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# Perlite impregnated with HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>: Magnetically separable catalyst for the synthesis of 3,3,6,6-tetramethyl-9-substituted-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-diones

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#### ABSTRACT

Phosphotungstic acid (HPA)/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-loaded Perlite has been prepared as a recyclable heterogeneous catalyst for the synthesis of xanthenes. The prepared catalyst has been characterized by Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM) with energy-dispersive X-ray (EDX) spectroscopy, transmission electron microscopy (TEM) with selected-area electron diffraction (SAED) pattern analysis, thermogravimetric analysis (TGA), and Brunauer–Emmett–Teller (BET) measurements. XRD peaks at  $2\theta = 9.08^{\circ}$  and  $26.73^{\circ}$  (HPA) and  $36.03^{\circ}$ ,  $39.72^{\circ}$ , and  $62.6^{\circ}$  ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) showed efficient loading of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the Perlite surface. TEM images of the prepared HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite corroborated the successful loading of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the Perlite. Advantages of this new protocol include facile handling, low cost, easy work-up procedure, and remarkable reusability over several cycles without loss of the catalytic activity.

#### 1. Introduction

Currently used heterogeneous catalysts have proven to be superior to their homogeneous predecessors. They have enabled synthetic routes to novel compounds in a cost-effective and benign manner. They are also well known for their ease of handling, low toxicity, and high-yielding transformations of organic compounds. Impregnated solid supports can act as facile and improved heterogeneous catalysts for synthetic organic transformations. They can retain their characteristics and provide excellent reaction enhancement [1–3]. Nanomaterials show outstanding properties, opening new possibilities for various applications [4–8]. Nano-sized and suitably blended solid-acid catalysts have proven to be suitable scavengers for biologically recalcitrant ions such as Cu(II), Cr(VI), and Cr(II), as well as noxious organic waste, as a result of their inherent characteristics of high porosity and large surface area. The most attractive feature of heterogeneous solid-acid catalysts is their safe and facile removal and handling [9–19].

Superior alternatives to homogeneous catalysts are solid supports incorporating immobilized magnetic nanoparticles, such as Fe<sub>2</sub>O<sub>3</sub> [20, 21], Fe<sub>2</sub>O<sub>5</sub>, Fe<sub>2</sub>O<sub>4</sub>, or Fe<sub>3</sub>O<sub>4</sub> [22], which are known for their ease of separation using a simple permanent magnet without any tedious steps, extended reactivity, and increased number of active sites. Among the various iron oxides, Fe<sub>2</sub>O<sub>3</sub> is highly versatile, of low toxicity, easily recoverable, and has been widely applied in various fields, such as nucleophilic substitution reactions [23], heterocycle synthesis [24], coupling reactions [25], catalysis [26], and sensors [27]. Owing to its conductivity, it is notably used in supercapacitors [28] and in conjunction with surfactants [29]. Solid supports incorporating magnetically separable materials are used in synthesis, as well as biomedical fields, such as bio-imaging, drug delivery, and so on [30,31]. Of these, those incorporating α-Fe<sub>2</sub>O<sub>3</sub> nanoparticles can be obtained by a range of techniques, such as sol-gel, microemulsion, dispersion, etc. The co-precipitation methodology has proved to be favorable for the preparation of stable composites that can be magnetically separated [32,33].

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Heteropoly acids (HPA) have been reported as better alternatives to conventional catalysts, owing to their protonating ability with superior active sites, possess advantages of high stability, non-toxicity, and non-corrosivity, and as such are exploited as benign systems for organic processes [34–36]. HPA-catalyzed transformations are usually free from side reactions and provide good yields. Developing a solid-acid catalyst with Keggin-type structured HPA supported on an inert material has proven to be a good choice for obtaining various heterocycles, due to the increased catalytic activity of such systems. A catalyst with a higher surface area will clearly show enhanced activity, and thus impregnating a solid inert silica-like material with HPA ensures excellent surface area and available active sites [37–39].

