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ARTICLE

p-Sulfonic acid calix[4]arene-functionalized alkyl-bridged organosilica in esterification reactions

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Two new *p*-sulfonic acid calix[4]arene- and *p*-sulfonic acid calix[6]arene-functionalized organosilica have been synthesized using the sol-gel method and applied as heterogeneous catalysts in esterification reactions. The catalytic performance was evaluated using the esterification of carboxylic acids with ethanol, and good catalytic activity (i.e., 55-88%) was observed under the optimum reaction conditions. This study reports the first promising example of successful employment of calix[*n*]arenes as a heterogeneous catalyst for catalytic esterification. The catalyst was easily separated by filtration and reused five times without any significant loss of activity.

Introduction

Esters are among the most important functional groups in organic synthesis due to their usefulness.[1] Esters have attracted more attention due to their wide applications in polymers, plastic derivatives, perfumes, flavours, chemicals, pharmaceutical and agrochemicals intermediates, and biodiesel.[2]

However, to develop an environmentally benign process and simplify the existing processes associated with homogeneous acid catalysts, substantial efforts have been focused on exploring heterogeneous solid acid catalysts, which offer significant advantages, such as easy recovery, little corrosion, low toxicity and environmental safety.[3] Recently, the combination of the chemical properties of organo-sulfonic acid catalysts and the physical properties of different nanomaterials has been a subject of great interest in heterogeneous catalysis.[3a,4]

In last two decades, research interest in calix[*n*]arene chemistry has increased dramatically due to their applications in several fields of chemistry related to supramolecular chemistry including molecular recognition[5], self-assembling systems[6], mechanically interlocked molecules[7], and nanoporous materials[8]. The application of calix[*n*]arenes as catalysts in organic transformations has become very popular.[9] In addition, we have recently reported excellent results for the esterification of carboxylic acids using *p*-sulfonic acid calix[4]arene ($CX4SO_3H$) or *p*-sulfonic acid calix[6]arene ($CX6SO_3H$) as a homogeneous catalyst (Fig. 1).[10] In this study, we report novel calix[*n*]arenes catalysts with Brønsted acid and heterogeneous properties as well as results from esterification reactions to synthesize carboxylic esters. To the best of our knowledge, this is the first application of *p*-sulfonic acid calix[*n*]arenes as heterogeneous catalysts in these esterification reactions.

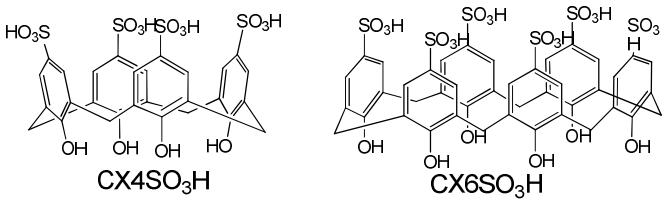

Fig. 1 Molecular structures of the two catalysts: *p*-sulfonic acid calix[4]arene ($CX4SO_3H$) and *p*-sulfonic acid calix[6]arene ($CX6SO_3H$).

Results and discussion

To develop catalytic methodologies with easy recovery, little corrosion, low toxicity and environmental safety for the esterification of carboxylic acids, we designed an effective system using calix[*n*]arenes as a heterogeneous catalyst (Scheme 1).

Scheme 1 Synthesis of catalysts **1a** and **1b**.

p-Sulfonic acid calix[4]arene ($CX4SO_3H$) and *p*-sulfonic acid calix[6]arene ($CX6SO_3H$) were synthesized in our laboratory

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(Scheme 1) according to previously reported protocols.[11] Catalysts **1a** and **1b** were synthesized using a sol-gel technique. A mixture of $CX4SO_3H$ or $CX6SO_3H$, water and a hydrochloric acid solution was added to tetraethyl orthosilicate. The mixture was stirred for 5 h at room temperature. Then, the mixture was allowed to stand for 3 days, and after breaking the formed hydrogel with a Teflon stick, the sample was dried in a vacuum for one week at room temperature (Scheme 1 and Fig. 2). Catalysts **1a** and **1b** were characterized based on acidity and XRD.

