# Mesoporous titania/tungstophosphoric acid composites: suitable synthesis of flavones

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Abstract Mesoporous $TiO_2/H_3PW_{12}O_{40}$ composites were synthesized by sol–gel reactions using urea as a low-cost template, and adding tungstophosphoric acid (TPA) at the same time as the template. The TPA concentration was varied in order to obtain TPA contents of 0, 10, and 20 (w/w) in the solid. The samples presented mesopores with a diameter higher than 3.0 nm. The specific surface area of the solids decreased with both the increase of the TPA content and the calcination temperature. From Fourier transform infrared and ^{31}P magic angle spinning-nuclear magnetic resonance studies it was observed that the main heteropolyoxometallate species present in the composites is the $[PW_{12}O_{40}]^{3-}$ anion, which was partially transformed into the $[P_2W_{21}O_{71}]^{6-}$ and $[PW_{11}O_{39}]^{7-}$ anions during the synthesis and drying step. The X-ray diffraction patterns of the modified samples only exhibited the characteristic peaks of the anatase phase of titanium oxide. The point of zero charge decreased with both the increase of TPA content in the solids and the calcination temperature. The materials were found to be efficient and recyclable catalysts for the synthesis of a series of flavones. The reaction was carried out in different reaction media: heterogeneous and solvent-free conditions. The solvent-free conditions represent the best green conditions. Initially, we optimize the reaction condition to obtain 6-chloroflavone by direct reaction of the cyclodehydration of 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione in the presence of a catalytic amount of mesoporous titania modified with tungstophosphoric acid catalyst. Reactions were performed in two conditions: low volume of toluene, at 110 °C, typically 24 h, and solvent-free at the same temperature, 1 h. In all cases the product (6-chloroflavone) was obtained with high selectivity. Conversions up to 76 and 92 % were obtained respectively, using the supported catalyst (TiTPA10). Optimal reaction conditions were applied to the preparation of six substituted flavones in both conditions.
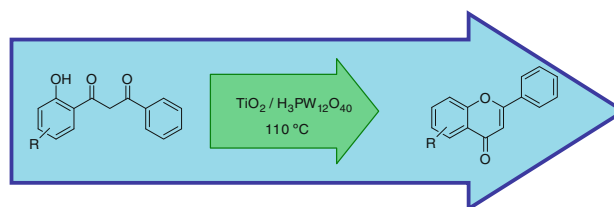
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1 Introduction

The search of new acid solids that can replace the classical acids for their use as catalysts in organic synthesis in liquid phase is constant due to the need for developing clean processes with environmental advantages [1]. The

Scheme 1 Synthesis of 6-chloroflavone
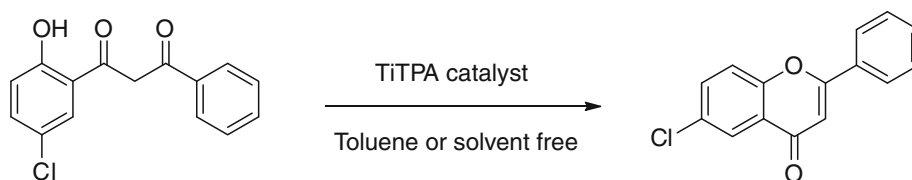
application of solid acids in organic transformation has an important role, because they have many advantages such as ease of handling, decreased plant corrosion, and more environmentally safe waste disposal procedures [2].

Heteropolyacids (HPA) are well-defined molecular arrangements with remarkable and useful applications. There is an increasing interest in the area of hetero-polycompound-induced organic transformations. In view of their remarkable catalytic properties, heteropolycompounds are applied both in bulk and supported form. For a long time, our efforts have focused on the development of environmentally benign synthetic methods using supported Keggin heteropolyacids, especially the protection and deprotection of organic functional groups and heterocycle synthesis [3–6].

Particularly different HPA have been used to modify TiO_2 and these materials are widely used as acid catalyst as well as oxidant. More recently they have been used as effective homogeneous photocatalyst in the oxidation of organic compounds, and in the degradation of pollutants in water [7].

On the other hand, compounds containing the chromone skeleton (4H-benzopyran-4-one) are widely distributed in the plant kingdom; they constitute a group of compounds in the flavonoid family [8]. These compounds have multiple biological properties, for example anti-inflammatory, antibacterial, antitumor [9], antioxidant [10], anti-HIV [11], vasodilator, antiviral, and antiallergenic [12]. Some flavonoids inhibit histamine release from human basophils and rat mast cells [13].