Catalyst systems based on the naturally occurring mineral Perlite have acquired significance lately due to characteristic features of ease of access, economy, reaction-enhancing ability at minimal loading, reduced time consumption, and high yield. The synthesis of heterocyclic compounds using Perlite-supported solid-acid catalysts has been widely investigated. Researchers have paid more attention to heterocycles due to their unique properties that underpin their numerous biological and pharmaceutical applications. Among these heterocycles, the synthesis of xanthenes is of substantial interest owing to their pharmacological activities, such as anti-oxidant, anti-microbial, anti-cancer, analgesic, and anti-inflammatory effects [40–43]. Hence, in continuation of our work on heterogeneous catalysis [44], we set out to prepare a solid-acid heterogeneous catalyst of phosphotungstic acid (HPA)/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite by a co-precipitation method. The activity of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite has been investigated in the synthesis of xanthenes.

#### 2. Experimental

#### 2.1. Synthesis of $\alpha$ -ferric oxide [45,46]

 $\alpha\text{-}Fe_2O_3$  was prepared by a co-precipitation method. FeCl\_2·4H\_2O (0.6 g) and FeCl\_3·6H\_2O (1.5 g) were dissolved in 2  $\scriptstyle\rm M$  HCl solution (30 mL). This mixture was then added dropwise with stirring to 25% NH\_4OH solution (75 mL), resulting in a solution of pH 11. Further 2  $\scriptstyle\rm M$  HCl was added dropwise until pH 2 was attained, and the resulting mixture was stirred for 2 h. It was then centrifuged, and the collected solid was washed with water to remove excess NH\_4OH. The obtained product was dried at 80 °C for 8 h.

#### 2.2. Synthesis of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>-loaded perlite

Perlite and ferric oxide in a 2:1 ratio were suspended in water/ ethanol (1:1; 25 mL) and the mixture was stirred for 8 h. The solvents were then evaporated and the residue was dried at 80  $^{\circ}$ C for 8 h.

#### 2.3. Synthesis of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite

 $\alpha$ -Ferric oxide/Perlite and phosphotungstic acid (H<sub>3</sub> [P(W<sub>3</sub>O<sub>10</sub>)<sub>4</sub>]·xH<sub>2</sub>O) (1:1.2) were suspended in acetonitrile, and the mixture was heated under reflux at 60 °C for 24 h. The solvent was then evaporated, and the residue was dried at 80 °C for 8 h and calcined at 300 °C for 3 h.

## 2.4. General procedure for the synthesis of 3,3,6,6-tetramethyl-9-substituted-tetrahydro-2H-xanthene-1,8-(5H,9H)-diones (1a-i)

A mixture of a diketone (2 mmol) and the requisite aromatic aldehyde (1 mmol) in acetonitrile was added to a dispersion of catalyst (0.1 g) in acetonitrile, and the resulting mixture was heated under reflux at 80 °C for the stipulated duration. Progress of the reaction was monitored by thin-layer chromatography (TLC), and on completion, the mixture was cooled and the catalyst was separated by means of an external magnet. The solvent was evaporated and the resulting crude product was recrystallized from ethanol. The structures of the xanthenes [47] obtained were confirmed by physical data and IR and NMR spectral

methods. The corresponding  ${}^{1}$ H and  ${}^{13}$ C NMR spectra are given as Figs. S1–S18 (see the Supporting Information).

3,3,6,6-Tetramethyl-9-phenyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1a): White solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2954.95, 1658.78, 1626.75, 1463.57, 1357.89, 1134.14, 1002.98, 694.37; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.30–7.08 (m, 5H, Ar–H), 4.75 (s, 1H, H-9), 2.46 (s, 4H, H-2, H-7), 2.25–2.22 (d, 2H, H-4), 2.18–2.15 (d, 2H, H-5), 1.10 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 0.99 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ 196.39 (carbonyl C=O), 162.24 (C-12, C-13), 115.69 (C-11, C-14), 144.08–126.38 (Ar–C), 50.75 (C-2, C-7), 40.89 (C-9), 32.21 (C-4, C-5), 31.84 (C-3, C-6), 29.27 (C–CH<sub>3</sub>), 27.34 (C–CH<sub>3</sub>).

