Res Chem Intermed
DOI 10.1007/s11164-015-2404-8

Sulfonated nanohydroxyapatite functionalized with 2-aminoethyl dihydrogen phosphate (HAP@AEPH$_2$-SO$_3$H) as a reusable solid acid for direct esterification of carboxylic acids with alcohols

Narges Yousefi Siavashi[1] · Batool Akhlaghinia[1] · Monireh Zarghani[1]

Received: 4 October 2015 / Accepted: 21 December 2015

Abstract Sulfonated nanohydroxyapatite functionalized with 2-aminoethyl dihydrogen phosphate (HAP@AEPH$_2$-SO$_3$H) efficiently catalyzed direct esterification of carboxylic acids and alcohols with high selectivity toward the formation of esters in good to excellent yields. Our results clearly show that HAP@AEPH$_2$-SO$_3$H can be easily recovered by simple filtration and reused for subsequent five runs without any significant impact on yields of products. The main advantage of this methodology is easy and ecofriendly catalyst preparation, easy catalyst separation, practical simplicity, safe reaction conditions, recyclable catalyst and high products yields.

Keyword Sulfonated nanohydroxyapatite functionalized with 2-aminoethyl dihydrogen phosphate (HAP@AEPH$_2$-SO$_3$H) · Direct esterification · Carboxylic acid · Alcohol

Introduction

Organic esters as key components in a variety of natural products are important structural units having wide applications in a variety of areas such as perfumes, flavors, pharmaceuticals, plasticizers, solvents and chemical intermediates [1, 2]. Accordingly, esterification of carboxylic acids constitutes a very important and widespread process in organic synthesis. Consequently, numerous chemical methods have been developed to construct ester linkage [3–25]. Particularly direct

Electronic supplementary material The online version of this article (doi:10.1007/s11164-015-2404-8) contains supplementary material, which is available to authorized users.

✉ Batool Akhlaghinia
akhlaghinia@um.ac.ir

[1] Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad 9177948974, Iran

Published online: 16 January 2016

coupling of carboxylic acids with alcohols is one of the simplest but yet highly challenging transformations in organic chemistry from both academic and industrial points of view. Although many strong homogeneous and conventional acid catalysts can normally promote these transformations toward ester formation [26–33], there are several crucial issues such as using corrosive, expensive, toxic reagents, harsh reaction conditions, tedious workups, non-recyclability of catalysts, acidic waste generation which constitutes real environmental problems. Therefore, in order to remove the above mentioned drawbacks and also promote green chemistry and atom efficiency by avoiding the use of large amounts of strong homogeneous and conventional acid catalysts, the replacement of current chemical processes with more environmentally benign alternatives is an increasingly attractive subject.

Solid acid catalysis as one of the economically and ecologically important fields in catalysis, have many advantages over liquid BrØnsted acid catalysts such as noncorrosive, effective separation of catalyst, waste reduction, and simplified purification of the products. The solid acid catalysts employed in the esterification reactions of carboxylic acids with alcohols include sulfonated polypyrene (S-PPR) [34], sulfonic acid-functionalized periodic mesoporous organosilicas [35], polymer-supported sulfonated magnetic resin [36] macroporous polymeric acid catalyst [37], ß-cyclodextrin-SO_3H [38], carbon material functionalized with NH_2^+ and SO_3H groups [39], SBA-15-functionalized sulfonic acid [40], H_3PO_4/TiO_2-ZrO_2 [41]. Unfortunately, the mentioned methods have several drawbacks such as, the use of expensive reagents, poor yields, long reaction times and tedious workup. In addition, some of them do not promote green synthesis and atom efficiency. Hence, development a new, simple, fast, efficient, and highly profitable direct esterification reaction under mild reaction conditions is still highly desirable and demanded.

Hydroxyapatite (HAP) is one of the most attractive inorganic compounds due to its excellent biocompatibility and surface active properties. Recently, there has been a growing interest in the synthesis of heterogeneous catalyst based on the grafting of various functional groups onto the surface of HAP because of good chemical stability, high surface area and simple preparation methods [42–50]. Owing to the potential advantages mentioned above, recently, we reported functionalized sulfonated nanohydroxyapatite by 2-aminoethyl dihydrogen phosphate (HAP@$AEPH_2$-SO_3H) as an efficient, eco-friendly and reusable heterogeneous solid acid catalyst in the synthesis of 4,4′-(aryl methylene)bis(1*H*-pyrazol-5-ol)s derivatives [51]. Herein we decided to extend these approaches by using HAP@$AEPH_2$-SO_3H for direct esterification of carboxylic acids with alcohols to affording high catalytic activity and selectivity that can be reused properly at least 5 times.

Experimental

General

The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were

recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Bruker Avance 300 and 400 MHz instruments in $CDCl_3$. Elemental analyses were performed using a Thermo Finnegan Flash EA 1112 Series instrument. Mass spectra were recorded with a CH7A Varianmat Bremen instruments at 70 eV; in *m/z* (rel %). Elemental compositions were determined with a Leo 1450 VP scanning electron microscope equipped with an SC7620 energy dispersive spectrometer (SEM–EDS) presenting a 133 eV resolution at 20 kV. Transmission electron microscopy (TEM) was performed with a Leo 912 AB (120 kV) microscope (Zeiss, Germany). BET surface area and pore size distribution were measured on a Belsorp mini II system at −196 °C using N_2 as adsorbate.

All of the known products were characterized by the FT-IR spectroscopy, mass spectrometry and comparison of their melting points with authenic samples. The structure of selected products was further confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy. The catalyst was prepared and characterized according the method reported previously [51]. All yields refer to isolated products after purification by recrystallization or thin layer chromatography.

Preparation of nanoHAP functionalized with $AEPH_2$ ($HAP@AEPH_2$)

To a solution of $Ca(NO_3)_2{\cdot}4H_2O$ (50 mL, 1.08 M, at pH adjusted to 10 with NH_4OH) in a three-necked 500 mL round-bottomed flask equipped with condenser, argon gas inlet tube and dropping funnel, solution of $(NH_4)_2HPO_4$ (50 mL, 0.65 M at pH adjusted to 10 with NH_4OH) was added at 90 °C with stirring. $AEPH_2$ (0.8 g, 5 mmol) was added to the resulting suspension. The precipitate was maintained in contact with the reaction solution for 5 h at 90 °C under stirring. Then suspension was centrifuged at 10,000 rpm for 10 min and repeatedly washed with CO_2-free distilled water (3 × 20 mL). The product (nanoHAP functionalized with $AEPH_2$) was dried at 50 °C overnight [51].