Moreover, some natural and synthetic flavonoid derivatives have shown a promising activity as insecticides. It is known that some flavonoids have a repelling property against certain species of phytophagous insects [14] and subterranean termites (*Genus Coptotermes*) [15] and there is an important amount of data about the role of flavonoids in insect-plant interactions [16]. In the past decade several papers about the antifeedant activity of flavonoid derivatives were published: various chromone and aurone derivatives showed activity against *Spodoptera litura* (Oriental leafworm moth) [14, 17–19], *Spodoptera littoralis* (Egyptian armyworm) [20], *Mythimna separate* (Oriental armyworm) [21], and other insects.

The fall armyworm, *Spodoptera frugiperda*, is a polyphagous pest that causes important damage in different regions of America and mainly affects corn crops in both tropical and subtropical areas. Recently, we found that flavone, particularly halogenated flavones (6-chloro, 7-chloro and 6-bromo), and showed insecticide activity for this pest. The significance of this pest in Argentina was pointed out by Virla et al. [22, 23].

One of the most commonly used methods consists of the cyclodehydration of 1-(2-hydroxyphenyl)-1,3-diketones [9]. This is usually a catalyzed reaction (Scheme 1) and it has been performed in different media. Some reaction conditions employed were the use of excess of sulfuric acid in glacial acetic acid [24], cationic exchange resins in isopropanol [25], $CuCl_2$ in ethanol [9], and ionic liquid under microwave irradiation [26]. Recently, we reported a more suitable method for their synthesis, including HPA [27–29], and carbon-supported triflic acid [30]

In the present work we describe the preparation and characterization of mesoporous titania modified with tungstophosphoric acid; also we present its use as a recyclable acid catalyst in the heterogeneous and solvent-free synthesis of flavones. Scheme 1 shows the synthesis of 6-chloroflavone using this protocol.

2 Experimental

Chemicals were purchased from Aldrich, Fluka and Merck chemical companies and were freshly used after purification by standard procedures (distillation and recrystallization). All catalysts were dried overnight prior to use. All the reactions were monitored by TLC on precoated silica gel plates (254 mm). Flash column chromatography was performed with 230–400 mesh silica gel. All the yields were calculated from crystallized products. All the products were identified by comparison of physical data (mp, TLC and NMR) with those reported or with those of authentic samples prepared by the respective conventional methods using sulfuric acid as catalyst. The melting points of the compounds were determined in sealed capillary tubes and are uncorrected. The ^{1}H-NMR and ^{13}C-NMR spectra were obtained on a Bruker instrument 400 MHz model as $CDCl_3$ solutions, and the chemical shifts were expressed in δ units with Me_4Si (TMS) as the internal standard. All the starting 1,3-diketones were prepared following a method described elsewhere [27].

2.1 Preparation of catalysts

The mesoporous titania samples modified with TPA concentration of 0, 10, and 20 by weight in the final material were prepared essentially following a procedure described in the literature [7]. Hereinafter, the samples will be named TiTPA00, TiTPA10, and TiTPA20, respectively. As an example, we describe the synthesis of the TiTPA10 samples. A titanium isopropoxide (Aldrich, 26.7 g) solution was prepared in absolute ethanol (186.6 g) under N_2 atmosphere and at 20 °C, continuously stirring for 10 min. Then, 0.33 mL of 0.28 M HCl aqueous solution was slowly added in order to catalyze the sol–gel reaction. After 3 h, 120 g of urea–ethanol–water (1:5:1 w/w) solution was added, together with 0.073 g tungstophosphoric acid ($H_3PW_{12}O_{40}$) dissolved in ethanol under stirring. The gel was dried at 20 °C and the solids were ground into powder and extracted with distilled water for three periods of 24 h, in order to remove the urea. Finally the solids were thermally treated at 110 °C for 2 h.

2.2 Catalysts characterization

The specific surface area (S_{BET}) and the average pore diameter (D_p) of the samples were estimated from the nitrogen adsorption–desorption isotherms using the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) method. The isotherms were obtained using Micromeritics ASAP 2020 equipment. The solids were previously degassed at 100 °C for 2 h.

The X-ray diffraction (XRD) patterns were recorded with Philips PW-1732 equipment with a built-in recorder, using Cu Kα radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5° and 60° 2θ at a scanning rate of 1° per minute.

The Fourier transform infrared (FT-IR) spectra of the solids were obtained using a Bruker IFS 66 FT-IR spectrometer and pellets in KBr in the 400–4,000 cm^{-1} wavenumber range.

The ^{31}P magic angle spinning-nuclear magnetic resonance (^{31}P MAS-NMR) spectra were recorded with Bruker Avance II equipment using the CP/MAS ^1H–^{31}P technique. A sample holder of 4 mm diameter and 10 mm in height was employed, using 5 μs pulses, a repetition time of 4 s, and working at a frequency of 121.496 MHz for ^{31}P at room temperature. The spin rate was 8 kHz/kHz and several hundred pulse responses were collected. Chemical shifts were expressed in parts per million with respect to 85 % H_3PO_4 as an external standard for ^{31}P-NMR.

