. Eur. Ceram. Soc*., 1999, **19**, 2875.
12 (a) B. M. Trost, *Science,* 1991, **254**, 1471; (b) R. A. Sheldon, *Pure Appl. Chem*., 2000, **72**, 1233; (c) A. Corma and H. Garcia, *Chem. Rev*., 2003, **103**, 4307.
13 F. Zelefack, D. Guilet, N. Fabre, C. Bayet, S. Chevalley, S. Ngouela, B. N. Lenta, A. Valentin, E. Tsamo and M. G. Dijoux-Franca, *J. Nat. Prod*., 2009, **72**, 954.

New Journal of Chemistry Accepted Manuscript

14 J. P. Poupelin, G. Saint-Ruf, O. Foussard-Blanpin, G. Narcisse, G. Uchida-Ernouf and R. Lacroix, *Eur. J. Med. Chem*., 1978, **13**, 67.

15 R. W. Lambert, J. A. Martin, J. H. Merrett, K. E. B. Parkes, G. J. Thomas, *PCT Int. Appl. WO*, 1997, **9**, 706, 178.

16 T. Hideo and J. Teruomi, *Jpn. Patent*, 1981, **56**, 005,480.

17 H. T. Nguyen, M. C. Lallemand, S. Boutefnouchet, S. Michel and F. Tillequin, *J. Nat. Prod*., 2009, **72**, 527.

18 (a) A. Arnone, L. Merlini and G. Nasini, *Tetrahedron Lett*., 1972, **13**, 3503; (b) B. Ravindranath and T. R. Seshadri, *Phytochemistry*, 1973, **12**, 2781; (c) K. N. Gurudutt and T. R. Seshadri, *Phytochemistry*, 1974, **13**, 2845; (d) N. Kumar and T. R. Seshadri, *Curr. Sci*., 1974, **43**, 611; (e) A. Arnone, L. Camarda, L. Merlini, G. Nasini and D. A. H. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1977, 2116; (f) J. Kinjo, H. Uemura, T. Nohara, M. Yamashita, N. Marubayashi and K. Yoshihira, *Tetrahedron Lett*., 1995, **36**, 5599.

19 B. Das, K. Laxminarayana, M. Krishnaiah and Y. Srinivas, *Synlett*. 2007, 3107.

20 J. Li, W. Tang, L. Lu and W. Su, *Tetrahedron Lett*. 2008, **49**, 7117.

21 J. M. Khurana and D. Magoo, *Tetrahedron Lett*. 2009, **50**, 4777.

22 G. C. Nandi, S. Samai, R. Kumar and M. S. Singh, *Tetrahedron*. 2009, **65**, 7129.

23 R.-Z. Wang, L.-F. Zhang and Z.-S. Cui, *Synth. Commun*., 2009, **39**, 2101.

24 S. Gao, C. H. Tsai and C.-F. Yao, *Synlett*, 2009, 949.

25 J. Li, L. Lu and W. Su, *Tetrahedron Lett*., 2010, **51**, 2434.

26 (a) A. Dömling, *Chem. Rev*., 2006, **106** 17; (b) A. M. Shestopalov, A. A. Shestopalov and L. A. Rodinovskaya, *Synthesis*, 2008, 1; (c) M. Syamala, *Org. Prep. Proced. Int*., 2009, ***41***, 1; (d) J. N. Sangshetti, N. D. Kokare, S. A. Kotharkara and D. B. Shinde, *J. Chem. Sci*., 2008, **120**, 463; (e) R. Murugavel and S. Kuppuswamy, *J. Chem. Sci*., 2008, **120**, 131.

27 (a) K. Bahrami, M. M. Khodaei and A. Farrokhi, *Synth. Commun*., 2009, **39**, 1801; (b) K.; Bahrami, M. M.; Khodaei and A. Farrokhi, *Synth. Commun*., 2010, **40**, 1492; (c) K. Bahrami, M. M. Khodaei, F. Naali and B. H. Yousefi, *Tetrahedron Lett*., 2013, **54**, 5293.