9-(2-Chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1b): Yellow solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2926.05, 1639.38, 1342.73, 1169.27, 738.74, 450.27; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.45–7.06 (m, 4H, Ar–H), 5.02 (s, 1H, H-9), 2.47 (s, 4H, H-2, H-7), 2.26–2.22 (d, 2H, H-4), 2.19–2.16 (d, 2H, H-5), 1.12 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 1.03 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  196.46 (carbonyl C=O), 162.95 (C-12, C-13), 139.82–126.28 (Ar–C), 113.64 (C-11, C-14), 50.65 (C-2, C-7), 40.76 (C-9), 31.97 (C-4, C-5), 31.82 (C-3, C-6), 29.23 (C–CH<sub>3</sub>), 27.32 (C–CH<sub>3</sub>).

9-(4-Chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1c): Yellow solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2924.09, 1631.78, 1520.91, 1327.03, 1168.86, 742.59; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.27–7.17 (m, 4H, Ar–H), 4.71 (s, 1H, H-9), 2.46 (s, 4H, H-2, H-7), 2.25–2.22 (d, 2H, H-4), 2.18–2.15 (d, 2H, H-5), 1.10 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 0.99 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$ 196.38 (carbonyl C=O), 162.45 (C-12, C-13), 142.70–128.22 (Ar–C), 115.27 (C-11, C-14), 50.69 (C-2, C-7), 40.85 (C-9), 32.21 (C-4, C-5), 31.47 (C-3, C-6), 29.28 (C–CH<sub>3</sub>), 27.29 (C–CH<sub>3</sub>).

9-(4-Bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1d): Light-yellow solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2926.01, 1654.92, 1363.67, 1157.29, 1145.39, 1001.02, 846.25, 697.53; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.34–7.16 (m, 4H, Ar–H), 4.70 (s, 1H, H-9), 2.46 (s, 4H, H-2, H-7), 2.25–2.22 (d, 2H, H-4), 2.18–2.15 (d, 2H, H-5), 1.10 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 0.99 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  196.37 (carbonyl C=O), 162.47 (C-12, C-13), 143.23–120.24 (Ar–C), 115.19 (C-11, C-14), 50.69 (C-2, C-7), 40.84 (C-9), 32.21 (C-4, C-5), 31.56 (C-3, C-6), 29.28 (C–CH<sub>3</sub>), 27.30 (C–CH<sub>3</sub>).

9-(4-Fluorophenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1e): White solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2951.67, 1654.46, 1602.92, 1503.63, 1364.10, 1196.92, 1145.39, 1005.86, 814.80; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.27–6.88 (m, 4H, Ar–H), 4.72 (s, 1H, H-9), 2.47 (s, 4H, H-2, H-7), 2.25–2.22 (d, 2H, H-4), 2.19–2.15 (d, 2H, H-5), 1.10 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 0.99 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  196.53 (carbonyl C=O), 162.41 (C-12, C-13), 139.95–129.81 (Ar–C), 115.50 (C-11, C-14), 50.70 (C-2, C-7), 40.84 (C-9), 32.21 (C-4, C-5), 31.20 (C-3, C-6), 29.26 (C–CH<sub>3</sub>), 27.28 (C–CH<sub>3</sub>).

3,3,6,6-Tetramethyl-9-(3,4,5-trimethoxyphenyl)-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1f): Yellow solid; IR (KBr, cm<sup>-1</sup>):  $\nu$ 2943.92, 1661.01, 1590.36, 1454.01, 1185.03, 1120.58, 1006.54, 830.53, 671.87; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  6.51 (s, 2H, Ar–H), 4.71 (s, 1H, H-9), 3.79 (s, 6H, Ar-CH<sub>3</sub>), 3.77 (s, 6H, m-OCH<sub>3</sub>), 3.69 (s, 3H, o-OCH<sub>3</sub>), 2.48 (s, 2H, H-2), 2.47 (s, 2H, H-7), 2.24–2.23 (m, 4H, H-4, H-5), 1.12 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 1.03 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  196.51 (carbonyl C=O), 162.35 (C-12, C-13), 152.80–136.57 (Ar–C), 115.50 (C-11, C-14), 60.71–56.10 (Ar-CH<sub>3</sub>), 50.75 (C-2, C-7), 40.91 (C-9), 32.19 (C-4, C-5), 31.81 (C-3, C-6), 29.38 (C–CH<sub>3</sub>), 27.20 (C–CH<sub>3</sub>).

