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Preparation of a Novel Poly(vinylsulfonic acid)-grafted Solid Phase Acid Catalyst and its Use in Esterification Reactions

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Supporting Information

Experimental

1. Synthesis procedure of PVS
Radical polymerization of the VSA (98.1 % acid form, 0.7 % water, 3 ppb Fe, < 20 ppb Ca, < 10 ppb Na, < 1 ppb Cr, <2 ppb Cu, Asahi Kasei FineChem Co. Ltd) using ammonium persulfate (0.1 wt\%) as the initiator in water (10 mol L\textsuperscript{−1}) at 60\textdegree C for 12 h was carried out according to a method described by Nishide et al. (\textit{Japanese Patent Application} 2008121421) to give the PVS polymer with \(M_w = 3.3 \times 10^4\), \(M_w/M_n = 1.8\) in the yield of 84 wt\%.

\textsuperscript{1}H NMR (500 MHz, D\textsubscript{2}O) \(\delta = 1.76-2.44\) (br, 2H, CH\textsubscript{2}), 3.39–3.74 (br, 1H, CH); IR (KBr, cm\textsuperscript{−1}) 1037 (\(\nu_{S=O}\)), 1199 (\(\nu_{S=O}\)).

2. Synthesis procedure of the ACV-attached PSt
ACV-attached PSt was synthesized according to a method described in the literature (J. Kobayashi et al., \textit{Anal. Chem.}, 2001, \textbf{73}, 2027). 4,4’-Azobis(4-cyanovaleric acid) (ACV; Fluka, 32mmol) and 1-(ethoxy-carbonyl)-2-ethoxy-1,2-dihydroquinoline (EEDQ; Aldrich, 64 mmol), an initiator and a condensing agent, respectively, were dissolved in DMF (400 mL) in three-necked flask. The solution was bubbled with Ar gas for 30 min. Aminomethylated polystyrene beads (4 mmol g\textsuperscript{−1} NH\textsubscript{2} loading, NH\textsubscript{2}-PSt; Aldrich, 4 g) were then immersed in the
solution, and the mixture was degassed again for 30 min before the reaction. The reaction was carried out at 25°C for 8 h under Ar atmosphere. The ACV-attached PST beads were washed with DMF and ethanol, consecutively, and dried in vacuo for 1 day. 9 g of the ACV-attached PST beads were obtained as a faint yellow. Elemental analysis: C: 70.6 %, H: 7.2 %, N: 12.3 %. Water uptake: 19 % under 25°C, 75% relative humidity (RH), 18 h.

3. Synthesis procedure of the PVS-grafted PST solid acid catalyst

PVS-grafted PST was synthesized as follows. VSA (98.1 % acid form, 0.7 % water, 3 ppb Fe, < 20 ppb Ca, < 10 ppb Na, < 1 ppb Cr, <2 ppb Cu, Asahi Kasei Finechem, 40 mmol) and the ACV-attached PST beads (0.5 g) were added in a round-bottom flask. The reaction was carried out at 65°C for 2 days under Ar atmosphere. PVS-grafted PST beads were filtered and extensively washed three times with water, methanol, and acetone by decantation so as to remove any un-immobilized PVS and monomers. The product was then dried in vacuo for 2 days at 90°C, and 0.8 g of the PVS-grafted PST beads were obtained as a pale brownish powder. Elemental analysis: C: 40.7 %, H: 6.0 %, N: 2.0 %, S: 17.6 %. The sulfonic acid group content was 5.2 mmol H⁺ g⁻¹ by titration experiment. Water uptake: 174 % under 25°C, 75% RH, 18 h.

4. Synthesis procedure of the PVS-grafted Sepharose®

First, epoxy-activated Sepharose was synthesized as follows. Suction-dried Sepharose® 6 FF (250 g, GE Healthcare), thoroughly washed with water (5 mL × 300 mL), was placed in a round bottom flask and mixed with 2 M NaOH (250 mL) and NaBH₄ (12.4 mmol) at room temperature for 2 h by means of an overhead mechanical stirrer. Epichlorohydrin (150 mL) was then added and the suspension stirred for a further 21 h. The resulting epoxy-activated gel was collected by vacuum filtration and washed with water (5 mL × 300 mL), 20% ethanol / water (5 mL × 300 mL), and once more with water (5 mL × 300 mL).