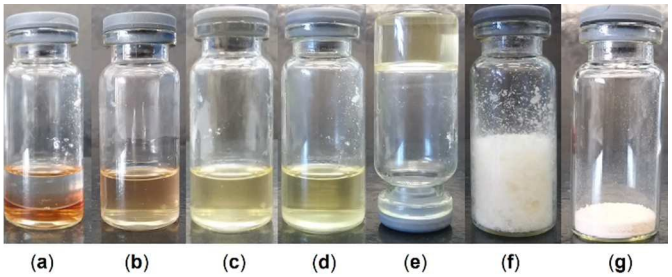

Fig. 2 Formation of the **1a**-based hydrogel induced by TEOS. (a) 0 h, (b) 1 h, (c) 24 h, (d) 72 h, (e) 72 h, (f) after breaking the formed hydrogel, and (g) hydrogel after washing and drying in a vacuum.

The ion exchange capacities of **1a** were determined by acid-base titration and potentiometric titration. The acid capacity of the sample (catalyst 15 %) was determined by titration with 5 x 10^{-3} M NaOH (aq).[12] The result in terms of mmol H^+/g for the catalyst was 0.32 mmol H^+/g catalyst. The strength of the acid sites can be classified according to the following scale: E > 100 mV (very strong sites); 0 <E< 100 mV (strong sites); −100 <E< 0 mV (weak sites) and E < −100 mV (very weak sites).[13] The acid strength for 15% catalyst was 205 mV, indicating the presence of very strong sites.

Typical XRD patterns of amorphous materials were observed for the supported **1a** samples in Fig. 3. The XRD pattern peaks were obtained between 5° and 50°. The absence of crystalline **1a** peaks in the XRD pattern of the supported samples cannot be ruled out because they may be less than 40 Å in size, which is beyond the detection limit of the XRD technique. The broad X-ray diffraction patterns may indicate long-range disordered nature

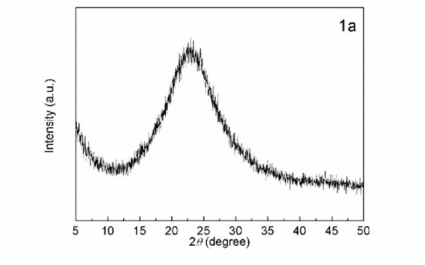

Fig. 3 XRD patterns of catalyst **1a**.

For the initial investigation of the use of **1a** and **1b** as catalysts for esterification, palmitic acid and ethanol were employed as substrates under the optimal reaction conditions (i.e., catalyst loading, time, and reuse of the catalyst). The results from the optimization of the catalyst concentration (2.0 mol %, 2.5 mol % and 5 mol %) are listed in Table 1. The evaluation of three concentrations of catalyst **1a** indicated a slight increase in the conversion of palmitic acid to ethyl palmitate (Table 1, entries 1-3). For catalyst **1b**, an increase in the catalyst concentration had a significant effect on the yield of ethyl palmitate (Table 1, entries 4-6). The differences observed between the catalytic activities of **1a** and **1b** may be due to the presence of water, which is a by-product of the esterification reaction.

Table 1 Effect of the amount of catalyst **1a** or **1b** and time on the conversion of ethyl palmitate.[a]

Entry	Catalyst	Catalyst (mol %)	Time (h)	Yield (%)[b]
1	**1a**	2	4	88
2	**1a**	2.5	4	91
3	**1a**	5	4	91
4	**1b**	2	4	67
5	**1b**	2.5	4	78
6	**1b**	5	4	87
7	**1a**	2	6	90
8	**1a**	2	8	93

[a]*Reaction conditions:* palmitic acid (100 mg) and ethanol (10 mL) was performed at 80 °C. [b]Analysed by GC-MS and ^{1}H NMR.

As described by Fernandes *et al.* in 2014, *p*-sulfonic acid calix[*n*]arenes catalytic activity is affected by increasing the amount of water, and this effect was more pronounced for *p*-sulfonic acid calix[6]arene.[10a] Therefore, catalyst **1a** exhibited the best conversion, and the concentration used for subsequent studies was 2 mol %. The effect of time on the conversion of palmitic acid to ethyl palmitate was also investigated (Table 1). The conversion of ethyl palmitate increased slightly from 88% to 90% and 93% with prolonged reaction times of 4 h, 6 h and 8 h (Table 1, entries 1, 7 and 8). Based on the conversion and selectivity results, a reasonable reaction time is 4 h.