The secondary electron micrographs of the samples were obtained by scanning electron microscopy (SEM), using Philips Model 505 equipment.

The acidity of the solids was measured by means of potentiometric titration. A known mass of solid was suspended in acetonitrile and stirred for 3 h. Then, the suspension was titrated with 0.05 N *n*-butylamine in acetonitrile using Metrohm 794 Basic Titrino apparatus with a double junction electrode.

2.3 Catalytic test

2.3.1 In heterogeneous conditions

A mixture of 1,3-diketone (0.25 mmol) dissolved in 1 mL toluene and the catalyst (100 mg) was refluxed with stirring for the indicated time. When the reaction time was over, the catalyst was filtered and washed twice with toluene (1 × 2 mL). The extracts were combined and washed with 3 M NaOH (2 × 1 mL), then with H_2O (1 × 1 mL), and dried with anhydrous sodium sulphate. The organic solution was concentrated in vacuum. All the solid crude products were recrystallized from methanol.

2.3.2 In solvent-free conditions

A mixture of 1,3-diketone (0.25 mmol) and catalyst (100 mg) was stirred at 110 °C for the indicated time. The reaction mixture was extracted with hot toluene (2 × 1 mL). The solution was washed with 3 M NaOH (2 × 1 mL) and H_2O (1 × 1 mL), then with H_2O (1 × 1 mL), and dried with anhydrous sodium sulphate. The organic solution was concentrated in vacuum. All the solid crude products were recrystallized from methanol.

2.3.3 Catalyst reuse

Stability tests of the catalysts (TiTPA10 and TiTPA20) were carried out running four consecutive experiments, under the same reaction conditions. After each test, the catalyst was separated from the reaction mixture by filtration, washed with toluene (2 × 1 mL), and then it was dried under vacuum and reused.

2.3.4 Characterization data of selected compounds

2.3.4.1 Flavone mp: 96–97 °C (methanol) (lit. mp: 96–99 °C, [28]); ^{13}C NMR (100 MHz, CDCl$_3$) d 107.5, 117.7, 123.8, 124.9, 125.6, 126.1, 129.1, 131.6, 131.9, 133.4, 155.8, 163.2, 177.9; ^1H NMR (400 MHz, CDCl$_3$) d 6.81 (s, 1H), 7.42 (ddd, 1H, J = 1.0, 7.2, 8.2 Hz), 7.47–7.57 (m, 4H), 7.69 (ddd, 1H, J = 1.7, 7.2, 8.3 Hz), 7.93–7.96 (m, 2H), 8.23 (dd, 1H, J = 1.8, 8.2 Hz).

2.3.4.2 6-Chloroflavone mp: 184–185 °C (methanol) (lit. mp: 184–185 °C, [28]); ^{13}C NMR (100 MHz, CDCl$_3$)
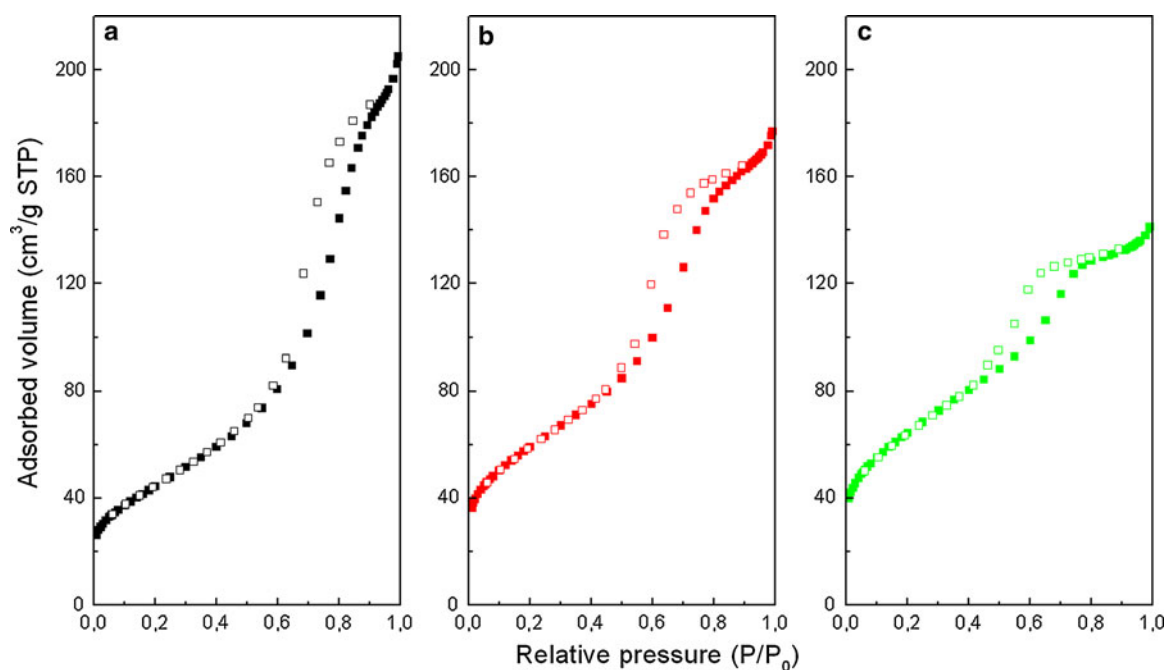
Fig. 1 N$_2$ adsorption–desorption isotherms of TiTPA00 (**a**), TiTPA10 (**b**), and TiTPA20 (**c**) samples. Adsorption branch (*full symbols*), desorption branch (*open symbols*)