Secondly, the aminated Sepharose was prepared as follows. An aliquot of the wet cake of the epoxy-activated gel (240 mL) was suspended in 2 M NH₄OH (240 mL) and gently shaken for 21 h at 28 °C. The aminated Sepharose gel was then washed with 10 volumes of distilled water,
The process after aminated carrier was similar to the procedures used for the preparation of the ACV-attached PSt and the PVS-grafted PSt. A PVS-grafted Sepharose product was not obtained, but degraded due to the high acidity of VSA.

5. Synthesis procedure of the PVS-grafted silica

PVS-grafted silica was synthesized using a 3-aminopropyl-functionalized silica gel (1 mmol g\(^{-1}\) NH\(_2\) loading, Aldrich) in a manner similar to the ACV-attached PSt and the PVS-grafted PSt. The PVS-grafted silica was obtained as a pale brownish powder. The sulfonic acid group content was 1.8 mmol H\(^+\) g\(^{-1}\) by titration experiment.

6. Synthesis procedure of the PSS-grafted PSt and its esterification ability

PSS-grafted PSt was synthesized using aminomethylated polystyrene beads (4 mmol g\(^{-1}\) NH\(_2\) loading, NH\(_2\)-PSt; Aldrich, 4 g) in a manner similar to the ACV-attached PSt and the PVS-grafted PSt. The grafting monomer, 4-styrenesulfonic acid was prepared by the cation-exchange reaction of sodium 4-styrenesulfonate (Aldrich). The PSS-grafted PSt was obtained as a pale yellowish powder. The sulfonic acid group content was 3.9 mmol H\(^+\) g\(^{-1}\). The molecular weight of the ungrafted free PSS polymer was \(M_n = 4.3 \times 10^3\), \(M_w = 1.3 \times 10^4\), \(M_w/M_n = 3.0\). The graft ratio of the PSS-grafted PSt was 98%. The conversion of the esterification of acetic acid with ethanol and 1-butanol catalysed by the PSS-grafted PSt for 4 h was 39 % and 27 %, respectively. The reaction rate constant of the esterification of acetic acid with ethanol and 1-butanol catalysed by the PSS-grafted PSt was \(4.4 \times 10^4\) L mol\(^{-1}\) s\(^{-1}\) and \(2.2 \times 10^4\) L mol\(^{-1}\) s\(^{-1}\), respectively.

7. Material characterization

The acid capacities of the PVS-grafted PSt were determined by the acid-base titration with 0.02 M NaOH solution using a Metrohm 808 Titrando autotitrator & 801 stirrer.

The organic content of the synthesized materials was quantified by elemental analysis performed on a Carlo Erba Elemental Analyser EA CHNS analyzer.
Fourier transform infrared (FT-IR) spectra of samples were recorded on JASCO FT/IR-6100 with KBr pellet technique. The effective range was from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\).

Thermal analyses were evaluated by thermogravimetry-differential thermal analysis (TG-DTA) and differential scanning calorimeter (DSC). TG-DTA curves of the samples were measured using a Rigaku TG8120 over a temperature range from 25°C to 450°C at the heating rate of 10°C min\(^{-1}\) under N\(_2\) atmosphere. \(T_g\) was measured using a TA Q200 differential scanning calorimeter over a temperature range from −80°C to 200°C at the heating rate of 10°C min\(^{-1}\) and at the cooling rate of 30°C min\(^{-1}\) under Ar atmosphere.

Water uptake of a hydrated sample was measured by immersing the sample in water at 25°C for 48 h. Then, the sample was removed, wiped and quickly weighed on a microbalance. Water uptake was calculated from:

\[
\text{Water uptake} = \frac{(W_s-W_d)}{W_d} \times 100 \text{ [wt%]}
\]

where, \(W_s\) and \(W_d\) are the weights of wet and dried samples, respectively.