The catalytic activities of the heterogeneous catalysts (**1a** and **1b**) were compared to those of the $CX4SO_3H$ and $CX6SO_3H$ homogeneous catalysts (Table 2). The $CX4SO_3H$ and $CX6SO_3H$ homogeneous catalysts exhibited catalytic activities that were similar to that of **1a** and higher than that of catalyst **1b** (Table 2, entries 1-4). Similarly, both strong Brønsted acid heterogeneous amberlyst 15 and $H_3PW_{12}O_{40}$ exhibited a lower activity than the **1a** catalyst, and the ethyl palmitate yield did not exceed 80% (Table 2, entries 5 and 6). The ethyl palmitate yield in the catalyst-free or matrix (TEOS) reactions was lower than 5% (Table 1, entries 7 and 8).

To determine if catalyst leaching occurred, an experiment using the optimal reaction conditions was performed for only 1 h.

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Then, the mixture was cooled, catalyst **1a** was removed by filtration, and the conversion of palmitic acid was confirmed. The mixture was heated again at 80 °C for 3 h but no significant reaction progress was observed, demonstrating that leaching did not occur.

Table 2 Effect of different catalysts on the conversion of palmitic acid to ethyl palmitate.[a]

Entry	Catalyst	Catalyst (mol%)	Yield (%)[c]
1	**1a**	2[b]	88
2	**1b**	2[b]	67
3	**$CX4SO_3H$**	2	91
4	**$CX6SO_3H$**	2	89
5	**Amberlyst 15**	2	79
6	**$H_3PW_{12}O_{40}$**	2	67
7	**TEOS**	2	< 5
8	**-**	2	< 5

[a]*Reaction conditions:* palmitic acid (100 mg); ethanol (10 mL) was performed at 80 °C and time (4 h). [b]Active phase ($CX4SO_3H$ or $CX6SO_3H$). [c]Analysed by GC-MS and ^1H NMR.

Once the optimal conditions for the formation of carboxylic esters using **1a** as the catalyst were determined, the scope of this protocol was further investigated (Table 3). According to the data in Table 1, good to high yields were obtained in the esterification reactions of carboxylic acids in the presence of catalyst **1a**. The carboxylic acids (Table 3) were converted to esters in yields ranging from 55-88% using catalyst **1a**.

Table 3 Esters yields obtained in esterification reactions catalysed by **1a**.[a]

Entry	Carboxylic acid	Yield (%)[b]
1	**palmitic acid**	88
2	**acetic acid**	83
3	**butyric acid**	86
4	**caprylic acid**	81
5	**oleic acid**	76
6	**stearic acid**	55
7	**myristic acid**	59

[a]*Reaction conditions:* carboxylic acid (0.40 mmols); ethanol (10 mL) and **1a** (2 mol%) was performed at 80 °C and time (4 h). [b]Analysed by GC-MS and ^1H NMR.

We also investigated the reuse of **1a** in these reactions. After completing the reaction, the catalyst was easily separated by filtration, washed with dichloromethane and subsequently oven dried at 80 °C for 2 h prior to use in a subsequent reaction process. Once dried, the residue was used in successive reactions, and the yields were monitored. **1a** was successfully used in five successive reactions without significant loss of catalytic activity (Fig. 4).

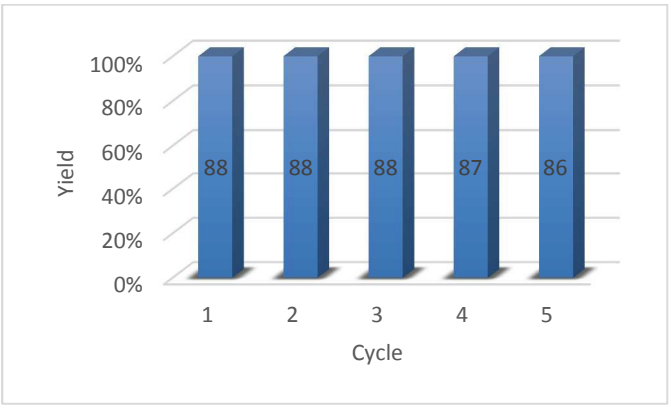

Fig. 4 Reuse of **1a** catalyst for the esterification of palmitic acid with ethanol.