3,3,6,6-Tetramethyl-9-(3,4-dimethylphenyl)-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1g): Light-yellow solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2958.79, 1752.73, 1656.07, 1604.74, 1456.87, 1196.57, 1134.25, 987.60, 892.28, 818.95; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.08 (s, 1H, Ar–H), 6.95 (d, 2H, Ar–H), 4.68 (s, 1H, H-9), 2.46 (s, 4H, H-2, H-7), 2.24–2.14 (m, 10H, H-4, H-5, Ar-(CH<sub>3</sub>)<sub>2</sub>), 1.09 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 1.00 (s,



Fig. 1. FTIR spectra of a) pure Perlite, b)  $\alpha\text{-Fe}_2O_3,$  c) HPA, and d) HPA/  $\alpha\text{-Fe}_2O_3/\text{Perlite}.$ 

6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  196.51 (carbonyl C=O), 162.08 (C-12, C-13), 141.56–125.50 (Ar–C), 115.84 (C-11, C-14), 50.79 (C-2, C-7), 40.90 (C-9), 32.23 (C-4, C-5), 31.35 (C-3, C-6), 29.24 (C-(CH<sub>3</sub>)<sub>2</sub>), 27.43 (C-(CH<sub>3</sub>)<sub>2</sub>), 19.86–19.39 (Ar-CH<sub>3</sub>).

3,3,6,6-Tetramethyl-9-(4-methylphenyl)-3,4,6,7-tetrahydro-2Hxanthene-1,8-(5H,9H)-dione (1h): White solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2941.14, 1659.44, 1448.63, 1173.98, 1133.03, 1001.72, 830.67, 687.32; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.18–7.01 (m, 4H, Ar–H), 4.71 (s, 1H, H-9), 2.45 (s, 3H, Ar-CH<sub>3</sub>), 2.24–2.14 (m, 7H, H-4, H-5, Ar-CH<sub>3</sub>), 1.09 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 0.99 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  196.45 (carbonyl C=O), 162.11 (C-12, C-13), 141.20–128.25 (Ar–C), 115.77 (C-11, C-14), 50.77 (C-2, C-7), 40.88 (C-9), 32.20 (C-4, C-5), 31.44 (C-3, C-6), 29.27 (C–CH<sub>3</sub>), 27.38 (C–CH<sub>3</sub>), 21.06 (Ar-CH<sub>3</sub>).

9-(4-Isopropylphenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione (1i): Light-yellow solid; IR (KBr, cm<sup>-1</sup>):  $\nu$  2958.79, 1658.53, 1608.95, 1460.21, 1357.33, 1191.23, 1046.21, 828.05, 711.53; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.18–7.04 (m, 4H, Ar–H), 4.73 (s, 1H, H-9), 2.99–2.96 (m, 1H, methine H), 2.46 (s, 4H, H-2, H-7), 2.25–2.22 (d, 2H, H-4), 2.20–2.16 (d, 2H, H-5), 1.29–1.27 (d, 6H, isopropyl CH<sub>3</sub>), 1.09 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>), 1.00 (s, 6H, (CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  196.84 (carbonyl C=O), 177.41–155.28 (C-12, C-13), 130.38–126.14 (Ar–C), 115.84 (C-11, C-14), 50.73 (C-2, C-7), 44.88, 40.88 (C-4, C-5), 32.21 (C-9), 34.48–33.60 (aliphatic C), 29.70–27.46 (C–CH<sub>3</sub>), 23.91–23.63 (aliphatic CH<sub>3</sub>).