Preparation of $HAP@AEPH_2$-SO_3H

To a magnetically stirred mixture of $HAP@AEPH_2$ (1 g) in 20 mL of dry dichloromethane, 0.5 mL (0.75 mmol) of chlorosulfuric acid was added drop by drop at room temperature. After 20 min the suspension was filtered and washed with 20 mL of dichloromethane and dried at room temperature to afford $HAP@AEPH_2$-SO_3H as a white powder [51].

Characterization of $HAP@AEPH_2$-SO_3H

$HAP@AEPH_2$-SO_3H as a novel, eco-friendly, reusable heterogeneous solid acid catalyst was synthesized according to the procedure presented in our previous report. The structure of the prepared catalyst was characterized by various spectroscopic analyses; including Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), elemental analysis (CHN), transmission electron microscopy (TEM) and X-ray powder

diffraction (XRD) which confirmed the successful preparation of the new catalyst [51].

The morphology and size of the HAP@AEPH$_2$-SO$_3$H were evaluated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Fig. 1). SEM images are shown in Fig. 1a, b. It can be seen that HAP@AEPH$_2$-SO$_3$H nanoparticles have uniform nanorods morphology. Moreover, the size of HAP@AEPH$_2$-SO$_3$H was observed by TEM as shown in Fig. 1c, d. TEM analysis of the HAP@AEPH$_2$-SO$_3$H revealed rod-like particles with a mean size range of 10–100 nm.

Furthermore energy dispersive spectrometer (EDS) was recorded at random area on the surface of HAP@AEPH$_2$-SO$_3$H for qualitative analysis (Fig. 2). The EDS spectrum shows the presence of C, O, P, S and Ca elements which confirmed successful modification surface of nanoHAP.

Additionally, FT-IR spectroscopy as an appropriate technique to approve the successful synthesis of catalyst was used. The FT-IR spectrum of HAP@AEPH$_2$-

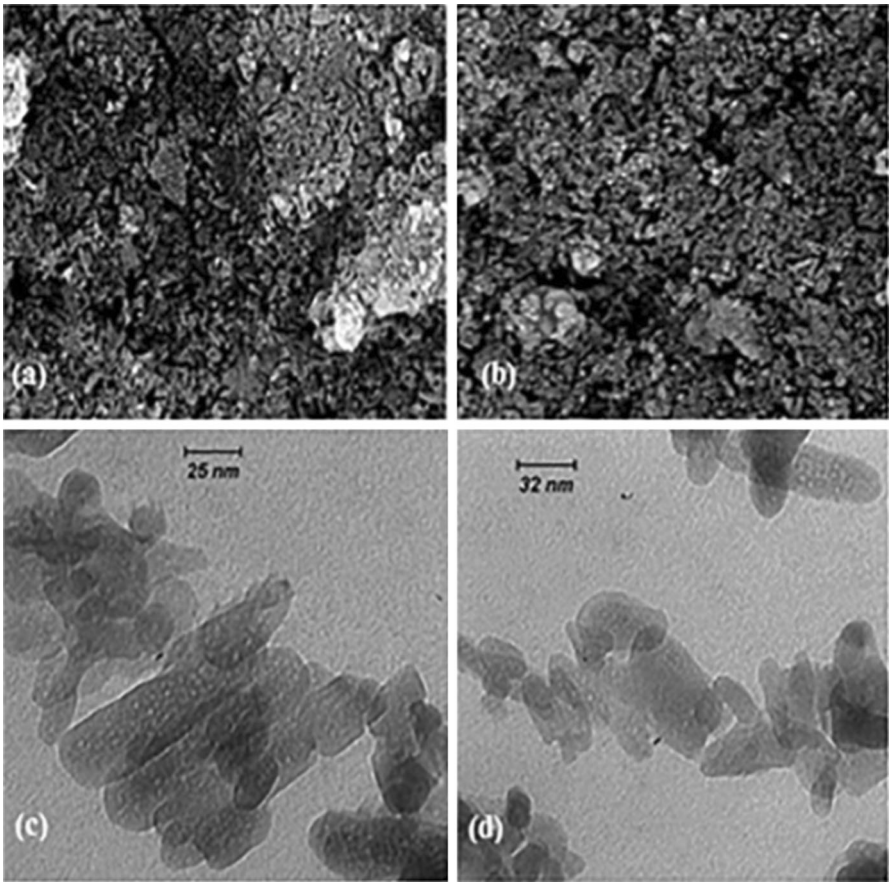


Fig. 1 **a**, **b** SEM images of HAP@AEPH$_2$-SO$_3$H, **c**, **d** TEM images of HAP@AEPH$_2$-SO$_3$H

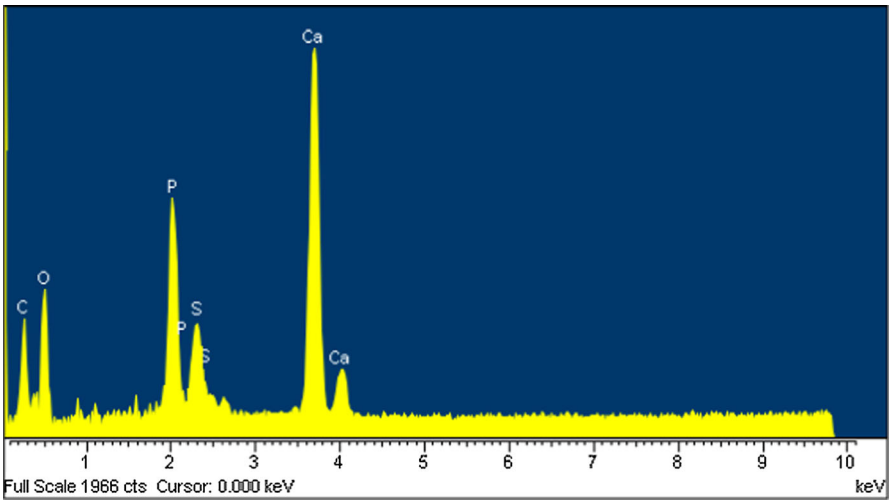


Fig. 2 The EDS analysis of HAP@AEPH$_2$-SO$_3$H

SO$_3$H is given in Fig. 3a. As can be seen from Fig. 3a, the absorption band at 3571 cm^{-1} could be attributed to hydroxyl ions in hydroxyapatite. Moreover, the broad band with a maximum at around 3450 cm^{-1} (due to stretching vibration) and the weak band at around 1637 cm^{-1} (due to bending vibration) are assigned to the crystal water and surface adsorbed water in hydroxyapatite. Another bands appearing at 1098, 1031, 962, 601, 571, and 471 cm^{-1} are related to the asymmetric, symmetric stretching and vibrational bending of the PO_4^{3-} ions respectively. Along with the primary absorption bands of nanoHAP, appearance of absorption bands at 2917, 2851, 1325 and 1155 cm^{-1} which are attributed to asymmetric and symmetric vibrational frequencies of –CH$_2$ and the asymmetric and symmetric stretching frequencies of S = O,respectively, revealed that new ligands (AEPH$_2$ and –SO$_3$H group) have been successfully attached onto the surface of nanoHAP.