The number-average molecular weight \((M_n)\), weight-average molecular weight \((M_w)\) and polydispersity index \((M_w/M_n)\) of the ungrafted free polymer sample was determined by gel permeation chromatography (GPC) at 40°C using a system equipped with a Tosoh guard column (TSKguardcolumn PW\(_{XL}\), 6.0 mm × 4 cm) and two TSKgel 10 \(\mu\)m columns (G3000PW\(_{XL}\) and G4000PW\(_{XL}\)) with a differential refractive index detector (Shimadzu, RID-10A). Water containing 20% acetonitrile and 0.2 M NaNO\(_3\) was used as an eluent at a flow rate of 1.0 mL min\(^{-1}\). The sample was calibrated with PSS standard samples with \(M_n\) value in the range of 1 000 000–910 g mol\(^{-1}\).

\(^1\)H Solid-state MAS NMR spectra were recorded on a JEOL CMX-400 spectrometer using a double-resonance MAS probe supporting rotors of 2.5mm o.d. The resonance frequency of \(^1\)H is 399.8 MHz. The dried samples were spun at 24 kHz. The \(\pi/2\) pulse lengths were set to 2 \(\mu\)s. A recycle delay of 3 s was used.

\(^{13}\)C Solid-state CP/MAS NMR spectra were recorded on a JEOL CMX-400 spectrometer using a double-resonance MAS probe supporting rotors of 5mm o.d. The resonance frequency of \(^{13}\)C is 100.5 MHz. The dried samples were spun at 10 kHz. A contact time of 5 ms and a recycle delay of 5 s were used. \(^{13}\)C chemical shift was referenced to hexamethylbenzene.
8. General procedures for the esterification reaction

The catalytic properties of the catalysts were tested for the esterification of acetic acid with different alcohols, such as methanol, ethanol, 1-butanol, 2-propanol, and 1-decanol (Kanto). A round-bottom flask fitted with a reflux condenser was used to prevent the escape of volatile liquid components. The flask with its content was heated at a constant temperature in an oil bath and stirred simultaneously magnetically. The mixture was heated over the range of 25–95°C, and then 100 mg of the dry catalyst was added and stirred continuously. In order to monitor the progress of the reaction, reaction products were collected at different time intervals, separated from solid catalyst particles by means of a syringe filter, and analyzed by $^1$H NMR in CDCl$_3$ using internal TMS as standard. $^1$H NMR spectra were recorded using a JEOL-Lambda 500 spectrometer. Commercial Amberlyst® 15 catalyst (Aldrich) and Nafion® silica composite catalyst (SAC-13, Alcrich) were also used for the same esterification as the heterogeneous catalyst control. Sulfuric acid, vinylsulfonic acid, methanesulfonic acid and benzenesulfonic acid were used as the homogeneous catalyst controls.

The kinetic data for the esterification reactions are known to correlate with second-order behaviour. The overall rate of ester production can then be written as

$$-r_A = \frac{d[E]}{dt} = k_{FW}\left([A][B] - \frac{[E][W]}{K}\right)$$

(1)

where the subscripts $A$, $B$, $E$ and $W$ refer to acid, alcohol, ester and water, respectively, $k_{FW}$ is forward reaction rate constant, $K$ is the equilibrium constant of the reaction.

The activation energy and frequency factor determined by the Arrhenius plot is given by;

$$k = A \exp\left(-\frac{E_a}{RT}\right)$$

(2)

where $E_a$, activation energy; $A$, frequency factor. From Eq. (2), a plot of $-\ln k_1$ versus $1/T$, at constant acid and alcohol concentrations, gives a straight line with the slope of $(E_a/R)$.

9. General procedure for the anticorrosion test

The anticorrosion properties of the samples were tested on a stainless steel (SUS304) at 100°C under an air atmosphere. SUS304 is an austenite type of stainless steel contained Ni (8-10.5%)
and Cr (18-20%). After the test, the stainless plate was observed visually and the surface corrosion condition of the stainless plate analyzed by X-ray photoelectron spectroscopy (XPS). XPS data were obtained using a JEOL JPS-9010TR spectrometer with an Mg Kα line source. All spectra were calibrated with respect to the position of the carbon 1s peak at 284.6 eV.

![Fig. S1](image)

**Fig. S1**  GPC chart of the ungrafted PVS polymer in the synthesis of the PVS-grafted PSt (The sample was calibrated with PSS standard samples and water containing 20% acetonitrile and 0.2 M NaNO₃ was used as an eluent at a flow rate of 1.0 mL min⁻¹.).