d 107.4, 119.9, 125.1, 125.2, 126.4, 129.2, 131.3, 131.5, 131.9, 134.0, 154.4, 163.6, 177.3; ^{1}H NMR (400 MHz, CDCl$_3$) d 6.85 (s, 1H), 7.52–7.56 (m, 4H), 7.64 (dd, 1H, J = 2.5, 8.8 Hz), 7.90–7.94 (m, 2H), 8.22 (d, 1H, J = 2.6 Hz).

2.3.4.3 7-Chloroflavone mp: 156–157 °C (methanol) (lit. mp: 156–157 °C, [28]); ^{13}C NMR (62.5 MHz, CDCl$_3$) d 107.1, 118.1, 122.4, 126.0, 126.3, 126.9, 129.2, 131.3, 131.7, 139.6, 156.0, 163.3, 177.8; ^{1}H NMR (250 MHz, CDCl$_3$) d 6.82 (s, 1H), 7.40 (dd, 1H, J = 1.9, 8.4 Hz), 7.50–7.55 (m, 3H), 7.60 (d, 1H, J = 1.9 Hz), 7.91–7.93 (m, 2H), 8.23 (d, 1H, J = 8.4 Hz).

2.3.4.4 7-Bromoflavone mp: 163–165 °C (methanol) (lit. mp: 164–165 °C, [28]); ^{13}C NMR (100 MHz, CDCl$_3$) d 107.5, 121.2, 122.4, 126.0, 126.4, 128.2, 128.6, 128.9, 131.4, 131.5, 155.3, 163.5, 177.0; 1H NMR (400 MHz, CDCl3) d 6.85 (s, 1H), 7.53– 7.57 (m, 3H), 7.62 (dd, 1H, J = 1.5, 8.2 Hz), 7.80 (d, 1H, J = 1.5 Hz), 7.91–7.94 (m, 2H), 8.18 (d, 1H, J = 8.2 Hz).

3 Results and discussion

3.1 Catalyst characterization

The N$_2$ adsorption–desorption isotherms of the TiO$_2$/ H$_3$PW$_{12}$O$_{40}$ composites calcined at 200 °C are presented in

Fig. 1. They can be classified as type IV, characteristic of mesoporous materials. The hysteresis loop of TPA-modified titania samples can be classified as H2 type. However, for the TiTPA00 sample the hysteresis loop noticeably resembles those of H1 type solids. H1 and H2 type hysteresis loops arise in solids consisting of particles crossed by nearly cylindrical channels or made by aggregates of spheroidal particles that present pores with uniform size and shape (type H1) or nonuniform size or shape (type H2) [22, 31]. The uniformity of the mesoporous structure of the modified samples would decrease with the incorporation of TPA during the synthesis.

The specific surface areas (S$_{BET}$) of TiTPA10 and TiTP20 samples (285 and 268 m^2/g, respectively) were lower than that of TiTP00 (355 m^2/g) (Table 1). The S$_{BET}$ values decreased with the increment of the TPA content. According to the microporous specific surface area (S$_{Micro}$) values (Table 1), calculated using the *t*-plot method, more than 90 % of the total specific surface area of the solids results from their mesoporous structure (S$_{Meso}$). The samples are mesoporous materials with a Dp higher than 3.0 nm and it decreased in the following way TiTPA00 (5.1 nm) > TiTPA10 (4.2 nm) > TiTPA20 (3.6 nm) when TPA content was increased. Additionally, the pore volume decreases in the same way (Table 1).