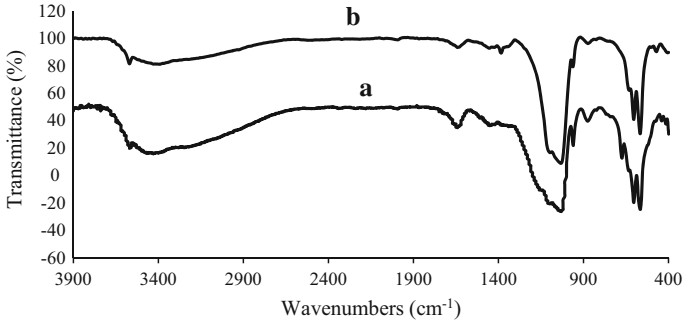


Fig. 3 FT-IR spectrum of **a** HAP@AEPH$_2$-SO$_3$H, **b** fifth reused HAP@AEPH$_2$-SO$_3$H

Table 1 Elemental analysis of the HAP@AEPH$_2$-SO$_3$H and the fifth reused catalyst

Samples	Elemental analysis (w/w %)		
	C	N	S
HAP@AEPH$_2$-SO$_3$H	2.419 (1.008 mmol/g)	1.409 (1.007 mmol/g)	3.32 (1.040 mmol/g)
Fifth reused HAP@AEPH$_2$-SO$_3$H	2.396 (0.998 mmol/g)	1.365 (0.975 mmol/g)	3.098 (0.970 mmol/g)

Table 2 BET surface area, pore volume and pour size of HAP@AEPH$_2$-SO$_3$H

Sample	Morphology	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
HAP@AEPH$_2$-SO$_3$H	Nanoparticle	130.2	0.391	12.011

To further investigate, the contents of organic fragments attached onto the surface of catalyst were determined by elemental analysis (Table 1). The elemental analysis of the catalyst revealed that carbon, nitrogen and sulfur contents of HAP@AEPH$_2$-SO$_3$H were estimated to be 2.419, 1.409 and 3.320 % respectively, which indicated that 1.008 mmol of AEPH$_2$ and 1.040 mmol of sulfonic acid were embedded on to 1.000 g of nanoHAP.

Additionally, nitrogen adsorption–desorption isotherm of the HAP@AEPH$_2$-SO$_3$H was investigated. Table 2 illustrates the average surface area, pore volume and pore size of the HAP@AEPH$_2$-SO$_3$H. By considering the BET results and comparing with literature, it can be seen that the surface area of HAP@AEPH$_2$-SO$_3$H is a little smaller than the pure HAP NPs [52].

Typical procedure for the preparation of benzhydryl benzoate in the presence of HAP@AEPH$_2$-SO$_3$H

HAP@AEPH$_2$-SO$_3$H (0.08 g, 8 mol %) was added to a solution of benzoic acid (1 mmol, 0.12 g) in dry dichloromethane (2 mL) at 41 °C. Benzhydrol (2 mmol, 0.368 g) was dissolved in dichloromethane (2 mL) and added to the reaction mixture dropwise during 1 h. Progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by filtration. The filtrate was washed with distilled water (3 × 4 mL), dried over Na_2SO_4, and concentrated in vacuo to give the crude product which was then purified by thin layer chromatography using EtOAc/*n*-hexane (2:8) to afford benzhydryl benzoate (0.264 g, 95 %).

Benzhydryl benzoate [53] (*Table 2, entry 1*) White solid; yield 95 %; mp 83–85 °C (Lit. 83.5–85.5 °C); FT-IR (KBr): υ_{max}/cm^{-1} 3056, 3023, 2917, 2851, 1713 (C=O), 1597, 1585, 1494, 1453, 1316, 1268 (C–O), 1176, 1110, 1022, 970, 894, 845, 754, 708, 598, 578; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.19 (d, J = 7.2 Hz, 2H, Ph), 7.61 (t, J = 7.2 Hz, 1H, Ph), 7.52–7.29 (m, 12H, Ph), 7.16 (s, 1H, $Ph_2\underline{C}H$); MS (EI): m/z (%) 288 (5) [M$^+$], 181 (61) [M$^+$–PhCO], 164 (100) [M$^+$–$PhCO_2$], 104 (87) [M$^+$–Ph_2CHO].

Benzhydryl 4-methylbenzoate [54] (*Table 2, entry 2*) White solid; yield 92 %; mp 108–110 °C (Lit. 110 °C); FT-IR (KBr): υ_{max}/cm^{-1} 3088, 3060, 3019, 2923, 2847, 1710 (C=O), 1608, 1503, 1450,1331, 1269 (C–O), 1179,1102, 979, 894, 841, 750, 696, 573, 469; MS (EI): m/z (%) 302 (5) [M^+], 301 (47) [M^+–1], 182 (41) [M^+–(*p*-MePhCO)], 165 (100) [M^+–(*p*-$MePhCO_2$)], 118 (90) [M^+–Ph_2CHO].

Benzhydryl 4-methoxybenzoate [55] (*Table 2, entry 3*) White solid; yield 95 %; mp 96–97 °C (Lit. 96–98 °C); FT-IR (KBr): υ_{max}/cm^{-1} 3064, 3027, 2966, 2937, 2839, 1707 (C=O), 1603, 1509, 1493, 1451, 1334, 1315, 1257 (C–O), 1165, 1098, 1025, 967, 894, 853, 820, 769, 742, 699, 616, 571, 506; MS (EI): m/z (%) 318 (10) [M^+], 317 (29) [M^+–1], 182 (82) [M^+–(*p*-MeOPhCO)], 166 (100) [M^+–(*p*-$MeOPhCO_2$)], 134 (93) [M^+–Ph_2CHO].

