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Trifluoromethanesulfonic acid supported on carbon used as catalysts in the synthesis of flavones and chromones

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ABSTRACT

Solid acid catalysts based on trifluoromethanesulfonic acid (TFMS) were synthesized using two different activated carbons as supports. They were characterized by FT-IR, DTA–TGA and BET, and their acidity was measured by potentiometric titration with *n*-butylamine. The new catalysts were checked for the cyclization of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione. The reaction experiments were performed using toluene as the solvent, at reflux. In all cases the product (flavone) was obtained with high selectivity. Conversions up to 84% were obtained using the supported catalyst $TFMSC_2$. The activity of the catalysts is strongly dependent on the textural properties of the support used to obtain them, particularly their mean pore size. Optimal reaction conditions were applied to the preparation of seven substituted flavones and chromones.

1. Introduction

The processes used in the industry for the manufacture of specialty chemicals in the field of pharmaceutical, agrochemical and flavor/fragrance products are largely based on stoichiometric organic syntheses, but these lead to a large quantity of by-products consisting of inorganic salts that now pose a serious waste-disposal problem [1]. The transformation used for the preparation of such fine chemicals is carried out in very environmentally unfriendly conditions, using homogeneous catalysts such as inorganic acids, Lewis acids, or organic bases that generate large amounts of corrosive and toxic waste products from which the catalysts are very difficult to recover [2].

Due to the environmental problem affecting all societies, the emphasis on the green aspects of chemical processes will be appreciated. In order to overcome these problems, the use of heterogeneous catalysts is a possibility. Different solid acid catalysts such as inorganic oxides, mixed oxides, including alumina, silica, titania, zirconia, zeolites, clays, Al–MCM-41, and supported reagents have been used [3].

Trifluoromethanesulfonic acid (TFMSA or triflic acid) is known to be a strong acid suitable to be used as catalyst for synthetic applications. It is used in different organic transformations including polymerization [4], Friedel Crafts acylation [4], Koch carbonylations [5], benzylation of aromatics [6], alkene coupling [7], and transalkylation [8]. However, the recovery of the triflic acid from the reaction mixture results in the formation of large amounts of waste. [9].

The design of acid-catalyzed reactions over solids needs further research in this area, and supported triflic acid or material with $-CF_2SO_3H$ groups is now becoming available to replace homogeneous acid solutions [10]. Different catalytic systems have been studied in which TFA is adsorbed on various solids such as acylation of 2-methoxynaphthalene [11] and acylation of alcohols over silica-embedded triflate catalysts [12], alkylation of hydroquinone with tert-butanol and alkylation of phenol and naphthols over silica-immobilized triflate derivatives [13,14], alkylation of isobutane with TFA absorbed on SiO_2 [15], acetalization of ethyl acetoacetate and benzoylation of biphenyl using triflic acid-functionalized mesoporous Zr-TMS catalysts [9], nitration and esterification of aromatic compounds over CF_3SO_3H/SiO_2 [10], and dithioacetalization and transdithioacetalization over polystyrene-supported aluminum chloride and triflic acid [16].

In previous studies [17–19], it was proved that mesoporous titania synthesized via sol–gel reactions using urea as a low-cost pore-forming agent is a support with suitable properties to obtain TFMSA-based catalysts for acidic reactions.

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Active carbons are solids that can be obtained with different pore size distributions, from the exclusively microporous types to those having a high proportion of meso- and macroporosity. Their specific surface areas can exceed 1000 m^2/g depending on the precursor type and the experimental conditions of the preparation stage. On the other hand, their different surface functional groups confer them distinct properties of interaction with the precursor.

Activated carbon has been used to prepare tungstophosphoric and tungstosilicic supported acid catalysts [20]. The solids thus obtained, which present strongly adsorbed species on the support, can be used as catalysts in liquid-phase reactions without an appreciable loss of the active phase, so being attractive for many processes in replacement of conventional liquid catalysts.

To the best of our knowledge, there have been no reports in the literature about the use of carbon as support of trifluoromethanesulfonic acid.

On the other hand, flavones and chromones are compounds belonging to the flavonoid group, which are found in a wide variety of plants [21]. They exhibit multiple biological properties: antibacterial, antifungal [22], anticancer [21], antioxidant [23], anti-HIV [24] and antifeedant activity [25].