![Fig. S2](image)

**Fig. S2**  FT-IR spectra of the NH₂-PSt and the PVS-grafted P
Fig. S3 ¹H solid-state MAS NMR spectra of dried samples; (a) PVS-grafted PSt (b) NH₂-PSt.
Fig. S4  $^{13}$C solid-state CP/MAS NMR spectra of dried samples; (a) PVS-grafted PSt (b) NH$_2$-PSt.
**Fig. S5** TG-DTA curve of the PVS-grafted PSt; inset: TG-DTA curve of the NH$_2$-PSt (black: TG curve, red: DTA curve).

![Graph](a) PVS-grafted PSt \( T_g = -24^\circ C \)

![Graph](b) PVS homopolymer \( T_g = -27^\circ C \)

![Graph](c) NH$_2$-PSt \( T_g = 126^\circ C \)

**Fig. S6** DSC curves of various samples recorded under Ar atmosphere with heating rate of 10°C/min and cooling rate of 30°C/min; (a) PVS-grafted PSt (b) PVS homopolymer (c) NH$_2$-PSt.
**Table S1**  Product conversion of the esterification of acetic acid with alcohols catalysed by various catalysts for 4 h\(^a\)

<table>
<thead>
<tr>
<th>catalyst \ alcohol</th>
<th>methanol</th>
<th>ethanol</th>
<th>2-propanol</th>
<th>1-butanol</th>
<th>1-decanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVS-grafted PSt methanol</td>
<td>68</td>
<td>60</td>
<td>24</td>
<td>48</td>
<td>26</td>
</tr>
<tr>
<td>Amberlyst(^\circ) 15 ethanol</td>
<td>62</td>
<td>46</td>
<td>9</td>
<td>30</td>
<td>19</td>
</tr>
<tr>
<td>Nafion(^\circ) SAC-13 methanol</td>
<td>28</td>
<td>23</td>
<td>4</td>
<td>18</td>
<td>14</td>
</tr>
<tr>
<td>PVS VSA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>58</td>
<td>-</td>
</tr>
<tr>
<td>VSA MSA</td>
<td>-</td>
<td>65</td>
<td>-</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>MSA BSA</td>
<td>-</td>
<td>64</td>
<td>-</td>
<td>66</td>
<td>-</td>
</tr>
<tr>
<td>BSA Sulfuric acid</td>
<td>-</td>
<td>68</td>
<td>-</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>No catalyst</td>
<td>8</td>
<td>7</td>
<td>1</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: acetic acid = 0.1 mol, alcohols = 0.1 mol, homogeneous acid catalysts = 0.45 mmol, heterogeneous acid catalysts = 0.1 g, temperature = 65\(^\circ\)C. \(^b\) PVS: poly(vinylsulfonic acid), VSA: vinylsulfonic acid, MSA: methanesulfonic acid, BSA: benzenesulfonic acid.

**Table S2**  TOF of the esterification of acetic acid with alcohols catalysed by various catalysts\(^a\)

<table>
<thead>
<tr>
<th>catalyst \ alcohol</th>
<th>acid capacity (mmol H(^+) g(^-1))</th>
<th>TOF(^b)</th>
<th>methanol</th>
<th>ethanol</th>
<th>2-propanol</th>
<th>1-butanol</th>
<th>1-decanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVS-grafted PSt</td>
<td>4.5(^c)</td>
<td>46</td>
<td>22</td>
<td>13</td>
<td>46</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>Amberlyst(^\circ) 15</td>
<td>4.7</td>
<td>18</td>
<td>13</td>
<td>5</td>
<td>18</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Nafion(^\circ) SAC-13</td>
<td>0.8</td>
<td>70</td>
<td>53</td>
<td>19</td>
<td>70</td>
<td>53</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Reaction conditions: acetic acid = 0.1 mol, alcohols = 0.1 mol, homogeneous acid catalysts = 0.45 mmol, heterogeneous acid catalysts = 0.1 g, temperature = 65\(^\circ\)C. \(^b\) TOF defined as mmol\(_{\text{product}}\) mmol\(_{\text{active site}}\)\(^{-1}\) h\(^{-1}\) determined at 1 h. \(^c\) The acid capacity was a value of the sample used for the esterification reactions.
Fig. S7  Arrhenius plot of the reaction rate constants for the esterification of 1-butanol with acetic acid catalysed by the PVS-grafted PSt.