Benzhydryl 4-nitrobenzoate [56] (*Table 2, entry 4*) White solid, yield 85 %, mp 131–132 °C (Lit. 131–132 °C); FT-IR (KBr): υ_{max}/cm^{-1} 3117, 3060, 2925, 2851, 1723 (C=O), 1693, 1604, 1521, 1491, 1433, 1347, 1311, 1279 (C–O), 1259, 1184, 1099, 1053, 976, 878, 741, 717, 699, 587, 510; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.33 (s, 4H, *p*-NO_2Ph), 7.47–7.35 (m, 10H, Ph), 7.17 (s, 1H, $Ph_2C\underline{H}$); MS (EI): m/z (%) 333 (7) [M^+], 182 (93) [M^+–(*p*-NO_2PhCO)], 166 (100) [M^+–(*p*-NO_2PhCO_2)], 151 (68) [M^+–Ph_2CHO].

Benzhydryl 3-nitrobenzoate [57] (*Table 2, entry 5*) White solid; yield 80 %; mp 93–95 °C (Lit. 95 °C); FT-IR (KBr): υ_{max}/cm^{-1} 3088, 3064, 3027, 2953, 2925, 2855, 1729 (C=O), 1617, 1527, 1494, 1452, 1349, 1290 (C–O), 1253,1191, 1126, 1094, 1065, 969, 912, 753, 719, 699, 600, 582; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.96-8.92 (m, 1H, *m*-NO_2Ph), 8.47–8.40 (m, 2H, *m*-NO_2Ph), 7.70–7.63 (m, 1H, *m*-NO_2Ph), 7.46–7.30 (m, 10H, Ph), 7.29–7.17 (m, 1H, $Ph_2C\underline{H}$); MS (EI): m/z (%) 333 (5) [M^+], 182 (80) [M^+–(*m*-NO_2PhCO)], 165 (100) [M^+–Ph_2CH], 105 (70) [M^+–(Ph_2CHO + NO_2)].

Benzhydryl 4-bromobenzoate [58] (*Table 2, entry 6*) White solid; yield 85 %; mp 90–92 °C; FT-IR (KBr): υ_{max}/cm^{-1} 3060, 3023, 2953, 2913, 2851, 1719 (C=O), 1587, 1494, 1482, 1452, 1395, 1267 (C–O), 1171, 1114, 1101, 1009, 970, 844, 747, 697, 600, 579, 461; MS (EI): m/z (%) 367 (67) [M^+], 182 (77) [M^+–(*p*-BrPhCO)], 166 (100) [M^+–(*p*-$BrPhCO_2$)], 105 (66) [M^+–(Ph_2CHO + Br)].

1-Phenylethyl benzoate [59] (*Table 2, entry 7*) Oil; yield 85 %; FT-IR (neat): υ_{max}/cm^{-1} 3087, 3063, 3033, 2980, 2930, 2854, 1717 (C=O), 1601, 1584, 1494, 1451, 1375, 1315, 1271 (C–O), 1209, 1176, 1109, 1067, 1027, 994, 936, 912, 868, 805, 760, 712, 597, 549; MS (EI): m/z (%) 226 (17) [M^+], 121 (65) [M^+–$PhCH_3CH$], 105 (100) [M^+–$PhCO_2$], 77 (82) [M^+–$PhCO_2$ $CHCH_3$].

1-Phenylethyl 4-methylbenzoate [60] (*Table 2, entry 8*) Oil; yield 90 %; FT-IR (neat): υ_{max}/cm^{-1} 3092, 3055, 3033, 2980, 2928, 2867, 1713 (C=O), 1612, 1580, 1494, 1452, 1380, 1330, 1270 (C–O), 1177, 1104, 1063, 1016, 910, 840, 753, 697, 549, 465; MS (EI): m/z (%) 240 (11) [M^+], 118 (100) [M^+–$PhCH_3CHO$], 105 (95) [M^+–(*p*-$MePhCO_2$)], 91 (82) [M^+–$PhCH_3CHOCO$].

1-Phenylethyl 4-methoxybenzoate [59] (*Table 2, entry 9*) Oil; yield 95 %; FT-IR (neat): υ_{max}/cm^{-1} 3068, 3031, 2979, 2934, 2838, 1709 (C=O), 1606, 1511, 1455, 1421, 1317, 1255 (C–O), 1167, 1100, 1062, 1029, 914, 848, 768, 698, 620, 551, 514; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 8.10 (dd, $J_1 = 6.9$ Hz, $J_2 = 2.7$ Hz, 2H, *p*-MeOPh), 7.52–7.29 (m, 5H, Ph), 6.97 (dd, $J_1 = 6.9$ Hz, $J_2 = 2.7$ Hz, 2H, *p*-MeOPh), 6.17 (q, $J = 6.6$ Hz, 1H, $OC\underline{H}(Ph)CH_3$), 3.88 (s, 3H, *p*-MeOPh), 1.72 (d, $J = 6.6$ Hz, 3H, $OCHC\underline{H}_3$); MS (EI): m/z (%) 256 (5) [M^+], 151 (73) [M^+–$PhCH_3CH$], 134 (100) [M^+–$PhCH_3CHO$], 105 (82) [M^+–(*p*-$MeOPhCO_2$)].

1-Phenylethyl 4-nitrobenzoate [56] (*Table 2, entry 10*) Oil; yield 85 %; FT-IR (neat): υ_{max}/cm^{-1} 3112,3059, 3031, 2982, 2937, 2859, 1727 (C=O), 1612, 1527, 1457, 1404, 1347, 1273 (C–O), 1212, 1098, 1061, 1008, 873, 848, 762, 720, 699, 554, 501, 423; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.32–8.29 (m, 2H, *p*-NO_2Ph), 8.27–8.24 (m, 2H, *p*-NO_2Ph), 7.49–7.34 (m, 5H, Ph), 6.18 (q, $J = 6.4$ Hz, 1H, $OC\underline{H}(Ph)CH_3$), 1.74 (d, $J = 6.4$ Hz, 3H, $OCHC\underline{H}_3$); MS (EI): m/z (%) 271 (5) [M^+], 166 (18) [M^+–$PhCH_3CH$], 149 (91) [M^+–$PhCH_3CHO$], 121 (76) [M^+–(*p*-NO_2PhCO)], 104 (100) [M^+–(*p*-NO_2PhCO_2)].

1-Phenylethyl 3-nitrobenzoate [61] (*Table 2, entry 11*) Oil; yield 80 %; FT-IR (neat): υ_{max}/cm^{-1} 3088, 3033, 2933, 2868, 1725 (C=O), 1616, 1533, 1495, 1453, 1351, 1292 (C–O), 1263, 1209, 1137, 1064, 1029, 994, 918, 843, 762, 719, 699, 596, 541; MS(EI): m/z (%) 271(5) [M^+], 150 (88) [M^+–$PhCH_3CHO$], 121 (75) [M^+–(*m*-NO_2PhCO)], 104 (100) [M^+–(*m*-NO_2PhCO_2)].