One of the most commonly used methods for the synthesis of flavones, chromones and their analogs is the cyclodehydration of 1-(2-hydroxyphenyl)-1,3-diketones. This reaction has been carried out under strongly acidic conditions using acetic acid and sulfuric acid [26].

In the present work, the synthesis and characterization of trifluoromethanesulfonic acid supported on two different activated carbons are presented. The acidic characteristics of the solids were determined by potentiometric titration with *n*-butylamine. The catalytic activity of the materials was tested in the production of flavone and chromone derivatives.

2. Experimental

2.1. Synthesis of supported trifluoromethanesulfonic acid catalysts

The supports employed were two commercial wood-based activated carbons ground to a mean particle size of 1 mm, named C_1 and C_2 hereinafter. Before being impregnated, these materials were washed first in a solution of NaOH 0.1 mol/dm^3 and then in HCl 0.1 mol/dm^3 to eliminate the soluble acidic and alkaline impurities. Finally, they were chemically treated in a solution of HNO_3 30% w/v heated by reflux for 2 h, and washed with distilled water up to neutral pH. The treatment with nitric acid makes the carbon more acidic [27] and shifted the isoelectric point from 6.9 to 2.7. Their textural features are shown in Table 1.

Trifluoromethanesulfonic acid, CF_3SO_3H, (0.01 mol, Alfa Aesar, 99%) was added dropwise to the mixture of mesoporous titania (2 g) and toluene (20 cm^3, Merck) at 90 °C under nitrogen atmosphere; then it was further refluxed for 2 h. Next, the sample was cooled, filtered, washed with acetone (Mallinckrodt AR) and dried at 100 °C for 24 h.

The solids were extracted with a mixture of dichloromethane and diethyl ether (50% v/v) (100 cm^3 of mixture per gram of catalyst) for three periods of 8 h using a Soxhlet apparatus in order to remove the acid weakly attached to the support. Afterwards, they were dried again at 100 °C for 24 h. The samples were named $TFMSC_1$ and $TFMSC_2$.

Table 1
Textural properties of carbons employed as supports.

Support	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (nm)
C_1	804	0.74	<2.5
C_2	478	0.82	<4.5

2.2. Catalysts characterization

The specific surface area of the solids was determined from N_2 adsorption–desorption isotherms at liquid-nitrogen temperature. They were obtained using Micromeritics ASAP 2020 equipment. The samples were previously degassed at 100 °C for 2 h.

FT-IR spectra of the supports and catalysts were obtained in the 400–4000 cm^{-1} wavenumber range using a Bruker IFS 66 FT-IR spectrometer.

The TGA–DTA measurements of the solids were carried out using a Shimadzu DT 50 thermal analyzer. The thermogravimetric and differential thermal analyses were performed under argon or nitrogen, respectively, using 25–50 mg samples and a heating rate of 10 °C/min. The studied temperature range was 20–700 °C.

The acidity of the solid samples was measured by means of potentiometric titration. The solid (0.05 g) was suspended in acetonitrile (Merck) and stirred for 3 h. The suspension was then titrated with 0.05 N *n*-butylamine (Carlo Erba) in acetonitrile at 0.05 cm^3/min. The electrode potential variation was measured with a Hanna 211 digital pH meter using a double-junction electrode.

2.3. Synthesis of flavone

1-(2-Hydroxyphenyl)-3-phenyl-1,3-propanedione was prepared following a procedure described elsewhere [28].

Initially, we tested the two catalysts in the cyclization of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavone. The reactions were carried out by adding the corresponding catalyst (40 mg) to a solution of 1 mmol of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione in refluxing toluene (4 ml, Baker). The suspension was stirred at 110 °C for 1 h. Then the catalyst was separated by filtration and washed twice with toluene (1 ml). The extracts were combined and washed with 10% sodium hydroxide, then with H_2O, and dried with anhydrous sodium sulfate. The organic solution was concentrated in vacuum. The solid crude product was recrystallized from methanol. The conversion was calculated as the ratio of mmoles of product to mmoles of initial propanedione.

