Silica-supported methanesulfonic acid — An efficient solid Brønsted acid catalyst for the Pechmann reaction in the presence of higher n-alkanes

J. Joshi, M.K. Mishra, and M. Srinivasarao

Abstract: A cost-effective and efficient solid Brønsted acid catalyst was synthesized by loading methanesulfonic acid (MSA) on silica and was used for the acid-catalyzed Pechmann reaction to test the catalytic activity and its reusability. Derivatives of 4-methylcoumarin were synthesized in good yields within short reaction times in the presence of environmentally friendly higher n-alkanes as solvents. The regeneration study of the spent catalyst showed satisfactory results.

Key words: silica supported solid acids, methanesulfonic acid, Brønsted acidity, Pechmann reaction, derivatives of 4-methylcoumarin.

Résumé : On a synthétisé un catalyseur acide de Brønsted efficace et rentable d’un point de vue coût en recouvrant de la silice avec de l’acide méthanesulfonique (AMS) et on l’a utilisé catalyseur acide pour la réaction de Pechmann dans le but d’évaluer son activité catalytique et la possibilité de le réutiliser. On a synthétisé des dérivés de la 4-méthylcoumarine avec de bons rendements, avec des temps de réaction relativement courts, dans des solvants à base d’alcanes supérieurs écologiques. L’étude de régénération du catalyseur utilisé a donné des résultats satisfaisants.

Mots-clés : acides solides supportés par de la silice, acide méthanesulfonique, acidité de Brønsted, réaction de Pechman, dérivés de la 4-méthylcoumarine.

[Traduit par la Rédaction]

Introduction

Methanesulfonic acid (CH₃SO₃H; MSA) is a strong Brønsted acid (pKₐ = −1.9) and has been reported as a potential acid catalyst for various acid-catalyzed reactions.¹⁻³ MSA is very cheap, has a lower tendency to oxidize organic compounds, is far less corrosive and toxic than widely used fluorosubstituted alkanesulfonic acids, like triflic acid and 1,1,2,2-tetrafluoroethanesulfonic acid, and the mineral acids. The problems associated with recovery and reuse of MSA from homogeneous conditions makes its application limited. To overcome these problems, a supported form of MSA could be the best alternative. The supported fluoro-substituted alkanesulfonic acids (triflic acid, 1,1,2,2-tetrafluoroethanesulfonic acid, etc.) have been synthesized and used for various acid-catalyzed organic transformations.⁴⁻¹⁰ However, supported MSA, which could be a cost-effective and eco-friendly solid acid catalyst, and an attractive alternative to supported fluorosubstituted alkanesulfonic acids for acid-catalyzed transformations, has not been reported in the literature. The present work was aimed at developing silica-supported MSA as a cost-effective, eco-friendly, and reusable solid acid catalyst. The synthesized catalyst was used for the Pechmann reaction to synthesize derivatives of 4-methylcoumarin.

Coumarins are heterocyclic natural products finding applications as pharmacologically and biologically active compounds.¹¹,¹² Coumarins are usually synthesized by acid-catalyzed Pechmann reaction of activated phenols and α-keto esters using homogeneous Brønsted¹⁴⁻¹⁶ and Lewis¹⁷,¹⁸ acid catalysts. It is to be noted that the homogeneous acids are corrosive, required in excess, and nonreusable, sometimes result in the formation of side products, and generate acidic waste. Various solid acid catalysts such as Amberlyst ion-exchange resins,¹⁹ zeolites,²⁰ montmorillonite K-10,²¹ sulfated zirconia,²² benzylsulfonic acid functionalized mesoporous Zr-TMS,²³ metal ion-exchanged ZAPO-5,²⁴ W/ZrO₂,²⁵ Nafion resin / silica nanocomposites,²⁶ polyaniline sulfate salt,²⁷ etc., have been found to be the best alternatives to homogeneous acids. However, most of the solid acids require either a longer reaction time²⁰⁻²⁵,²⁷ or a higher reaction temperature²²,²⁴,²⁷ to achieve maximum yield. The syntheses using some of the solid acids are not cost-effective because of either tedious methods of synthesizing the catalysts²⁷ or the use of large amounts of catalysts.¹⁹,²⁰,²⁶ In addition, the solid acid catalyzed Pechmann reactions are usually carried out using nonpolar solvents like tetrahydrofuran (THF),toluene, etc.,¹⁹,²⁰ which are volatile, hazardous, and nonrecoverable. To the best of our knowledge, there is no report...
available on the application of higher \( n \)-alkanes as nonpolar solvents in heterogeneous catalysis. Hence, an attempt was also made in the present work to use higher \( n \)-alkanes as environmentally friendly nonpolar solvents for Pechmann reactions.