In a previous study [7], based on FT-IR and ^{31}P MAS-NMR results, it was reported that the main species present in the TiO$_2$/H$_3$PW$_{12}$O$_{40}$ composites is the [PW$_{12}$O$_{40}$]$^{3-}$ anion. However, due to the limited pH range stability of the

**Table 1** Textural properties of the catalyst calcined at 110 °C

Sample	S_{BET} (m^2/g)	S_{MICRO} $(m^2/g)^a$	D_p $(nm)^b$	Total pore volume $(cm^3/g)^c$
TiTPA00	355	24	5.1	0.190
TiTPA10	285	17	4.2	0.182
TiTPA20	268	12	3.6	0.165

[a] Specific surface area of micropores was obtained from t-plot analysis

[b] Average pore diameter was calculated using the BJH formula from the desorption branch

[c] Total pore volume was calculated by the BJH method

$[PW_{12}O_{40}]^{3-}$ anion in solution, it was partially transformed into a dimeric species $[P_2W_{21}O_{71}]^{6-}$ (sample TiTPA10) and into the dimeric anion together with the $[PW_{11}O_{39}]^{7-}$ (sample TiTPA20). The generation of lacunar and dimeric species such as $[PW_{11}O_{39}]^{7-}$ and $[P_2W_{21}O_{71}]^{6-}$ could be due to pH changes because of urea decomposition occurring during the sol–gel synthesis, as has been proposed by Pope [32] through the equilibrium:

$$[PW_{12}O_{40}]^{3-} \Leftrightarrow [P_2W_{21}O_{71}]^{6-} \Leftrightarrow [PW_{11}O_{39}]^{7-} \quad (1)$$
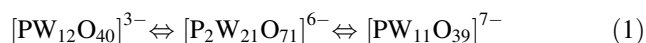
The XRD patterns of the TiTPA00 sample (Fig. 2a) show weak broad peaks in the same position where the characteristic peaks of the anatase phase are placed 25.3° (1 0 1), 37.9° (0 0 4), 47.8° (2 0 0), and 54.3° 2θ. This is indicative of a solid poorly crystallized and mostly amorphous. On the other hand, the XRD patterns of the samples modified with TPA displayed (Fig. 2b, c) the same broad band. Diffraction lines attributed to crystalline TPA (Fig. 2d) or its decomposition products were not observed, indicating that TPA is highly dispersed or present as an amorphous phase in the $TiO_2/H_3PW_{12}O_{40}$ composites.

According to the SEM images (Fig. 3), the samples consist of spherical particles, whose size increased from 200 to 500 nm when the TPA content was raised. However, when the image is magnified (insert, Fig. 3), it is observed that the spherical particles are formed by the aggregation of smaller particles (see arrows), as was reported by Bakarjieva et al. [33] for titania samples obtained by the hydrolysis of $TiOSO_4$ aqueous solution using urea as the precipitation agent. Additionally, the spherical particles are present as clusters, whose size also increased when the TPA content was raised.

The acidity measurements of the catalysts by means of potentiometric titration with n-butylamine let us estimate the number of acid sites and their acid strength. It was suggested that the initial electrode potential (Ei) indicates the maximum acid strength of the sites, and the value of meq n-butylamine/g solid where the plateau is reached indicates the total number of acid sites. The acid strength of these sites may be classified according to the following
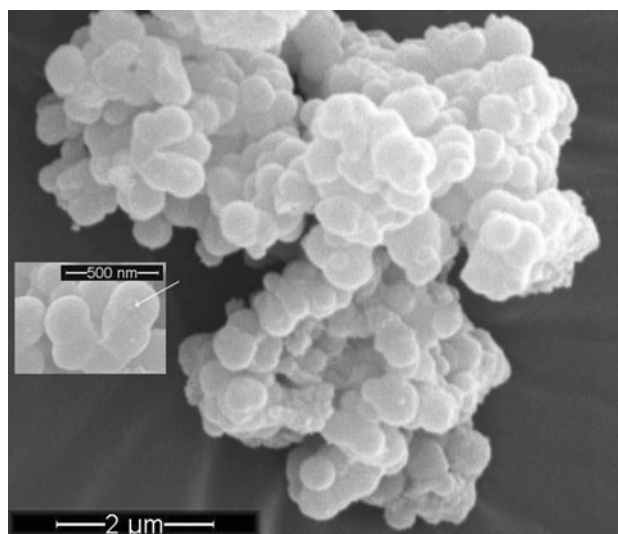