Experimental

Chemicals and Reagents. All of the chemicals were obtained from commercially available sources and used without further purification. The reactions did not require anhydrous conditions. The GC-MS analyses were carried out on a Shimadzu GC-2010 Plus gas chromatograph coupled with a MS QP2010 Ultra Shimadzu mass spectrometer (Tokyo, Japan), using a DB5 capillary column (30 m length, 0.25 mm id, 0.25 mm film thickness). The ^1H- and ^{13}C-NMR spectra were recorded on a Varian Mercury spectrometer at 300 MHz and 75 MHz, respectively.

General procedure for the synthesis of calix[*n*]arenes. $CX4SO_3H$ and $CX6SO_3H$ were synthesized in our laboratory according to previously published procedures. First, *p-tert*-butylcalix[4]arene and *p-tert*-butylcalix[6]arene were prepared using the Gutsche and Iqba method.[11a] Second, *p-tert*-butylcalix[4]arene or *p-tert*-butylcalix[6]arene were dealkylated by treatment with aluminium chloride in the presence of toluene and phenol according to the method described by Ungaro and co-workers.[11b] The preparation of $CX4SO_3H$ and $CX6SO_3H$ was carried out by treatment of calix[4]arene and calix[6]arene with concentrated sulfuric acid (98% wt) (Shinkai *et al.*).[11c]

General procedure for the synthesis of 1a and 1b. 1a and **1b** were synthesized using a sol-gel technique. A mixture of $CX4SO_3H$ (0.600 g) or $CX6SO_3H$ (0.500 g), water (4.5 mL or 3.7 mL, respectively) and 1 mol L^{-1} hydrochloric acid (0.5 mL or 0.4 mL, respectively) was added to tetraethyl orthosilicate (12.50 mL or 10.40 mL, respectively). The mixture was stirred for 5 h at room temperature. Then, the mixture was allowed to stand for 3 days, and after breaking the formed hydrogel with a Teflon stick, the sample was dried under vacuum for one week at room temperature. The powder was washed with distilled water (3 x 10 mL) and dried under vacuum.

Acidity in aqueous media

The acid capacity was determined by titration with 5 x 10^{-3} M NaOH (aq).[12] In a typical experiment, 30 mg of solid **1a** was added to 10 mL of deionized water. The resulting suspension was allowed to equilibrate and the titrated by dropwise addition of a 5 x 10^{-3} M NaOH solution using phenolphthalein (0.2 %) as the pH indicator.

Acidity in non-aqueous media

The catalyst acidity of **1a** (50 mg, catalyst 15 %) was determined by potentiometric titration of a suspension consisting of the solid catalyst in acetonitrile using a solution

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containing *n*-butylamine in acetonitrile (0.025 N) in a Metrohm 794 Basic Titrino apparatus with a double junction electrode.[13]

X-ray Diffraction

The crystallographic phase of supported **1a** was analysed by *ex situ* XRD. The XRD patterns were collected using a Rigaku DMax 2500PC instrument that was operated at 40 kV and 150 mA with Cu Kα (λ=1.5406 Å) radiation. The data were collected in a 2θ range from 5° to 50° with a 0.5° divergence slit and a 0.3 mm receiving slit in fixed time mode with a 0.02° step size.

General procedure for the synthesis of esters. Carboxilic acid (0.40 mmol.) and 2 mol% of the catalyst (CX4SO_3H or CX6SO_3H, active phase) were combined with ethanol (10 mL) in a 50 mL round-bottom flask equipped with a stir bar. The reaction was refluxed (80 °C) for the appropriate amount of time (4 h). After completion of the reaction, the reaction mixture was concentrated under vacuum to afford the crude product, which was analysed by GC-MS.

Conclusions

In conclusion, the results clearly demonstrate the possibility of preparing new *p*-sulfonic acid calix[4]arene heterogeneous catalyst **1a** with a high catalytic activity for the esterification of carboxylic acids. The corresponding ester products were obtained in good to high yield (55-88 %) with excellent selectivity. Some of the other advantages of catalyst **1a** include easy product separation and purification, non-corrosive, and low cost. In addition, the catalyst is considered to be eco-friendly because it can be reused five times. The solid catalyst is highly specific and active, and its stability under liquid-phase reaction conditions indicates the potential for applications in a continuous flow reactor, which would further decrease the cost of ester production.

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Notes and references

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