**Experimental**

**Chemicals**

Tetraethylorthosilicate, ethyl acetoacetate, and pyrogallol were procured from s.d. Fine Chemicals, India. Hydrochloric acid, methanol, \( n \)-hexadecylamine (HDA), resorcinol, nitrobenzene, petroleum ether, \( n \)-butylamine, and acetonitrile were from Merck, USA. \( n \)-Octadecane, \( n \)-hexadecane, \( n \)-dodecane, phloroglucinol, methoxyphenol, and \( m \)-cresol were procured from National Chemicals, India. Methanesulfonic acid was procured from Loba Chemie, India.

**Synthesis of silica-supported methanesulfonic acid (SiO\(_2\)-MSA) solid acid catalyst**

The silica support was synthesized by hydrolysis of tetraethylorthosilicate (TEOS) using HDA as the template. The pH of the TEOS (20 g) and methanol (50 mL) solution was adjusted in the range of 2–3 by adding a few drops of concentrated hydrochloric acid. Water (7.2 mL) was then added to the acidic TEOS solution with stirring and the solution was kept for 30 min. The HDA solution, prepared by dissolving HDA (2.4 g, 0.01 mol) in methanol (50 mL), was added to the TEOS solution with vigorous stirring and the solution was aged for 5 days at room temperature. The gel was filtered and washed with methanol to remove surfactant template, which was confirmed by FT-IR analysis of the dried silica. The gel was dried at room temperature for 24 h and then at 120 °C for 12 h. To load a nominal amount of MSA (\( \sim 1 \) mmol MSA / g of silica) on the silica support, 10 g of dried silica gel was treated with MSA solution (5 mL of MSA in 50 mL of carbon tetrachloride) at room temperature with stirring for 24 h. The gel was filtered and washed with methanol and then with petroleum ether to remove free MSA. The gel was dried at room temperature for 24 h and later at 120 °C for 6 h.

**Characterization of SiO\(_2\)-MSA catalyst**

The catalyst was characterized by N\(_2\) adsorption–desorption isotherm, FT-IR, FT-IR of the pyridine-adsorbed sample, potentiometric titration, thermal analysis (TGA-DTA), and CHN/S/O elemental analysis. The Brunauer–Emmett–Teller (BET) surface area and average pore diameter of the samples were measured by N\(_2\) adsorption–desorption isotherm studies using a Quantachrome NOVA 1000e surface area analyzer. The sample was degassed under vacuum at 120 °C for 4 h prior to adsorption measurement, to evacuate the physisorbed moisture. The surface area was determined by using the BET equation, and the average pore diameter of the samples was measured by the Barrett, Joyner, and Halenda method (BJH).\(^{28}\) The loading of MSA over the silica support was confirmed by FT-IR study using a FT-IR spectrophotometer (Shimadzu IRPrestige-21) with a diffuse reflectance scanning disc technique by mixing the sample with dried KBr (in a 1:20 wt ratio) in the range of 400–4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). The type of surface acidity (Brønsted or Lewis) in the samples was characterized by FT-IR study of the pyridine-adsorbed samples. For this the sample (0.2 g) was activated at 120 °C for 2 h. The activated sample was cooled in a desiccator under vacuum and was exposed to pyridine (25 mL) vapor for 12 h. The pyridine-adsorbed sample was degassed under vacuum for 15 min to remove physically adsorbed pyridine from the sample. The FT-IR spectra of the samples adsorbed with pyridine (mixed with KBr in a 1:20 wt ratio) were recorded in the range of 400–4000 cm\(^{-1}\). The amount of acidity and the strength of the acid sites in the samples were measured by potentiometric titration.\(^8\) The sample (0.05 g) was suspended in acetonitrile and stirred for 3 h. The suspension was titrated with 0.05 N \( n \)-butylamine in acetonitrile at 0.05 mL/min. The electrode potential variation was measured using a potentiometric titrator (Chemito, India). The TGA-DTA of the samples was carried out by a Shimadzu DTG-60H, by heating the sample in the range of 50–1000 °C with a heating rate of 10 °C/min under nitrogen flow (30 cm\(^3\)/min). The amount of MSA loaded on the silica was calculated from the TGA results (\( W_{\text{MSA}} \)) using the following equation:\(^8\)