1-Phenylethyl 4-bromobenzoate [59] (*Table 2, entry 12*) Oil; yield 85 %; FT-IR (neat): υ_{max}/cm^{-1} 3088, 3062, 3028, 2973, 2927, 2870, 1721 (C=O), 1589, 1492, 1451, 1370, 1268 (C–O), 1209, 1172, 1099, 1028, 1011, 951, 906, 853, 758, 699, 637, 544, 469; MS (EI): m/z (%) 305 (9) [M^+], 182 (73) [M^+–$PhCH_3CHO$], 121 (73) [M^+–(*p*-$BrPhCO$)], 105 (100) [M^+–(*p*-$BrPhCO_2$)].

Benzhydryl 2-phenylacetate [62] (*Table 2, entry 13*) Oil; yield 95 %; FT-IR (neat): υ_{max}/cm^{-1} 3087, 3063, 3031, 2927, 2859, 1742 (C=O), 1602, 1586, 1495, 1452, 1341, 1245 (C–O), 1144, 1077, 984, 916, 742, 698, 597, 549, 531; MS (EI): m/z (%) 302 (5) [M^+], 182 (47) [M^+–$PhCH_2CO$], 165 (100) [M^+–$PhCH_2CO_2$], 90 (77) [M^+–Ph_2CHCO_2].

Benzhydryl 2,2-diphenylacetate [63] (*Table 2, entry 14*) White solid; yield 85 %; mp 105–107 °C (Lit. 107–108 °C); FT-IR (KBr): υ_{max}/cm^{-1} 3088, 3064, 3029, 2929, 2851, 1734 (C=O), 1597, 1495, 1449, 1346, 1304, 1278 (C–O), 1187, 1141, 1078, 1003, 977, 914, 784, 741, 695, 603, 549, 473; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) *δ*: 7.35–7.26 (m, 20H, Ph), 7.00 (s, 1H, $Ph_2C\underline{H}O$), 5.25 (s, 1H, $Ph_2C\underline{H}$); MS (EI): m/z (%) 378 (3) [M^+], 180 (10) [M^+–Ph_2CHCO], 166 (100) [M^+–Ph_2CHCO_2].

((E)-Benzhydryl 3-(3-nitrophenyl)acrylate) (*Table 2, entry 15*) White solid; yield 90 %; mp 100–102 °C; FT-IR (KBr): υ_{max}/cm^{-1} 3105, 3076, 3035, 2949, 2851, 1725 (C=O), 1639, 1613, 1523, 1491, 1446, 1356, 1328, 1213 (C–O), 1161, 998, 972, 918, 865,808, 743, 699, 661, 563; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) *δ*: 8.43 (s,

1H, *m*-NO_2Ph), 8.268 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 1H, *m*-NO_2Ph), 7.87–7.80 (m, 2H, *m*-NO_2Ph, HC = CH), 7.60 (t, J = 8.1 Hz, 1H, *m*-NO_2Ph), 7.47–7.29 (m, 10H, Ph), 7.08 (s, 1H, Ph_2CH), 6.74 (d, J = 15.9 Hz, 1H, HC = $CHCO_2$); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ: 121.2, 122.5, 124.6 127.2, 128.1, 128.4, 128.6, 130.04, 133.7, 136.07, 139.9, 142.5, 148.7, 165.1; MS (EI): m/z (%) 359 (66) [M^+], 183 (79) [M^+–(*m*-NO_2PhCH = CHCO)], 166 (100) [M^+–(*m*-NO_2PhCH = $CHCO_2$)], 102 (72) [M^+–(Ph_2CHCO_2 + NO_2)]; CHN ($C_{22}H_{17}NO_4$) calc. (%) C (73.53), H (4.77), N (3.90); found (%) C (72.75), H (4.89), N (3.74).

1-Phenylethyl 2-phenylacetate [64] (*Table 2, entry 16*) Oil; yield 90 %; FT-IR (neat): υ_{max}/cm^{-1} 3088, 3063, 3031, 2980, 2931, 2872, 1732 (C=O), 1609, 1495, 1453, 1344, 1254 (C–O), 1213, 1157, 1063, 1029, 1009, 952, 849, 759, 722, 698, 547; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ: 7.44-7.37 (m, 10H, Ph), 6.04 (q, J = 6.6 Hz, 1H, OCH(Ph)CH_3), 3.76 (s, 2H, PhCH_2), 1.64 (d, J = 6.6 Hz, 3H, OCH(Ph)CH_3); MS (EI): m/z (%) 240 (7) [M^+], 122 (25) [M^+–$PhCH_2CO$], 105 (100) [M^+–$PhCH_2CO$], 91 (73) [M^+–$PhCH_3CHOCO$].

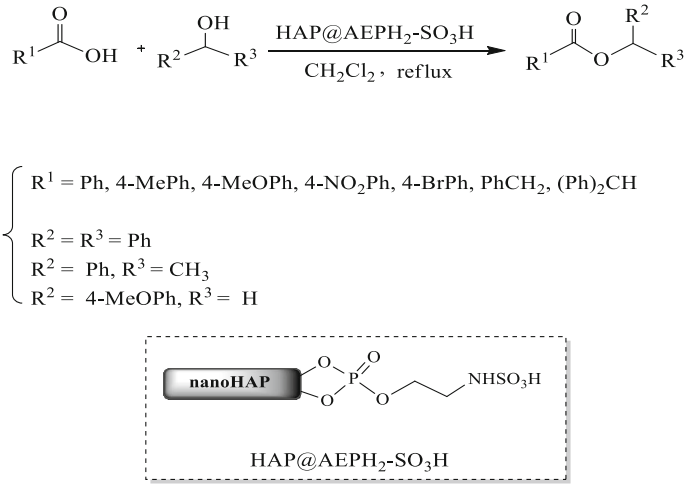
4-Methoxybenzyl benzoate [15] (*Table 2, entry 17*) Oil; yield 70 %; FT-IR (neat): υ_{max}/cm^{-1} 3067, 3035, 3006, 2961, 2927, 2855, 1717 (C=O), 1613, 1585, 1515, 1452, 1374, 1272 (C–O), 1175, 1109, 1069, 1030, 959, 926, 825, 711, 575, 524; MS (EI): m/z (%) 242 (3) [M^+], 136 (20) [M^+–PhCO], 121 (100) [M^+–$PhCO_2$], 100 (94) [M^+–(*p*-$MeOPhCH_2CO$)].