Then the best performing catalyst was chosen to study the reaction as a function of time by means of UV/Vis spectroscopy. The absorbance values of samples at different reaction times were determined at 420 nm, using a UV/Vis spectrometer LAMBDA 35, Perkin Elmer.

Flavone. mp: 97–98 °C (methanol) (lit. mp: 98 °C [28]); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.3, 117.9, 123.7, 124.9, 125.5, 126.0, 129.0, 131.5, 131.8, 133.5, 155.9, 163.1, 177.9; ^1H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 1H), 7.41 (ddd, 1H, J = 1.0, 7.2, 8.2 Hz), 7.49–7.56 (m, 4H), 7.68 (ddd, 1H, J = 1.7, 7.2, 8.3 Hz), 7.92–7.95 (m, 2H), 8.23 (dd, 1H, J = 1.8, 8.2 Hz).

2.4. Synthesis of substituted flavones and chromones

The best performing catalyst was used to prepare different substituted flavones and chromones. All the starting 1,3-diketones were prepared following a procedure described elsewhere [29].

A mixture of 1,3-diketone (1 mmol) dissolved in 4 ml toluene and catalyst (40 mg) was refluxed with stirring for 5 h. The reaction was followed by TLC using TLC aluminum sheets (silica gel 60 F_{254} Merck). When the reaction time was over, the catalyst was separated by filtration and washed twice with toluene (1 ml). The extracts were combined and washed with 10% sodium hydroxide, then with H_2O, and dried with anhydrous sodium sulfate. The organic solution was concentrated in vacuum. All the solid crude products were recrystallized from methanol or hexane. The conversion was calculated as the ratio of mmoles of products to mmoles of initial propanedione.

7-Chloroflavone: mp: 159–160 °C (methanol) (lit. mp: 156–157 °C [30]); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 107.2, 118.2, 122.4, 126.0, 126.3, 126.8, 129.0, 131.3, 131.7, 139.6, 156.0, 163.2, 177.9; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.82 (s, 1H), 7.42 (dd, 1H, *J* = 1.9, 8.4 Hz), 7.52-7.55 (m, 3H), 7.61 (d, 1H, *J* = 1.9 Hz), 7.90–7.93 (m, 2H), 8.22 (d, 1H, *J* = 8.4 Hz).

7-Bromoflavone: mp: 164–165 °C (methanol) (lit. mp: 167–168 °C [30]); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.5, 121.1, 122.4, 126.0, 126.4, 128.1, 128.6, 128.9, 131.3, 131.5, 155.3, 163.5, 177.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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).

2-(2-Naphthyl)chromone: mp: 162–163 °C (methanol) (lit. mp: 164–165 °C [31]); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.9, 118.1, 122.3, 124.0, 125.2, 125.7, 126.7, 126.9, 127.6, 128.0, 128.7, 128.7, 129.1, 132.9, 133.8, 134.5, 156.3, 163.4, 178.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 7.43 (ddd, 1H, *J* = 1.6, 6.6, 7.9 Hz), 7.54–7.60 (m, 2H), 7.63 (d, 1H, *J* = 8.0 Hz), 7.72 (ddd, 1H, *J* = 1.6, 6.6, 7.9 Hz), 7.87–8.05 (m, 4H), 8.23 (dd, 1H, *J* = 1.5, 7.9 Hz), 8.46 (s, 1H).

2-(1-Naphthyl)chromone: mp: 142–143 °C (methanol) (lit. mp: 138–139 °C [31]); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.1, 118.2, 124.0, 124.8, 125.0, 125.3, 125.8, 126.6, 127.4, 127.9, 128.7, 130.3, 130.7, 131.5, 133.7, 133.8, 156.7, 165.4, 178.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H), 7.49 (dt, 1H, *J* = 0.9, 7.6 Hz), 7.55–7.63 (m, 4H), 7.74 (dt, 1H, *J* = 1.8, 7.8 Hz), 7.79 (dd, 1H, *J* = 1.2, 7.2 Hz), 7.96–7.99 (m, 1H), 8.05 (d, 1H, *J* = 8.3 Hz), 8.15–8.18 (m, 1H), 8.34 (dd, 1H, *J* = 1.5 Hz).