The temperature dependence of the reaction rate constants of the PVS-grafted PSt followed Arrhenius’ law. The activation energy of the esterification of acetic acid with 1-butanol was found to be 51 kJ mol\(^{-1}\) (12 kcal mol\(^{-1}\)) in the presence of the PVS-grafted PSt. This value can be compared to 70 kJ mol\(^{-1}\) (17 kcal mol\(^{-1}\)) in the presence of Nafion \textsuperscript{®} SAC-13 and 115 kJ mol\(^{-1}\) (28 kcal mol\(^{-1}\)) in the absence of catalyst, respectively. The presence of the PVS-grafted PSt resulted in an activation energy of approximately 20 kJ mol\(^{-1}\) lower than the case of Nafion \textsuperscript{®} SAC-13, and half of the value in the absence of catalyst. The frequency factor of the PVS-grafted PSt was 3.5×10\(^4\) L mol\(^{-1}\) s\(^{-1}\).

Table S3  Activation energy and frequency factor of the PVS-grafted PSt

<table>
<thead>
<tr>
<th>catalyst</th>
<th>activation energy (E_a) (kJ mol(^{-1}))</th>
<th>frequency factor (A) (L mol(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVS-grafted PSt</td>
<td>51</td>
<td>3.5×10(^4)</td>
</tr>
<tr>
<td>Nafion \textsuperscript{®} SAC-13</td>
<td>70</td>
<td>1.1×10(^7)</td>
</tr>
<tr>
<td>No catalyst</td>
<td>115</td>
<td>8.1×10(^{12})</td>
</tr>
</tbody>
</table>
**Fig. S8** Anticorrosion test of the PVS-grafted PST using stainless steel plate (SUS304) at 100°C under air atmosphere; inset: the case of sulfuric acid.

**Fig. S9** XPS spectrum of the stainless steel plate (SUS304) over the region of O 1s (a) and the region of S 2p$_{3/2}$ (b) by anticorrosion test of (i) sulfonic acid, (ii) PVS-grafted PST, and (iii) blank.
10. General procedures for Friedel-Crafts reaction and condensation reaction

The catalytic performance of the catalysts was tested for the Friedel-Crafts reaction and the condensation reaction. In order to analyze the reaction products, the reaction mixtures were collected and separated from solid catalyst particles by means of a syringe filter, and analyzed by $^1$H NMR in CDCl$_3$ using internal TMS as standard. $^1$H NMR spectra were recorded using a JEOL-Lambda 500 spectrometer. Commercial Amberlyst® 15 catalyst (Aldrich) and Nafion® silica composite catalyst (SAC-13, Aldrich) were also used for the same reaction as the heterogeneous catalyst control.

(a)

\[
\begin{align*}
\text{Catalyst} & \quad \text{90°C, 1h} \\
\text{OCH}_3 + \text{O} & \quad \text{OCH}_3 + \text{OH}
\end{align*}
\]

i) PVS-grafted PSt = 0.2 g, ii) Amberlyst 15 = 0.2 g, iii) Nafton SAC-13 = 0.2 g

Scheme S1

$p$-Methoxyacetophenone was prepared by acetylation of 10 mmol of anisole with 10 mmol of acetic anhydride over 0.2 g of catalyst at 90°C for 1 h in 30 mL round-bottomed flask.