4-Methoxybenzyl hexanoate [65] (*Table 2, entry 18*) Oil; yield 70 %; FT-IR (neat): υ_{max}/cm^{-1} 3060, 3031, 2999, 2953, 2929, 2835, 1736 (C=O), 1610, 1583, 1510, 1462, 1439, 1300, 1246 (C–O), 1175, 1111, 1036, 809, 747, 578, 538; MS (EI): m/z (%) 236 (10) [M^+], 121 (92) [M^+–$CH_3(CH_2)_4CO_2$], 115 (42) [M^+–(*p*-$MeOPhCH_2$)].

Results and discussion

Following our interest in application of solid acids in organic transformation [51, 66–73] we speculated on the possibility of using HAP@$AEPH_2$-SO_3H to activate carboxylic acids for a nucleophilic substitution at the carbonyl groups to achieve ester linkage (Scheme 1).

The optimization of the reaction conditions was carried out for the reaction of benzoic acid with benzhydrol in the presence of HAP@$AEPH_2$-SO_3H under various reaction parameters in order to achieve the maximum chemical yield at the lowest reaction time and lowest reaction temperature. The representative results are shown in Table 3. On the basis of our previous reports [66, 67] we found that in acidic media, the yield of esterification reaction was influenced by the rate of addition of benzhydrol to the reaction mixture. Quick addition of benzhydrol leads to the formation of excess amount of symmetric ether which was obtained from self-condensation of benzhydrol. To minimize self-condensation of benzhydrol in all of the following reactions, addition of benzhydrol should be performed drop by drop, which consumes more times. In this manner, the corresponding ester was obtained

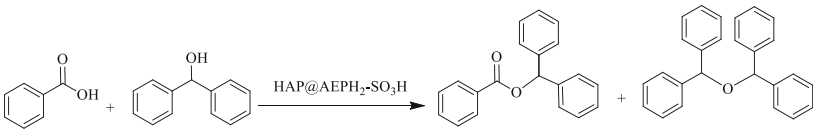


Scheme 1 Direct esterification of different structurally carboxylic acids with different alcohols in the presence of HAP@AEPH$_2$-SO$_3$H

as the chief product. In the absence of any catalyst, there was no conversion to benzhydryl benzoate (Table 3, entry 1). Applying 1/1 molar ratio of benzoic acid/benzhydrol in the presence of 4 mol % of catalyst in refluxing CH_2Cl_2 leads to formation of desired product and (benzhydryloxy)diphenylmethane as by product (Table 3, entry 2). Low yield of corresponding product was obtained even after long reaction time, when the same reaction condition was performed at room temperature (Table 3, entry 3). In an effort to develop better reaction conditions, different molar ratios of reactants were examined on model reaction (Table 3, entries 4–7). The maximum yield of benzhydryl benzoate with trace amount of by product was obtained by using 1/2 molar ratio of benzoic acid/benzhydrol. To improve direct esterification reaction the effect of catalyst loading was investigated on model reaction (Table 3, entries 8–10). According to this study, the best result of benzhydryl benzoate was produced in the presence of 8 mol % of catalyst with lowest yield of by product (Table 3, entry 9). The catalytic effect of HAP@AEPH$_2$-SO$_3$H was studied in different solvents as well as solvent free conditions. No product was obtained when the reaction was performed in refluxing H_2O and THF and also in solvent free condition (Table 3, entries 11–12, 22). As shown in Table 3, the catalytic effect of HAP@AEPH$_2$-SO$_3$H was efficiently decreased in $CHCl_3$, CH_3CN, 1, 2-dichloroethane, CH_3NO_2, 1,4-dioxane and toluene (Table 3, entries 13–21).

After optimizing the reaction parameters, generality of the method was tested with other carboxylic acids and alcohols. The results are summarized in Table 4. From this Table, it is clear that, in the presence of HAP@AEPH$_2$-SO$_3$H, the desired esters can be obtained in good to excellent yields. In comparison, benzhydrol condensed with aromatic carboxylic acids more quickly than 1-phenylethanol due to more stability of diphenylmethylium cation than 1-phenylethan-1-ylium cation

Table 3 Direct esterification of benzoic acid with benzhydrol in the presence of HAP@AEPH$_2$-SO$_3$H under different reaction conditions



A B

Entry	Molar ratio of benzoic acid/ benzhydrol	Catalyst (mol %)	Solvent	Temperature (°C)	Time (h)	Conversion[a] (%)	Selectivity A/B (%)
1	1/1	0	CH_2Cl_2	Reflux	24	0	0:0
2	1/1	4	CH_2Cl_2	Reflux	2	70	90:10
3	1/1	4	CH_2Cl_2	R.T	24	30	20:10
4	1/1.2	4	CH_2Cl_2	Reflux	2.5	80	90:10
5	1/1.5	4	CH_2Cl_2	Reflux	3	90	90:10
6	1/2	4	CH_2Cl_2	Reflux	3.5	100	90:10
7	1/2.5	4	CH_2Cl_2	Reflux	4	100	85:15
8	1/2	6	CH_2Cl_2	Reflux	3.5	100	95:5
9	1/2	8	CH_2Cl_2	Reflux	2.5	100	95:5
10	1/2	2	CH_2Cl_2	Reflux	4.5	90	80:20
11	1/2	8	H_2O	Reflux	24	0	0:0
12	1/2	8	THF	Reflux	24	0	0:0
13	1/2	8	$CHCl_3$	Reflux	5	95	85:15
14	1/2	8	CH_3CN	Reflux	8	80	75:25
15	1/2	8	CH_3CN	40	24	50	10:40
16	1/2	8	1,2-DCE	Reflux	3	100	80:20
17	1/2	8	1,2-DCE	40	24	45	25:15
18	1/2	8	CH_3NO_2	Reflux	12	95	70:30
19	1/2	8	1,4-Dioxane	Reflux	20	70	60:40
20	1/2	8	Toluene	Reflux	7	75	70:30
21	1/2	8	$CHCl_3$	40	24	65	40:60
22	1/2	8	Solvent free	40	24	0	0:0