7-Chloro-2-(2-naphthyl)chromone: mp: 219–220 °C (hexane) (lit. no data); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 108.1, 118.2, 122.4, 122.7, 126.1, 127.0, 127.2, 127.2, 127.9, 128.2, 128.7, 129.1, 129.1, 133.0, 134.8, 139.8, 156.5, 163.5, 177.4; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.93 (s, 1H), 7.39 (dd, 1H, *J* = 2.0, 8.6 Hz), 7.55–7.63 (m, 2H), 7.66 (d, 1 H, *J* = 2.0 Hz), 7.86–7.98 (m, 4 H), 8.18 (d, 1 H, *J* = 8.6 Hz), 8.45 (s, 1 H).

7-Chloro-2-(1-naphthyl)chromone: mp: 198–199 °C (methanol) (lit. mp: 198–199 °C [32]); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.3, 118.3, 122.5, 124.7, 125.1, 126.2, 126.7, 127.2, 127.6, 128.0, 128.8, 130.2, 130.3, 131.7, 133.7, 139.9, 156.8, 165.6, 177.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 (s, 1 H), 7.46 (dd, 1 H, *J* = 1.9, 8.5 Hz), 7.58–7.63 (m, 4 H), 7.78 (dd, 1 H, *J* = 1.1, 7.2 Hz), 7.97–7.99 (m, 1 H), 8.06 (d, 1H, *J* = 8.2 Hz), 8.12–8.14 (m, 1H), 8.26 (d, 1H, *J* = 8.6 Hz).

7-Methyl-2-(1-naphthyl)chromone: mp: 162–163 °C (methanol) (lit. no data); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 21.8, 113.0, 118.0, 121.9, 124.9, 125.0, 125.6, 126.5, 126.8, 127.3, 127.8, 128.7, 130.5, 130.9, 131.4, 133.8, 145.2, 156.9, 165.1, 178.1; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.50 (s, 3H), 6.65 (s, 1H), 7.27 (d, 1H, *J* = 9.3 Hz), 7.32 (s, 1H), 7.54–7.60 (m, 3H), 7.75 (dd, 1H, *J* = 0.8, 6.7 Hz), 7.92–7.96 (m, 1H), 8.01 (d, 1H, *J* = 8.3 Hz), 8.11–8.15 (m, 1H), 8.18 (d, 1H, *J* = 8.1 Hz).

3. Results and discussion

3.1. Catalyst characterization

The specific surface areas (S_{BET}) of the $TFMSC_1$ and $TFMSC_2$ catalysts (798 and 465 m^2/g, respectively) are slightly lower than that of the corresponding support. However, both the mean pore diameter and pore volume remain unchanged.

The FT-IR spectrum of the $TFMSC_1$ and $TFMSC_2$ samples displays bands at 1269, 1180, and 1035 cm^{-1} in addition to those ascribed to the supports. The first two bands are due to the S=O stretching mode of the adsorbed trifluoromethanesulfonic acid and the last one is assigned to the C–F stretching [33].

TGA diagrams of C_1 (Fig. 1) and C_2 supports showed a rapid decrease in weight below 100 °C and a continuous weight loss from 160 °C to 600 °C. The first step is due to the loss of physically adsorbed water, and the second to carbon degradation. [20]. The DTA diagrams of both supports only presented an endothermic peak at 75–80 °C, associated with the loss of physically adsorbed water.

From the comparison between the TGA diagrams of $TFMSC_1$ and C_1 samples, we can conclude that the elimination of the TFMS firmly adsorbed onto the support took place between 130 and 480 °C. The amount of acid that was firmly adsorbed onto the support (W_{TFMS}) was estimated from TGA diagrams using the following expression:

$$W_{TFMS} = (W_{TFMSCx} - W_{Cx})/FW_{TFMS}$$

where W_{TFMSCx} is the weight loss of TFMS catalyst from 130° C to 500 °C (mg/g), W_{Cx} is the weight loss of C_x support from 130° C to 500 °C (mg/g), FW_{TFMS} is the CF_3SO_3H molecular weight.