Fig. 2 SEM image of TiTPA00 sample. The *inset* shows a magnified image and the *arrow* indicates the presence of the smallest nanoparticles
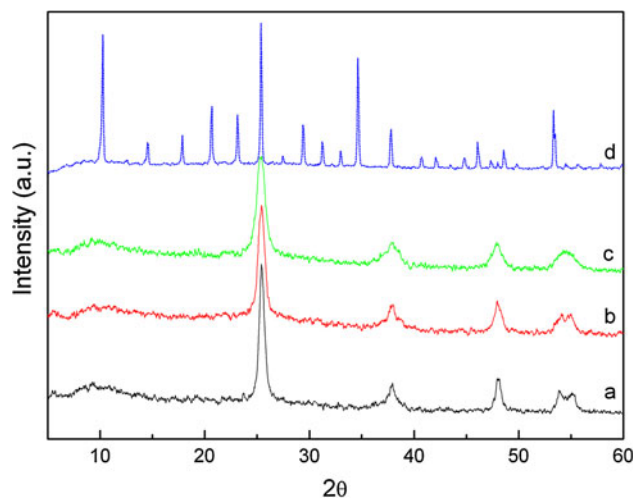

Fig. 3 XRD patterns of the of TiTPA00, TiTPA10, TiTPA20 and TPA

scale: Ei > 100 mV (very strong sites), 0 < Ei < 100 mV (strong sites), −100 < Ei < 0 (weak sites) and Ei < −100 mV (very weak sites) [34, 35].

The acid strengths of samples TiTPA10 (Ei = 348 mV) and TiTPA20 (Ei = 342 mV) were quite similar and markedly higher than that of sample TiTPA00 (Ei = 140 mV) (Fig. 4). However, they were lower than that of bulk TPA (Ei = 620 mV) [36] and almost independent of TPA concentration. The lower acid strength of the TiTPA samples compared to bulk TPA could be assigned to the fact that the protons in $H_3PW_{12}O_{40}.6H_2O$ are present as $H^+(H_2O)_2$ species, whereas in the TiTPA samples they are interacting with the oxygen of Ti–OH groups or in a higher hydration state $(H^+(H_2O)_n)$. This is in agreement with previous work [36]
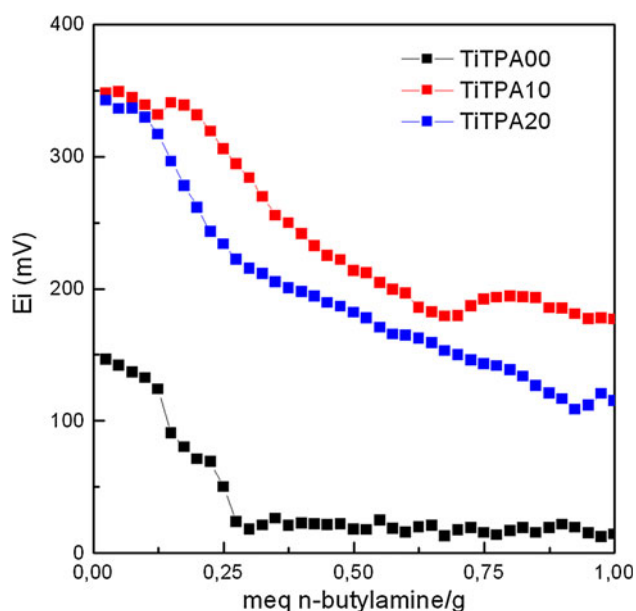
Fig. 4 Potentiometric titration curves of TiTPA00, TiTPA10, and TiTPA20 samples
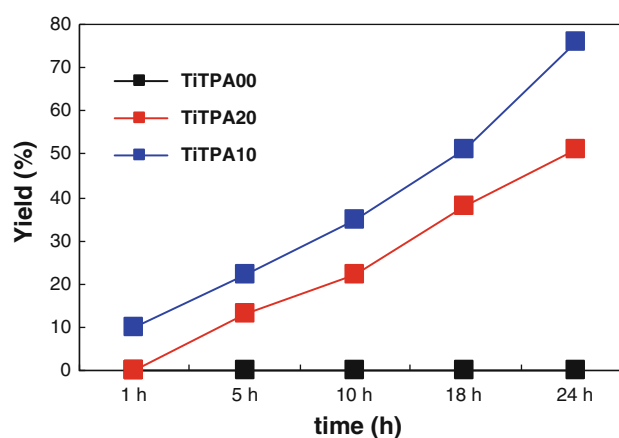

Fig. 5 Yield (%) of 6-chloroflavone versus time (h) for the different catalysts (TiTPA00, TiTPA10 and TiTPA20). Reaction conditions: 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione, 0.25 mmol; catalyst, 100 mg; solvent: toluene, 1 mL; temperature, 110 °C; reaction time, 24 h; stirring

reporting that $H_3PW_{12}O_{40} \cdot 21H_2O$, where the protons are highly hydrated, displayed lower acid strength ($E_i = 538$ mV) than $H_3PW_{12}O_{40} \cdot 6H_2O$, while the partially substituted salts $Cs(K)_{2.9}H_{0.1}PW_{12}O_{40}$ containing bare protons showed E_i in the range 900–1,000 mV.