[a] The corresponding data referred to the conversion of benzoic acid

(compare entries 1–6 with 7–12). Electron density of aromatic carboxylic acids plays an essential role in the reaction rate. Comparatively electron–donating groups on aromatic rings accelerates the esterification reaction whilst esterification of aromatic carboxylic acids bearing electron withdrawing substituents was completed in longer reaction times (compare entries 2–3 with 4–6 and entries 8–9 with 10–12). Aliphatic carboxylic acids also followed this manner in direct esterification reaction in the presence of HAP@AEPH$_2$-SO$_3$H (Table 4, entries 13–16). Difference in reactivity between diphenylacetic acid and the other aliphatic carboxylic acids can be rationalized by the steric effects of two phenyl groups. On the basis of the results obtained from Table 4 and according to the proposed mechanism in Scheme 2, the

stability of carbocation **II** and the nucleophilicity of carboxylic acid are thought to be two effective factors in the esterification reaction. The electron-rich aryl ring increases the nucleophilicity of carboxylic acid and accelerates the formation of intermediate **III** which in turn facilitates the formation of desired product. We also tested the direct esterification reaction of carboxylic acids with tertiary alcohols (triphenyl methanol, *t*-butyl alcohol), secondary and primary aliphatic alcohols (2-heptanol, 3-phenyl 1-propanol) in the presence of HAP@AEPH$_2$-SO$_3$H. Unfortunately, the catalyst was not effective in esterification of carboxylic acids with the above mentioned alcohols even under forced conditions (16 mol % of catalyst). Although, the catalyst was effective in promoting the reaction of carboxylic acids with electron-rich primary benzylic alcohol (Table 4, entry 17), but the esterification reaction of carboxylic acids with primary benzylic alcohols bearing electron withdrawing groups were not successful even after long period of time.

The present protocol, in its entirety, simply involves the reaction of carboxylic acids with primary/or secondary benzylic alcohol in the presence of a catalytic amount of HAP@AEPH$_2$-SO$_3$H, and warming the reaction mixture to afford the desired product. The reactions are reasonably fast, but because of acidic media, to prevent formation of any by-products (symmetrical ethers or alkenes in the case of 1-phenyl ethanol), the addition of benzylic alcohols should be carried out drop by drop, which prolonged the reaction times.

In all of experiments, the completion of the reaction was confirmed by the disappearance of the carboxylic acids on TLC followed by the disappearance of acidic OH stretching frequency at 3400–2400 cm^{-1} in FT-IR spectra. Also, absorption bands at 1742–1707 and 1292–1213 cm^{-1} due to carbonyl and C–O group of esters in FT-IR spectra confirmed the ester formation. In the ^{13}C NMR spectrum, a signal at 165 ppm is assigned to the quaternary carbonyl carbon. The structures of all synthesized compounds were confirmed spectroscopically and found to be comparable in all respects with pure samples.

According to these observations we propose the mechanism reported in Scheme 2. It is speculated that in the presence of HAP@AEPH$_2$-SO$_3$H the protonated species **I** was produced initially which subsequently generates the corresponding stable benzylic carbocation **II**. This idea is supported by performing the reaction in the absence of catalyst. Without any catalyst, the esterification reaction is not performed even after a long period of time (Table 3, entry 1). The formation of benzylic carbocation **II** was also confirmed by the fact that the more stable carbocation reacts more quickly with carboxylic acid (compare the reaction rate of benzhydrol with 1-phenyethanol). Nucleophilic attack of carboxylic acid to benzylic carbocation **II** produced the protonated ester **III** which was followed by releasing of the acidic catalyst. Then the solid acid catalyst re-enters to the catalytic cycle. As the addition of benzylic alcohol to the reaction mixture was performed drop by drop the formation of any symmetric ether **IV** as by product was prohibited. Also, as the reaction was performed at low temperature (41 °C) dehydration of **I** through benzylic cation **II** which leads to alkene **V**, did not happen in the esterification reaction in the presence of HAP@AEPH$_2$-SO$_3$H [74–76]. Further studies to elucidate the details of the mechanism are ongoing.

Table 4 Direct esterification of various carboxylic acids with alcohols catalyzed by HAP@AEPH$_2$-SO$_3$H

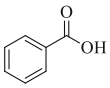
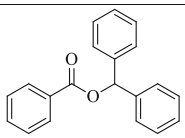
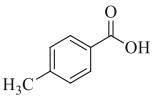
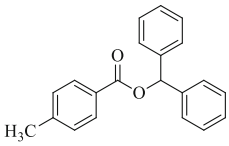
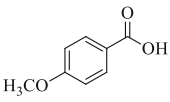
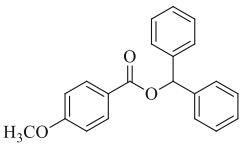
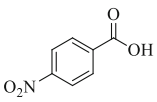
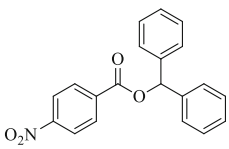
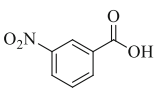
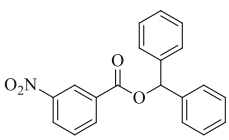
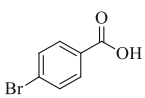
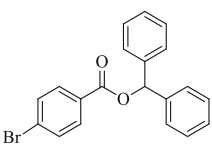
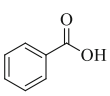
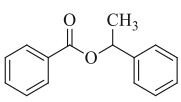
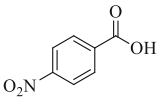
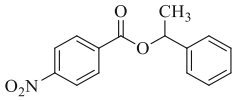
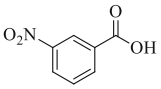
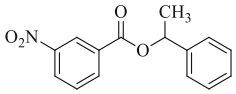
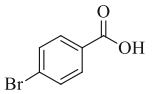
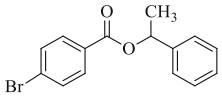
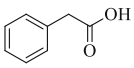
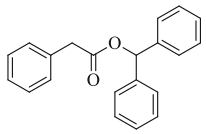
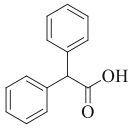
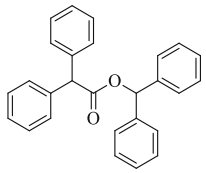
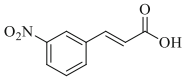
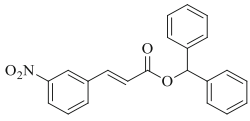
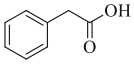
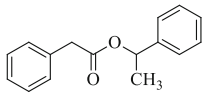
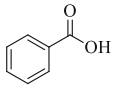
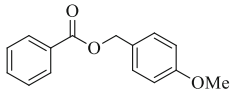
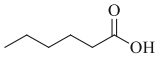
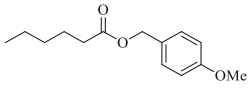
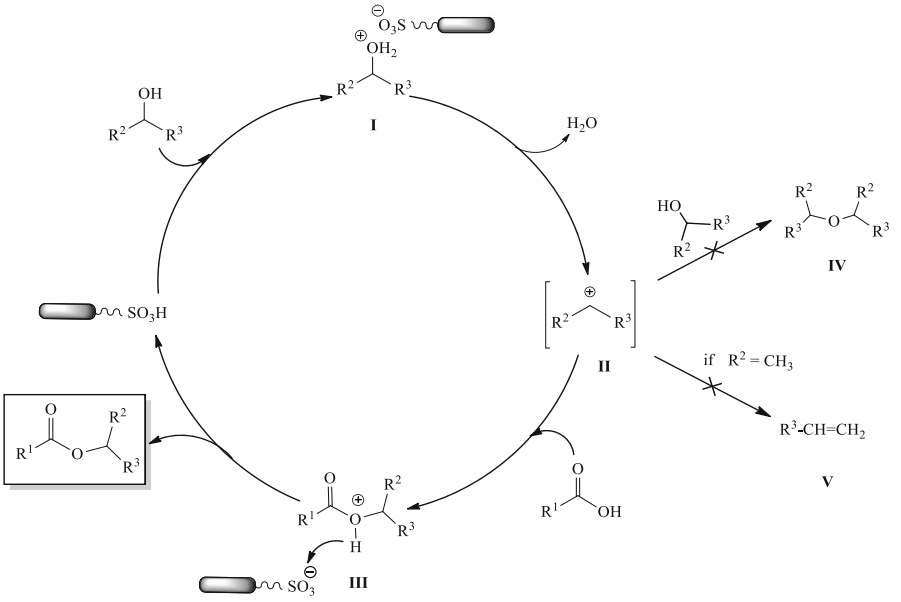
Entry	Carboxylic acid	Alcohol	Product	Time (h)	Isolated[a] Yield (%)
1		benzhydrol		2.5	95
2		benzhydrol		2	92
3		benzhydrol		1.5	95
4		benzhydrol		3.5	85
5		benzhydrol		3.5	80
6		benzhydrol		4	85
7		1-phenylethanol		3	85