The amount of TFMS firmly adsorbed on C_2 (W_{TFMS} = 0.75 mmol CF_3SO_3H/g) was higher than that on C_1 (W_{TFMS} = 0.68 mmol CF_3SO_3H/g). The interaction between the trifluoromethanesulfonic acid and carbon could be assumed to be of electrostatic type due to the transfer of protons to the different functional groups of activated carbon [34]. At low pH values, groups such as hydroxyl, diol or ether can be protonated, together with other less basic groups. The amount and type of groups available to be protonated depend on the nature and physicochemical treatments of the carbon. The lower W_{TFMS} value obtained for C_1 was the result of a lower concentration of this kind of group in the support.

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. As a criterion to interpret the obtained results, it was suggested that the initial electrode potential (Ei) indicates the maximum acid strength of the sites, and the value of meq amine/g solid where the plateau is reached indicates the total number of acid sites [35]. Nevertheless, the end point of the titration given by the inflexion point of the curve is a good measure to carry out a comparison of the acidity of different samples. On the other hand, the acid strength of these sites may be classified according to the following 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).

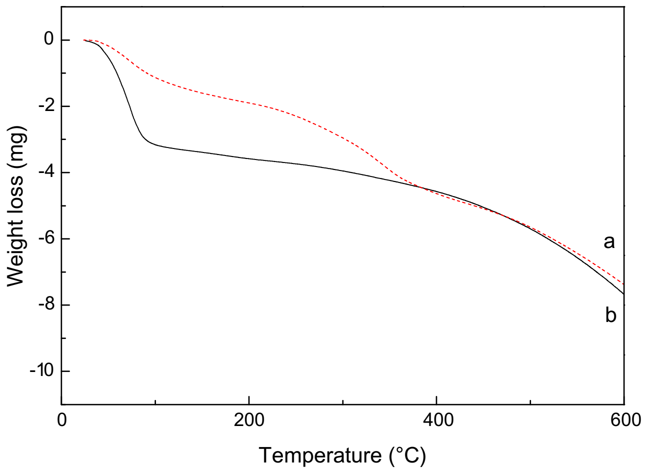


Fig. 1. TGA diagrams of $TFMSC_1$ (a) and C_1 (b) samples.

The titration curves of the catalysts are shown in Fig. 2. According to the previous classification, both $TFMSC_1$ (Ei = 682 mV) and $TFMSC_2$ (Ei = 647 mV) samples present very strong acid sites. The acid strength of the $TFMSC_1$ catalyst was slightly higher than that of the $TFMSC_2$ one, probably because the C_1 (Ei = 135 mV) support displayed a higher acid strength than C_2 (Ei = 6 mV).

The $TFMSC_1$ catalyst showed a lower number of acid sites than $TFMSC_2$, as a consequence of the lower amount of acid firmly adsorbed on the support.

3.2. Catalytic activity

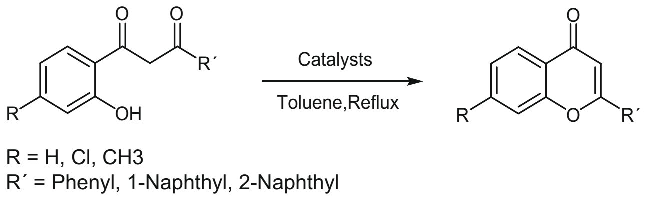
Initially, $TFMSC_1$ and $TFMSC_2$ were used as catalysts for the cyclization reaction of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione to flavone (Scheme 1), in refluxing toluene, for a reaction time of 1 h. Under such conditions, a higher conversion was attained using the $TFMSC_2$ catalyst (53%) than using $TFMSC_1$ (11%), probably as a result of the higher content of TFMS and the higher mean pore diameter. In all the cases, flavone was the only product formed.

In order to study the influence of the particle size on the conversion, we performed some tests using $TFMSC_1$ and $TFMSC_2$ catalysts ground in a mortar. The conversion using different solid fractions obtained by grinding and sieving both the $TFMSC_1$ and $TFMSC_2$ catalysts is shown in Fig. 2. It can be observed that the particle size does not have an important influence on the catalyst performance.

The 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione conversion obtained using $TFMSC_2$ as a function of time is shown in Fig. 3. The reaction time required for reaching the maximum conversion was 300 min. It was observed that for the same reaction time, the conversion obtained when the C_2 support was used as catalyst was lower than 5%.