Fig. 2. XRD patterns of a) pure Perlite, b)  $\alpha\text{-}Fe_2O_3,$  c) HPA, and d) HPA/  $\alpha\text{-}Fe_2O_3/Perlite.$ 

#### 3. Results and discussion

#### 3.1. Characterization of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite

The immobilization of the solid-acid catalyst by loading HPA and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the surface of Perlite was studied by FTIR measurements. The IR spectrum of pure Perlite is depicted in Fig. 1a. The vibrations at 677.01, 985.62, 1066.64, 1527.62, and 3578.60 cm<sup>-1</sup> correspond to Si–O–Si bending, Si–O–Al bending, Si–O stretching, Si–OH stretching, and O–H stretching, respectively [48].

The IR spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, HPA, and HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite are displayed in Fig. 1b, c, and 1d, respectively. In Fig. 1b, the vibrations at 1041.56, 810.10, 594.08, and 439.77 cm<sup>-1</sup> can be ascribed to Fe–O stretchings and bendings, and are characteristic of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [49]. The stretching frequencies at 1074.35, 964.41, and 900.76 cm<sup>-1</sup> in Fig. 1c correspond to P–O, W=O, and W–O–W vibrations, respectively. Fig. 1d indicates characteristic vibrations at 3348.42, 1656.02, 1527.89, and 1066.20/1049.28 cm<sup>-1</sup>, corresponding to O–H stretching, Si–OH stretching, Si–O–Si stretching, and Si–O–Al bending vibrations, respectively. Further peaks at 810.10, 601.79, 547.78, and 439.77 cm<sup>-1</sup> can be ascribed to Fe–O stretchings of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The vibrations at 897.42 and 982.36 cm<sup>-1</sup> can be attributed to W–O–W and W=O, and correspond to Keggin-type HPA in HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite [50].



Fig. 3. SEM images of a)  $\alpha\mbox{-}Fe_2O_3$  and b) HPA/ $\alpha\mbox{-}Fe_2O_3/\mbox{Perlite}.$ 



Fig. 4. EDX of a) α-Fe<sub>2</sub>O<sub>3</sub> and b) HPA/α-Fe<sub>2</sub>O<sub>3</sub>/Perlite.

The synthesized catalysts were analyzed by the powder XRD technique. The XRD patterns of pure Perlite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, HPA, and HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite are shown in Fig. 2. The XRD patterns corroborate the crystalline nature of the product and the effective loading of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HPA on Perlite. The XRD pattern of Perlite shows a strong band at 24.74°, evidencing its amorphous nature (Fig. 2a). The 2 $\theta$  and hkl indices in Fig. 2b conform well with JCPDS no. 87–1164, confirming the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [49]. In Fig. 2c, the peaks at 2 $\theta$  = 10.38°, 20.58°, 26.24°, 28.51°, 31.86°, and 38.18° can be attributed to Keggin-type HPA. The XRD pattern of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite is displayed in Fig. 2d. It features the peaks of both HPA and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, consistent with efficient loading of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the Perlite surface.

The surface morphology of the prepared catalyst was examined by SEM. The SEM image (Fig. 3a) shows the prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to be spherical in nature, and the clusters formed are due to magnetic dipole interactions, evidencing the magnetic nature of the prepared compound [49]. Fig. 3b depicts the SEM image of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite, which reveals the effective and uniform loading of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the Perlite (see arrow marks) as well as the layer structure of the latter [44].

Fig. 4 depicts the percentage compositions of the elements in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>8</sub>/Perlite. As is evident from Table 1, the additional peak for W (23%) and the increase in Fe content corroborate the loading of HPA and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on Perlite.

TEM images and SAED patterns of the prepared materials ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite), along with particle size distributions of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, are given in Figs. 5 and 6. From the TEM images, the morphology of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was seen to be spherical and of nanometer dimensions (Fig. 5a and b). The diffraction pattern (Fig. 5c) of the compound is consistent with the nano- and polycrystalline nature of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. TEM images of the prepared HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite indicate the successful loading of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (see arrow marks) (Fig. 5d and e). The layered structure of Perlite can clearly be seen, and the spherical particles of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> are embedded on the surface of layered Perlite sheets (Fig. 5d and e). The diffraction pattern of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite (Fig. 5f) with irregular spots showed the catalyst to be semicrystalline and polycrystalline in nature. The particle size distribution curve from the TEM results showed that the prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> consisted of 70% of 20–30 nm particles, with an average particle size of 24.65 nm (Fig. 6).