On the other hand, the TiTPA10 sample displayed a higher number of acid sites determined by potentiometric titration than TiTPA20 (Fig. 4). This is assigned to the higher specific surface area and lower particle agglomerates of the TiTPA10 sample, which allows us to obtain materials with a higher amount of protons exposed on the surface than in the TiTPA20 sample.

3.2 Catalytic tests

We presented here the application of a heterogeneous system for the preparation of halogenated flavones in the presence of mesoporous titania/tungstophosphoric acid composites as reusable catalyst. The flavone synthesis involving the reaction of the cyclodehydration of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodiones using toluene or no reaction solvent was studied.

Before attempting detailed catalytic work, a noncatalytic reaction using 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione (0.25 mmol) and toluene (1 mL) was examined and it was observed that, under the experimental conditions (110 °C, 24 h), no formation of 6-chloroflavone was detected, indicating that from a practical point of view the reaction is not taking place in the absence of a catalyst.

The catalytic activity of TiTPA00, TiTPA10, and TiTPA20 catalysts in the reaction is displayed in Fig. 5. In all

cases, toluene was used as solvent at reflux temperature (110 °C). Under these experimental conditions, no detectable reaction occurred when the sample without TPA (TiTPA00) was used as catalyst.

In such conditions, the conversion attained using the TiTPA10 catalyst (76 %, 100 °C, 24 h) was higher than that reached using TiTPA20 (45, 100 °C, 24 h). Taking into account that he acid strengths of TiTPA10 ($E_i = 348$ mV) and TiTPA20 ($E_i = 342$ mV) samples were quite similar, we attribute the higher conversion of the TiTPA10 sample to the fact this material displayed a higher number of acid sites determined by potentiometric titration than TiTPA20 (Fig. 4). Additionally, we consider that the higher mesoporous surface area of the TiTPA10 sample (it is about 10 % higher than that of the TiTPA20) can be also responsible of its better catalytic activity.

Then, the influence of the reaction temperature on 6-chloroflavone synthesis was investigated using the best catalyst (TiTPA10) and the results are illustrated in Table 2. In order to obtain the optimal temperature, five temperatures (20, 50, 70, 90 and 110 °C, Table 2) were tested.

The tested experimental reaction conditions were: 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione, 0.5 mmol; toluene, 1 mL; 0.01 mmol catalyst (TiTPA10); time, 24 h. No reaction was observed at 20 and 50 °C (entries 1 and 2 in Table 2).

A temperature increase leads to a higher 6-chloroflavone yield. For example, the yield of 6-chloroflavone, for a reaction time of 24 h at 50 °C, was only 14 % (entry 3, Table 2) for TiOTPA10 catalysts, whereas at 90 °C the conversion was 54 % (entry 4, Table 2). Finally at 110 °C (toluene reflux) the yield was 76 % (entry 5, Table 2). For

this reason, 110 °C was employed as the ideal temperature to continue with the analysis of other reaction variables.

Table 3 displays the effect of the amount of catalyst (TiTPA10) on the yield of 6-chloroflavone in the reaction. The experimental reaction conditions were: 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione, 0.25 mmol; toluene, 1 mL; 24 h 110 °C, and a variable amount of TiTPA10 catalyst (25, 50, 100 and 150 mg, respectively). It can be seen that the conversion of yields increased from 20 to 76 % when the amount of TiTPA10 increased from 25 to 100 mg (Table 3, entries 1, 2 and 3). No relevant change of reaction yield was observed with further increase in the amount of TiTPA10 (150 mg) (74 %, Table 3, entry 4). Thus 100 mg of TiTPA10 is the suitable amount in this reaction.

The reusability of the catalysts was investigated in the sequential reaction of the cyclization of 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione using the catalysts TiTPA10 and TiTPA20. At the end of each run the catalyst was removed, washed with toluene, dried in vacuum at 40 °C and reused. The results, which are summarized in Table 4, showed that the catalysts were reused three consecutive runs and no appreciate loss of their catalytic activity was observed. Under the same reaction conditions, 6-chloroflavone yields were 75, 73 and 70 % when TiTPA10 was used as catalyst, and 48, 50 and 47 % when using TiTPA20 as catalyst.