On the other hand, the spent $TFMSC_2$ catalyst was washed with toluene, dried at room temperature and then reused. The change of conversion with time for the washed catalyst is compared with that of the fresh one in Fig. 3. As can be seen, the conversion is lower when the reaction is performed with the reused catalyst. The lowering of activity could be due to the adsorption of reagent and/or product onto the catalyst surface.

To gain an insight into this behavior, the spent $TFMSC_2$ catalyst was refluxed in chloroform, a more polar solvent, for 2 h. The analysis of the extract indicates that the spent catalyst retains flavone. Substituted 1,3-propanedione could not be detected.



Scheme 1. Synthesis of flavones.

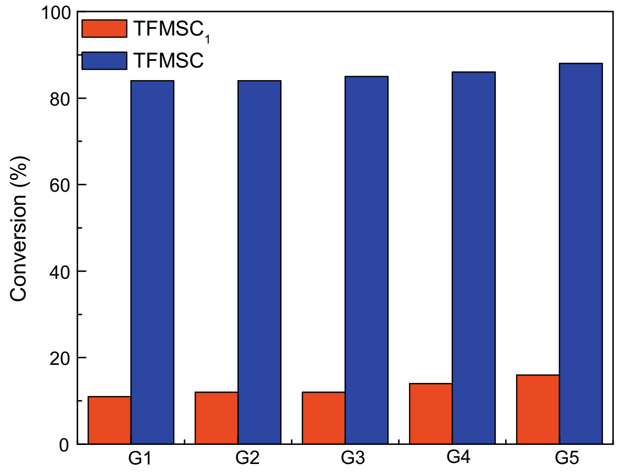


Fig. 3. 1-(2-Hydroxyphenyl)-3-phenyl-1,3-propanedione conversion at 3 h under reaction using different ground fractions of $TFMSC_1$ and $TFMSC_2$ catalysts: G1: ground in a mortar, G2: sieve 20 (>840 μm), G3: sieve 20–30 (840–590 μm), G4: sieve 30–40 (590–420 μm), G5: sieve 40–140 (420–105 μm).

We found that after this treatment, the activity of the catalyst could be completely restored (Fig. 3). The catalyst treated in this way displayed a similar yield during the second and the third reuse (92% and 93%, respectively).

In order to evaluate the possible catalyst solubilization, an additional test was performed. The $TFMSC_2$ sample was refluxed in toluene for 2 h, filtered and dried in vacuum till constant weight. The activity of the so treated catalyst was the same as that of the fresh

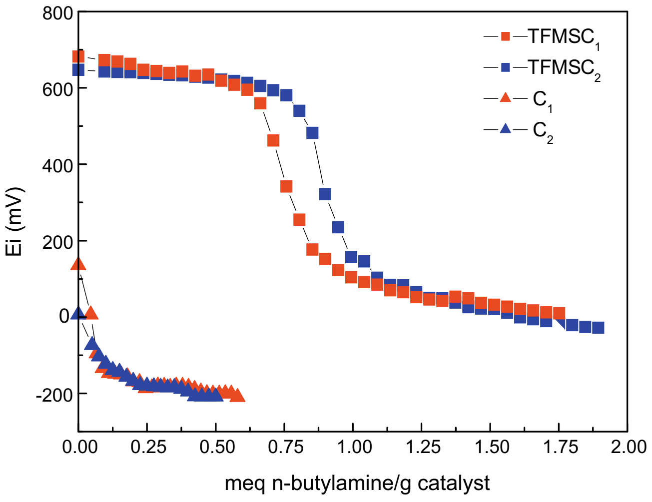


Fig. 2. Potentiometric titration curves of $TFMSC_1$ and $TFMSC_2$ catalysts and the corresponding supports.