28 (a) K. Bahrami, M. M. Khodaei and F. Naali, *J. Org. Chem*., 2008, **73**, 6835; (b) K. Bahrami, M. M. Khodaei and M. Sheikh Arabi, *J. Org. Chem*., 2010, **75**, 6208; (c) K. Bahrami, M. M. Khodaei and M. Soheilizad, *J. Org. Chem*., 2009, **74**, 9287; (d) K. Bahrami, M. M. Khodaei and P. Fattahpour, *Catal. Sci. Technol*., 2011, **1**, 389; (e) K. Bahrami, M. M. Khodaei, H. Targhan and M. Sheikh Arabi, *Tetrahedron Lett*., 2013, **54**, 5064; (f) K. Bahrami, M. M. Khodaei, F. Naali and B. H. Yousefi, *Tetrahedron Lett*., 2013, **54**, 5293.

29 (a) R. Schenk and G. Römer, *Ber. Dtsch. Chem. Ges*., 1924, **57**, 1343; (b) H. R. Allcock, *J. Am. Chem. Soc*., 1964, **86**, 2591; (c) J. C.; Graham and D. H. Marr, *Can. J. Chem*., 1972, **50**, 3857; (d) M.; Hashimoto, Y.; Obora, S.; Sakaguchi and Y. Ishii, *J. Org. Chem*., 2008, *73*, 2894; (e) R. K. Voznicova, J.; Taraba, J.; Prihoda and M. Alberti, *Polyhedron*, 2008, **27**, 2077; (f) H. R. Allcock, J. L. Desorcie and P. J. Harris, *J. Am. Chem. Soc*., 1983, **105**, 2814; (g) O. Rolland, L. Griffe, M. Poupot, A. Maraval, A. Ouali, Y. Coppel, J. J. Fournie, G. Bacquet, C. O. Turrin, A. M. Caminade, J. P. Majoral and R. Poupot, *Chem. Eur. J*., 2008, **14**, 4836.

30 Z.-H. Zhang, P. Zhang, S.-H. Yang, H.-J. Wang and J. Deng, *J. Chem. Sci*., 2010, **122**, 427.

31 K. Tabatabaeian, A. Khorshidi, M. Mamaghani, A. Dadashi, M. Khoshnood Jalali, *Can. J. Chem*., 2011, **89**, 623.

32 L.-P. Mo and H.-L. Chen, *J. Chin. Chem. Soc*., 2010, **57**, 157.

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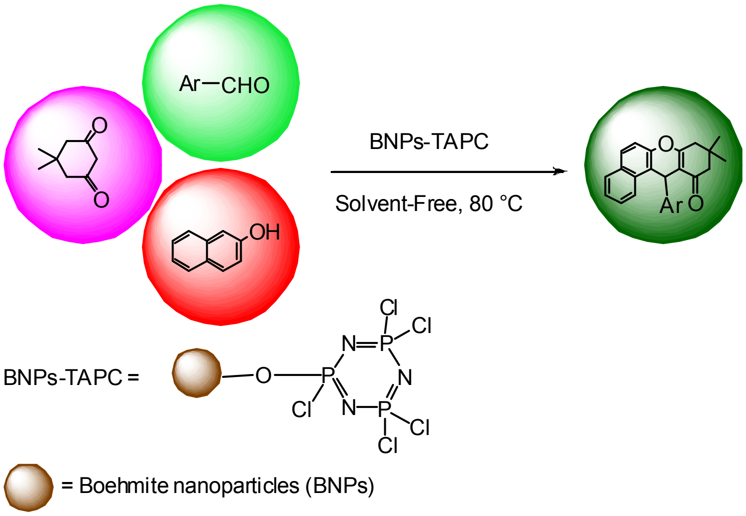
Graphical Abstract

A one-pot multi-component, green, and highly efficient protocol has been described for the synthesis of a wide range of 12-aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones using TAPC supported on boehmite nanoparticles (BNPs-TAPC) as an eco-friendly and recyclable nanocatalyst in excellent yields under solvent-free conditions.



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