Table 2 Effect of temperature on 6-chloroflavone yields (%)

Entry	Temperature (°C)	Yield (%)[a]
1	25	–
2	50	–
3	70	14
4	90	54
5	100	76

Reaction conditions: 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione, 0.25 mmol; solvent: toluene, 1 mL; catalyst: TiTPA10, 100 mg; reaction time: 24 h; stirring

[a] Isolated yield

Table 3 Effect of amount of catalyst on 6-chloroflavone yields (%)

Entry	Catalyst amount (%)	Yield (%)[a]
1	25	20
2	50	55
3	100	76
4	150	74

Reaction conditions: 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione, 0.25 mmol; solvent: toluene, 1 mL; catalyst: TiTPA10; reaction time: 24 h; temperature, 110 °C; stirring

[a] Isolated yield
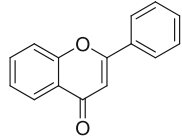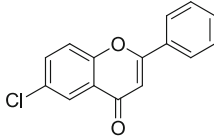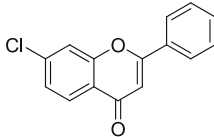
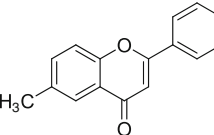**Table 4** Catalyst reuse in 6-chloroflavone synthesis
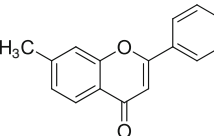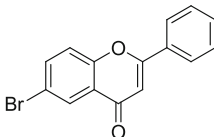
Entry	Cycle	Yield (%) TiTPA20[a]	Yield (%) TiTPA10[a]
1	0	51	76
2	1	48	75
3	2	50	73
4	3	47	70

Reaction conditions: 1-(2-hydroxy-5-chlorophenyl)-3-phenyl-1,3-propanodione, 0.25 mmol; solvent: toluene, 1 mL; catalyst: TiTPA10; 100 mg, reaction time: 24 h; temperature, 110 °C; stirring

[a] Isolated yield

Table 5 Preparation of flavones by TiOTPA10 in toluene and in solvent-free condition

Entry	Product	Yield (%) in toluene	Yield (%) solvent-free
1		72	78
2		76	92
3		70	74
4		70	76
5		71	76
6		69	72

Reaction conditions: In toluene: reaction conditions: substrate, 0.25 mmol; solvent: toluene, 1 mL; catalyst: TiTPA10; 100 mg, reaction time: 24 h; temperature, 110 °C; stirring

Reaction conditions: Solvent-free: reaction conditions: substrate, 0.25 mmol; catalyst: TiTPA10; 100 mg, reaction time: 1 h; temperature, 110 °C; stirring

An additional test was performed in order to evaluate the possible catalyst solubilization. A TiTPA10 sample was refluxed in toluene for 24 h, filtered and dried in vacuum till constant weight. The activity of the so-treated catalyst was the same as that of the fresh catalyst (76 % in 24 h). The refluxed toluene was used as solvent for attempting the reaction without adding the catalyst. After 24 h no product was detected and the starting material was quantitatively recovered.

Finally, the reaction was extended to various 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanodiones substrates by using the catalytic amount (100 mg) of TiTPA10 as active catalyst. TiTPA10 was used in toluene at 110 °C and without reaction solvent at the same temperature. The results are summarized in Table 5. In both cases, the desired products were obtained with high selectivity, almost free of secondary products. The solvent-free condition appears to be more convenient because the reaction yields are higher and the reaction times are shorter.

4 Conclusions

Mesoporous titania/tungstophosphoric acid composite materials were prepared using urea as pore-forming agent, via sol–gel reactions. FT-IR and ^{31}P MAS-NMR results indicated that the main species present in the samples is the $[PW_{12}O_{40}]^{3-}$ anion, which was partially transformed into $[P_2W_{21}O_{71}]^{6-}$ and $[PW_{11}O_{39}]^{7-}$ anions during the synthesis and drying steps. The prepared catalysts presented suitable acid and textural properties to use them as catalysts in heterogeneous acid reactions. The best catalytic performance was shown by the TiTPA10 sample that displayed the highest specific surface area and number of acid sites.

The described procedure for the synthesis of flavones using mesoporous titania modified with tungstophosphoric acid in toluene as solvent and in no reaction solvent results in a clean and useful alternative; the advantages of this methodology are operative simplicity, use of a reusable and noncorrosive solid acid catalyst, soft reaction conditions, low reaction times, and good yields. The use of a solid acid catalyst instead of the usual soluble acid catalyst (sulfuric, hydrochloric, etc.) contributes to a reduction in waste generation by allowing an easy separation and recovery without any loss of its catalytic activity.

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