(b)

\[
\begin{align*}
\text{Catalyst} & \quad \text{50°C} \\
\text{O} & \quad \text{O}
\end{align*}
\]

i) PVS-grafted PSt = 0.18 g, ii) Amberlyst 15 = 0.18 g, iii) Nafton SAC-13 = 0.18 g

Scheme S2

2,2-Bis(5-methylfuryl)propane was prepared by condensation of 22 mmol of 2-methylfuran with 55 mmol of acetone over 0.18 g of catalyst at 50°C in 30 mL round-bottomed flask.
Table S4  Product conversion and TOF of the acylation of anisole with acetic anhydride catalysed by various catalysts<sup>a</sup>

<table>
<thead>
<tr>
<th>catalyst</th>
<th>acid capacity (mmol H&lt;sup&gt;+&lt;/sup&gt; g&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>conversion (%)</th>
<th>TOF&lt;sup&gt;b&lt;/sup&gt;</th>
<th>p-selectivity&lt;sup&gt;c&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVS-grafted PST&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50</td>
<td>5.4</td>
<td>98</td>
</tr>
<tr>
<td>Amberlyst® 15</td>
<td>4.7</td>
<td>54</td>
<td>5.6</td>
<td>97</td>
</tr>
<tr>
<td>Nafion® SAC-13</td>
<td>0.8</td>
<td>25</td>
<td>15</td>
<td>96</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: anisole = 10 mmol, acetic anhydride = 10 mmol, heterogeneous acid catalysts = 0.2 g, temperature = 90°C.  
<sup>b</sup> TOF defined as mmol<sub>product</sub> mmol<sub>active site</sub><sup>−1</sup> h<sup>−1</sup> determined at 1 h.  
<sup>c</sup> Selectivity toward p-methoxyacetophenone. The other product was the o isomer.  
<sup>d</sup> The sample was a same acid capacity used for the esterification reactions.

Table S5  Product conversion and TOF of the synthesis of 2,2-bis(5-methylfuryl)propane using the PVS-grafted PST in comparison with commercial solid acid catalysts and literature precedents.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>acid capacity (mmol H&lt;sup&gt;+&lt;/sup&gt; g&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>time (h)</th>
<th>conversion (%)</th>
<th>TOF&lt;sup&gt;a&lt;/sup&gt;</th>
<th>selectivity&lt;sup&gt;b&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVS-grafted PST&lt;sup&gt;c&lt;/sup&gt;</td>
<td>4.5&lt;sup&gt;e&lt;/sup&gt;</td>
<td>2</td>
<td>82</td>
<td>11</td>
<td>99</td>
</tr>
<tr>
<td>PVS-grafted PST&lt;sup&gt;e&lt;/sup&gt;</td>
<td>4.5&lt;sup&gt;e&lt;/sup&gt;</td>
<td>6</td>
<td>98</td>
<td>4.4</td>
<td>98</td>
</tr>
<tr>
<td>Amberlyst® 15</td>
<td>4.7</td>
<td>2</td>
<td>63</td>
<td>7.7</td>
<td>94</td>
</tr>
<tr>
<td>Nafion® SAC-13</td>
<td>0.8</td>
<td>2</td>
<td>49</td>
<td>36</td>
<td>96</td>
</tr>
<tr>
<td>Mesoporous silica-perfluoroSO&lt;sub&gt;3&lt;/sub&gt;H&lt;sup&gt;d&lt;/sup&gt;</td>
<td>0.2</td>
<td>6</td>
<td>86</td>
<td>49</td>
<td>98</td>
</tr>
<tr>
<td>HMS-propylSO&lt;sub&gt;3&lt;/sub&gt;H&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>24</td>
<td>73</td>
<td>&lt;1.7</td>
<td>98</td>
</tr>
<tr>
<td>MCM-41-propylSO&lt;sub&gt;3&lt;/sub&gt;H&lt;sup&gt;f&lt;/sup&gt;</td>
<td>1.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>24</td>
<td>85</td>
<td>&lt;2.0</td>
<td>96</td>
</tr>
</tbody>
</table>

<sup>a</sup> TOF defined as mmol<sub>product</sub> mmol<sub>active site</sub><sup>−1</sup> h<sup>−1</sup>.  
<sup>b</sup> Selectivity for 2,2-bis(5-methylfuryl)propane, based on 2-methylfuran.  
<sup>c</sup> Reaction conditions: 2-methylfuran = 22 mmol, acetone = 55 mmol, heterogeneous acid catalysts = 0.18 g, temperature = 50°C.  
<sup>d</sup> D. J. Macquarrie et al., Chem. Commun., 2005, 2363.  
<sup>f</sup> The sample was a same acid capacity used for the esterification reactions.  
<sup>g</sup> Based on the lowest value in the range quoted in reference.