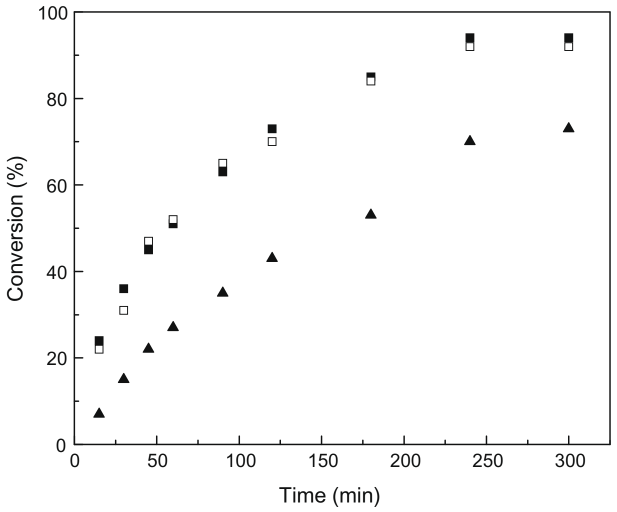
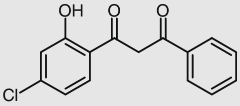
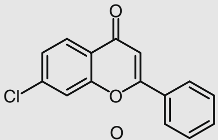
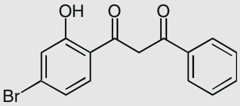
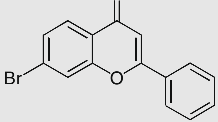
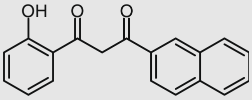
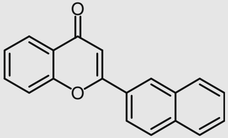
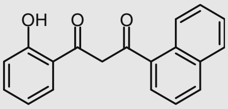
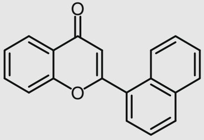
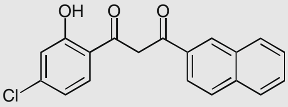
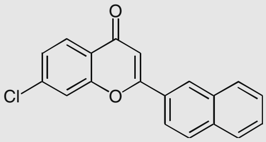
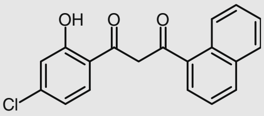
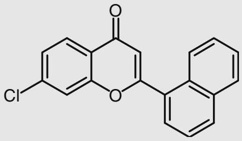
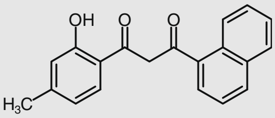
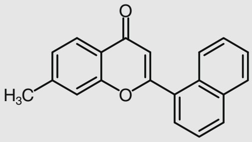


Fig. 4. Conversion of 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione as a function of time for: fresh (■), washed (▲) and refluxed (□) $TFMSC_2$ catalyst.

Table 2
Synthesis of flavones and naphthylchromones using $TFMSC_2$ in toluene at reflux for 300 min.

Entry	Diketone	Flavone/chromone 2	Yield 2 (%)
1			86
2			87
3			88
4			86
5			86
6			82
7			82

catalyst (92% in 5 h). The refluxed toluene was used as solvent for attempting the reaction without adding the catalyst. After 5 h flavone was not detected and the starting material was quantitatively recovered (Fig. 4).

In Table 2, we report the catalytic activity of $TFMSC_2$ in the preparation of substituted flavones and 2-naphthylchromones from 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones (see Scheme 1). The experiments were carried out in refluxing toluene in the presence of 40 mg catalyst, till consumption of 1,3-diketone or until no changes in the composition of the reaction mixture were observed for TLC. In all cases, the desired products were obtained with high selectivity, and almost free of secondary products. The unchanged starting materials were recovered nearly quantitatively. Yields of flavones were similar to those of naphthylchromones (see Table 2).

4. Conclusions

The $TFMSC_1$ and $TFMSC_2$ catalysts were prepared by adsorption of trifluoromethanesulfonic acid (TFMS) on two activated carbons with different textural properties used as supports.

According to the potentiometric titration measurements, the catalysts present very strong acid sites. Their acid strength and the amount of acid firmly adsorbed depend on the type of activated carbon used as support.

The $TFMSC_2$ catalyst used as solid catalyst provided interesting yields in the cyclization reaction of 1-(2-hydroxyphenyl)-3-aryl-1,3-propanediones to flavones and chromones, also leading to an easy separation and recovery of the catalysts for further use. Moreover, as a significant decrease of the catalytic activity was not observed, they can be recycled without any activity loss.

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