The thermal stability of the HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite catalyst was examined by TGA. Fig. 7 shows a gradual thermal decomposition up to 180 °C, corresponding to the loss of water. Thereafter, the decrease from 200 to 400 °C indicates a 4% loss of Keggin-type HPA, and this is followed by a sudden loss at around 500 °C, corresponding to complete loss of HPA. A steady loss after 600 °C reflects the removal of hydroxyl groups from the surface of Perlite [51,52].

Surface area analysis of the Perlite and HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite was performed by the BET method. The pore volumes, pore diameters, and surface areas are tabulated in Table 2, from which it can be seen that there was an increase in surface area and pore volume of Perlite after HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> loading.

#### 3.2. Catalytic activity of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite

In order to test the effectiveness of the HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite catalyst, 9-substituted xanthenes were prepared by reactions of a diketone with aromatic aldehydes in its presence (Scheme 1).

#### Table 1

Composition of the prepared HPA/α-Fe<sub>2</sub>O<sub>3</sub>/Perlite catalyst.

Sample	0	Fe	Na	Al	Si	K	Са	W
Perlite	20.28	1.04	3.09	11.05	60.24	4.33	0.82	-
HPA/α-Fe <sub>2</sub> O <sub>3</sub> /Perlite	30.69	4.12	1.20	3.91	33.76	1.95	0.01	23.77

The reaction conditions were initially optimized for the reaction of dimedone with benzaldehyde to afford 3,3,6,6-tetramethyl-9-phenyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione. The synthesis of xanthenes was first evaluated using bare Perlite and Perlite/Fe<sub>2</sub>O<sub>3</sub>. Only a trace amount of product was obtained with Perlite, whereas utilization of 0.1 g of Perlite/Fe<sub>2</sub>O<sub>3</sub> produced an appreciable yield of 89%. Accordingly, the efficiency of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite was evaluated further. The amount of catalyst was varied from 0.01 to 0.20 g (Table 3). The zero yield from the uncatalyzed reaction proved the need for a catalyst. The reaction with 0.1 g of catalyst was found to proceed with significant yield. An increase in the amount of the catalyst raised the yield from 89 to 95% (Table 3), but a further increment in the catalyst loading beyond 0.1 g decreased the yield. Thus, the catalyst amount was optimized at 0.1 g for this reaction.

Temperature and solvent effects were also examined to optimize the protocol. The reaction was carried out at various temperatures (60–110 °C) with the optimized catalyst loading. At 80 °C, the yield of the product was satisfactory. Increasing the temperature beyond 80 °C did not produce a beneficial effect on the yield (Table 4). Thus, further reactions were controlled at 80 °C.

Furthermore, the reaction was attempted in different solvents, namely ethanol, water, and acetonitrile, at 80  $^\circ C$  using 0.1 g of catalyst

in each case (Table 5). Of the solvents used, acetonitrile showed good reaction progress, giving a 95% yield within 1 h (Table 5). The rapid attainment of high yield made acetonitrile the preferred solvent for further reactions. Hence, the preparation of xanthene in the presence of 0.1 g of catalyst at 80 °C using acetonitrile as solvent was identified as



Fig. 6. Particle size distribution of α-Fe<sub>2</sub>O<sub>3</sub>.



Fig. 5. TEM images and SAED patterns of a–c)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and d–f) HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite.



Fig. 7. TGA for HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite.

#### Table 2

Pore analysis of Perlite and HPA/α-Fe<sub>2</sub>O<sub>3</sub>/Perlite.

Catalyst	Surface area (m <sup>2</sup> /g)	Pore volume (cc/ g)	Pore diameter (Å)
Perlite HPA/α-Fe <sub>2</sub> O <sub>3</sub> /	1.874 2.084	$\begin{array}{c} 2.899 \times 10^{-3} \\ 3.661 \times 10^{-3} \end{array}$	3.910 3.485
Perlite			



10	4-01
1d	4-Br
1e	4-F
1f	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>
1g	3,4-(CH <sub>3</sub> ) <sub>2</sub>
1ĥ	4-CH <sub>3</sub>
1i	4-isopropyl

Scheme 1. Synthesis of xanthenes.