\[
W_{\text{MSA}} = \frac{W_{\text{SiO-MSA}}}{FW_{\text{MSA}}}
\]

where \( W_{\text{SiO-MSA}} \) = weight loss (mg/g) of SiO\(_2\)-MSA catalyst from 25 to 500 °C, \( W_{\text{SiO}} \) = weight loss (mg/g) of SiO\(_2\) support from 25 to 500 °C, and \( FW_{\text{MSA}} \) = molecular weight of CH\(_3\)SO\(_3\)H. Percentage of sulfur in the catalysts was also analyzed by CHNS/O elemental analysis (PerkinElmer 2400) to estimate the amount of methanesulfonic acid loaded on the silica.

**Catalytic activity of SiO\(_2\)-MSA for synthesis of 4-methylcoumarin derivatives by the Pechmann reaction**

The derivatives of 4-methylcoumarin were synthesized by the SiO\(_2\)-MSA catalyzed Pechmann reaction of a phenol (resorcinol, phloroglucinol, pyrogallol, \( m \)-methylphenol, \( m \)-methoxyphenol, or phenol) and ethyl acetoacetate (Scheme 1). The reaction was carried out by adding preactivated (at 120 °C for 1 h) catalyst to the mixture of phenol and ethyl acetoacetate, with or without solvent, at constant temperature under stirring. After the completion of reaction, the reaction mixture was cooled and methanol (\( \sim 10 \) mL) was added to dissolve the product. The reaction mixture was filtered to separate the catalyst and the product was crystallized by cooling the filtrate.

**Characterization of the products**

The products were recrystallized in ethanol–water (95:1) solution and the isolated yields were calculated. The products were characterized by melting point and by FT-IR and \(^1\)H NMR spectroscopy, and the data were matched with those reported in the literature. Melting points were measured by a melting point apparatus (Choudhary Instruments, India) and are uncorrected. Infrared spectra were recorded on a FT-IR spectrophotometer (Shimadzu IRPrestige-21) in KBr with transmittance in cm\(^{-1}\). \(^1\)H NMR spectra were determined on a NMR spectrometer (Bruker Avance DFX, 200 MHz) as dimethyl sulfoxide (DMSO-\(d_6\)) solutions. Chemical shifts (\( \delta \)) were expressed in ppm downfield from the internal standard tetramethylsilane.
Scheme 1. SiO₂ methanesulfonic acid (MSA) catalyzed Pechmann reaction of phenols and ethyl acetoacetate to synthesize derivatives of 4-methylcoumarin.

Table 1. Physicochemical and catalytic properties of SiO₂ support and SiO₂ methanesulfonic acid (MSA) catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S_{BET} (m²/g)</th>
<th>Dp (Å)</th>
<th>Brønsted acidity band area (A/cm)</th>
<th>Lewis acidity band area (A/cm)</th>
<th>N_{MSA} (µmol/g)</th>
<th>W_{MSA} (µmol n-butylamine / g)</th>
<th>Acid site (wt %)</th>
<th>Yield of 7-hydroxy-4-methylcoumarin (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ support</td>
<td>373</td>
<td>31</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂–MSA</td>
<td>362</td>
<td>31</td>
<td>5.3</td>
<td>Nil</td>
<td>1000</td>
<td>1200</td>
<td>1200</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: S_{BET}, BET surface area; Dp, average pore diameter; N_{MSA}, the amount of MSA loaded on silica calculated from the sulfur content; W_{MSA}, amount of MSA loaded on silica calculated from TGA analysis.

1. IR study of pyridine-adsorbed sample.
2. Calculated from sulfur wt % obtained by CHNS/O analysis.
3. By TGA analysis.
4. By potentiometric titration with n-butylamine.
5. Resorcinol (10 mmol), ethyl acetoacetate (20 mmol), catalyst (0.25 g), 160 °C, 12 h.

7-Hydroxy-4-methylcoumarin

mp: 185–190 °C (lit. mp 188 °C), FT-IR (KBr, cm⁻¹): 3159 (ν_{OH}), 1674 (ν_{C=O}). ^{1}H NMR (DMSO-d₆): δ: 10.54 (s, 1H, –OH), 7.56 (d, 1H, Ar–H), 6.79 (d, 1H, Ar–H), 6.72 (s, 1H, Ar–H), 6.12 (s, 1H, –C=CH₂), 2.36 (s, 3H, –CH₃).