Table 4 continued

Entry	Carboxylic acid	Alcohol	Product	Time (h)	Isolated[a] Yield (%)
10		1-phenylethanol		4	85
11		1-phenylethanol		4.5	80
12		1-phenylethanol		5	85
13		benzhydrol		2.5	95
14		benzhydrol		3.5	85
15		benzhydrol		3	90
16		1-phenylethanol		3	90
17		4-methoxy benzyl alcohol		3	75
18		4-methoxy benzyl alcohol		4.5	70

[a] The data referred to isolated yield of the corresponding ester



Scheme 2 Proposed mechanism for direct esterification of carboxylic acid with alcohol in the presence of HAP@$AEPH_2$-SO_3H

Catalyst re-usability was assessed in the direct esterification of benzoic acid with benzhydrol. To this end, the reaction was stopped after 2.5 h (i.e. at 100 % conversion of benzoic acid) and the catalyst removed by centrifugation and washed with ethylacetate three times. Table 5 shows the results obtained after five re-use cycles. As can be seen, no significant loss of activity of the catalyst was observed after 5 runs. In another word the heterogeneous catalyst can be used for five successive times in the new experiments without any significant impact on yields of products with purity similar to that obtained in the first run.

In order to study the stability of the catalyst in the reaction mixture, the FT-IR spectrum and elemental analysis are employed to give detail investigation of the fifth reused catalyst. Figure 3b represents the FT-IR spectrum of the fifth reused HAP@$AEPH_2$-SO_3H nanoparticles. As shown in Fig. 3b, there was no significant leaching of organic segments ($AEPH_2$ and -SO_3H) from the catalyst surface after five runs of the reaction. Moreover, elemental analysis of the reused catalyst is presented in Table 1. Based on this analysis (C 2.396 %, N 1.365 % and S 3.098 %) no considerable leaching of organic segments occurred in the reaction mixture away from the surface of HAP@$AEPH_2$-SO_3H.

Table 5 Reaction of benzoic acid with benzhydrol in the presence of reused catalyst

Run	Time (h)	Conversion (%)	Isolated yield (%)
1	2.5	100	95
2	2.5	100	95
3[a]	2.5/3	95/100	95
4[a]	2.5/3	95/100	90
5	3	95	90

[a] The second numbers in the third columns correspond to conversion after 3 h

Table 6 Comparison efficiency of various catalysts in the direct esterification of benzoic acid with 1-phenylethanol

Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Yield (%)	Reference
1	$TiO(acac)_2$	Xylene	138.5	36	97	[77]
2	$ClHC = N^+ MeCl^{-}$[a]	THF	R.T	16	66	[78]
3	5,5′-Dimethyl-3,3′-azoisoxazole/ PPh_3	CH_3CN	82	11	55	[79]
4	PS-SI[b]	H_2O	80	48	90.7	[80]
5	RHAPhe–Ru[c]	Solvent-free	85	12	82	[81]
6	Et–PMO–Me– $PrSO_3H$[d]	Solvent-free	60	6	>99	[35]
7	HAP@$AEPH_2$-SO_3H	CH_2Cl_2	41	3	85	Present study

[a] (Chloromethylene)dimethylammonium chloride

[b] Polymer-supported sulfonamide, the corresponding data referred to the direct esterification of *n*-butyric acid with *n*-butanol

[c] *L*-(*N*-α-acetylphenylalanine)–Ru(III) complex, the corresponding data referred to the direct esterification of acetic acid with ethyl alcohol

[d] Sulfonic acid-functionalized periodic mesoporous organosilicas, the corresponding data referred to the direct esterification of acetic acid with benzyl alcohol

To further evaluate the overall utility of the current methodology, we compared our results with those of the other methods reported for direct esterification of carboxylic acids with alcohols (Table 6). As shown in Table 6, this method avoids disadvantages of the other procedures such as long reaction times, expensive catalysts, toxic reagents, high temperature and low yield [35, 77–81]. Consequently, HAP@$AEPH_2$-SO_3H can be considered as a novel, eco-friendly and reusable solid acid catalyst for this reaction.

Conclusion

In conclusion, we have developed an efficient process, for preparation of esters using HAP@$AEPH_2$-SO_3H as a recyclable catalyst. The HAP@$AEPH_2$-SO_3H is able to promote the esterification of a variety of carboxylic acids with benzylic alcohols in high yields under mild reaction conditions. The yields for the esterification reaction were excellent in the range of 78–99 %. After completion of the reaction the HAP@$AEPH_2$-SO_3H were removed by filtration, which could be reused five times without any loss of activity. Stability and recyclability of HAP@$AEPH_2$-SO_3H and the easy workup make the present system an alternative way to construct ester bonds from carboxylic acids and alcohols in future.

Acknowledgments The authors gratefully acknowledge the partial support of this study by Ferdowsi University of Mashhad Research Council (p/3/33830).

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