#### Table 3

Effect	of	catalyst	loading	in	the	synthesis	of	3,3,6,6-tetramethyl-9-phenyl-
3,4,6,7	-te	trahydro	-2H-xantl	hen	e-1,8	8-(5H,9H)-	dio	ne.

Catalyst	Catalyst amount (g) <sup>a</sup>	Yield (%) <sup>b</sup>
_	_	none
Perlite	0.1	trace
α-Fe <sub>2</sub> O <sub>3</sub> /Perlite	0.1	89
HPA/a-Fe <sub>2</sub> O <sub>3</sub> /Perlite	0.01	84
HPA/a-Fe <sub>2</sub> O <sub>3</sub> /Perlite	0.05	89
HPA/α-Fe <sub>2</sub> O <sub>3</sub> /Perlite	0.1	95
HPA/α-Fe <sub>2</sub> O <sub>3</sub> /Perlite	0.15	93
HPA/a-Fe <sub>2</sub> O <sub>3</sub> /Perlite	0.2	90

 $^{a}$  Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol), solvent = acetonitrile, time = 60 min at 80 °C.

<sup>b</sup> Isolated yield.

#### Table 4

Effect of temperature in the synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione.

Temperature (°C) <sup>a</sup>	Yield (%) <sup>b</sup>
60	72
70	86
80	95
90	95
100	95
110	95

 $^{\rm a}$  Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol), solvent = acetonitrile, time = 60 min.  $^{\rm b}$  Isolated yield.

#### Table 5

Effect of solvent in the synthesis of 3,3,6,6-tetramethyl-9-phenyl-3,4,6,7-tetrahydro-2H-xanthene-1,8-(5H,9H)-dione.

Solvent <sup>a</sup>	Yield (%) <sup>b</sup>	Time (h)
water ethanol CH-CN	87 91 95	12 8
CH <sub>3</sub> CN	95	1

 $^{\rm a}$  Reaction conditions: benzaldehyde (1 mmol), dimedone (2 mmol).  $^{\rm b}$  Isolated yield.

#### optimal.

Having identified the optimal conditions, this protocol was extended to various substituted xanthenes. Besides the appreciable results obtained, application of the reaction was studied for several aromatic aldehydes (Table 6). As is evident from Table 6, the proposed protocol proved to be applicable to a variety of substituted aldehydes. Neither electron-withdrawing nor electron-releasing groups had any appreciable influence on the reaction outcome. To study the effectiveness of this protocol, the results were correlated with previously published results (Table 7). Although previous reports of the use of heteropoly acids for the synthesis of xanthenes quoted comparable yields, reaction times were longer and reusability of the catalyst was difficult. The use of iron oxide and composites thereof has produced satisfactory yields, but the reaction temperature was relatively high. Hence, to reconcile these differences, we set out to combine the properties of HPA and Fe<sub>2</sub>O<sub>3</sub> by preparing a composite on Perlite. The strong adsorbability, chemical and thermal stability, low toxicity, and natural occurrence of Perlite, mainly comprising silica and alumina, make it a good support for the assembly of heterogeneous catalysts. These remarkable properties prompted us to prepare HPA/α-Fe<sub>2</sub>O<sub>3</sub>/Perlite. The proposed strategy is promisingly superior to preceding methods.

The reusability of the catalyst for the synthesis of xanthene from

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#### Table 6

Preparation of 3,3,6,6-tetramethyl-9-substituted-3,4,6	,7-tetrahydro-2H-xanthene-1,8	3-(5H,9H)-diones using HPA/α-Fe <sub>2</sub> O <sub>3</sub> /Perlite.
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Product	R	Product structure <sup>a</sup>	Yield (%) <sup>b</sup>	Time (min)	m.p. (°C)	Ref. m.p. (°C)
1a	Н	$\sim$	95	60	203–205	203-204 [53]
1b	2-Cl		91	45	229-231	228–230 [54]
1c	4-Cl		93	48	228–229	230–231 [53]
1d	4-Br		94	50	231–232	230–231 [55]
1e	4-F	F F	92	55	222-223	224–225 [54]
1f	3,4,5-(OCH <sub>3</sub> ) <sub>3</sub>		91	50	184–185	186–188 [56]
1g	3,4-(CH <sub>3</sub> ) <sub>2</sub>	Me Me	89	55	220–221	-
1h	4-(CH <sub>3</sub> )		85	70	211-212	211–214 [57]
1i	4-isopropyl	СН	80	75	213–214	-

<sup>a</sup> Reaction conditions: aldehyde (1 mmol), dimedone (2 mmol), catalyst (0.1 g) under reflux in CH<sub>3</sub>CN.

<sup>b</sup> Isolated yield.

benzaldehyde was evaluated. The catalyst used in the reaction could be easily removed by means of a permanent magnet (Fig. 8).

#### 4. Conclusion

The catalyst was separated from the product after the reaction by simple filtration. It was washed with hot ethanol, dried, and reused for further reaction. The results revealed that the prepared catalyst could be reused up to five times without incurring a significant loss of activity (Table 8).

The heterogeneous solid-acid catalyst HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite has been prepared and used for the synthesis of substituted xanthenes. After optimizing the protocol, the optimal conditions were applied to the synthesis of various substituted xanthenes. The favorable immobilization of the HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on the Perlite was evident from FTIR, XRD, SEM-EDX, TEM, TGA, and BET studies. The efficiency of HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/

#### Table 7

Effectiveness of  $HPA/\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Perlite compared with other described catalysts in the synthesis of 9-substituted xanthenes.

Catalyst	Catalyst amount	Temp. (°C)	Time	Yield (%)	Ref.
<sup>a</sup> SBSSA	0.03 g	RT	10 h	98	[53]
MCM-41-SO <sub>3</sub> H	0.05 g	60	60 min	84	[47]
<sup>b</sup> SBSAN	0.05 g	50	2 h	95	[55]
Amberlyst-15	200 mg	reflux	5 h	92	[58]
HPWA/MCM-41	0.25 g	100	5 h	87	[59]
<sup>c</sup> SBNPSA	0.03 g	reflux	2–3 h	89	[60]
H <sub>14</sub> NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub>	0.4 mol%	120	1.5–1.9 h	90	[61]
H <sub>5</sub> PMo <sub>11</sub> TiO <sub>40</sub>	1 mol%	90	20-45 min	90	[62]
Fe <sub>3</sub> O <sub>4</sub> NPs	0.02 g	100	30-40 min	89	[63]
γ-Fe2O3@HAp-Ag NPs	15 mg	60	30 min	95	[64]
Fe <sub>2</sub> O <sub>3</sub>	20 mol%	RT	2 h	90	[65]
$HPA/\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Perlite	0.1 g	80	60 min	95	our work

<sup>a</sup> SBSSA: silica-bonded S-sulfonic acid.

<sup>b</sup> SBSAN: silica boron-sulfuric acid nanoparticles.

<sup>c</sup> SBNPSA: silica-bonded *N*-propyl sulfamic acid.

#### Table 8

Reusability of HPA/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Perlite.								
Run	1	2	3	4	5			
Yield (%)	95	95	93	91	91			



Fig. 8. Magnetic separation of catalyst.

Perlite in organic transformations has been analyzed by synthesizing xanthenes in high yields in short reaction times. The benign nature of the catalyst has been exemplified by reusability tests. The HPA/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ Perlite catalyst has been shown to be effective for preparing xanthene and its derivatives. Further, the versatility of this catalyst holds promise for its application to various other reactions.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpcs.2021.110192.

#### Authors statement

Komalavalli Lakshminarayanan is involved in the preparation of the materials and specifically writing the initial draft. Amutha Parasuraman contributed in the supervision and leadership responsibility for the research activity planning and execution, including mentorship external to the core team. Manawwer Alam and Naushad Ahmad are involved in materials characterization. Balu Krishnakumar is involved in material characterization's discussion and correcting the manuscript. Annamalai Raja and Misook Kang both are involved in the validation of the manuscript and overall replication/reproducibility of results/experiments and other research outputs.

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