5,7-Dihydroxy-4-methylcoumarin

mp: 283–285 °C (lit. mp 284–285 °C), FT-IR (KBr, cm⁻¹): 3159 (ν_{OH}), 1670 (ν_{C=O}). ^{1}H NMR (DMSO-d₆): δ: 10.5 (s, 1H, –OH), 10.3 (s, 1H, –OH), 6.3 (s, 1H, Ar–H), 6.2 (s, 1H, Ar–H), 5.9 (s, 1H, –C=CH₂), 2.5 (s, 3H, –CH₃).

7,8-Dihydroxy-4-methylcoumarin

mp: 242–245 °C (lit. mp 242–244 °C), FT-IR (KBr, cm⁻¹): 3231 (ν_{OH}), 1648 (ν_{C=O}). ^{1}H NMR (DMSO-d₆): δ: 10.0 (s, 1H, –OH), 9.4 (s, 1H, –OH), 7.1 (d, 1H, Ar–H), 6.8 (d, 1H, Ar–H), 6.1 (s, 1H, –C=CH₂), 2.3 (s, 3H, –CH₃).

Results and discussion

Characterization of SiO₂–MSA

The physicochemical characteristics of the silica and the supported catalyst are given in Table 1. The average pore diameter for the samples was 31 Å. The SiO₂–MSA had a slightly lesser BET surface area (362 m²/g) compared with the silica support (373 m²/g), which is attributed to the loading of MSA on the silica surface (Table 1).

The FT-IR spectrum (Fig. 1) of SiO₂ exhibits a broad band in the range of 2800–3750 cm⁻¹ (ν_{ν=O, ν=H} for –OH groups of silica and adsorbed water) including small peaks at 3650 (ν_{ν=O, ν=H}, for free silanols =Si–OH) and 1630 cm⁻¹ (δ_{ν=O, δ=H}, for adsorbed water). In the FT-IR spectrum of SiO₂–MSA the peak for silanols (3650 cm⁻¹) disappeared and the broadness of the band in the –OH region increased. This spectral change indicates that MSA is bonded with free silanols of silica by the reaction of MSA and silanols. A similar observation was also reported for silica-supported triflic acid. The FT-IR spectrum of SiO₂–MSA shows a peak at 1337 cm⁻¹ for the ν_{ν=O, ν=H} stretching mode of the –SO₃H group and a small peak at 1425 cm⁻¹ for the δ_{ν=O, δ=H} bending mode of the –CH₃ group. A peak for SO₂ deformation was found at 554 cm⁻¹. The FT-IR spectrum of pyridine-adsorbed catalyst (Fig. 2) shows peaks at 1489, 1554, 1620, and 1635 cm⁻¹. The peak at 1554 cm⁻¹ is a characteristic peak of adsorbed pyridine on Bronsted acid sites, showing the presence of a significant amount of Bronsted acidity. There is no peak in the range of 1440–1450 cm⁻¹ for adsorbed pyridine on Lewis sites. Thus, the catalyst has predominantly Bronsted acidity showing 5.3 A/cm peak area of the band at 1554 cm⁻¹ (Table 1). The reaction of the –SO₃H group of MSA and silanols results in
formation of protonated silanols, which hold methanesulfonate ions on the silica surface (Scheme 2). The protonated silanols bonded with methanesulfonate ions on the silica surface act as Brønsted acid sites.

The initial electrode potential ($E_i$), obtained by potentiometric titration with $n$-butylamine, indicates that the catalyst possesses very strong acid sites ($E_i = 612$ mV) compared with those of the silica support (Fig. 3). The total number of acid sites in the catalyst was found to be 1200 mmol $n$-butylamine/g of catalyst (Table 1).

TGA-DTA profiles of SiO$_2$ support and SiO$_2$–methanesulfonic acid (MSA) catalyst are given in Figs. 4a and 4b showing two-stage weight loss in SiO$_2$–MSA. The weight loss that occurred from 50 to 150 °C corresponds to the removal of adsorbed water. The second stage weight loss in the range of 300–450 °C is attributed to the decomposition of loaded MSA. The amount of MSA loaded on silica, calculated from TGA analysis ($W_{\text{MSA}}$), was 1200 µmol/g (Table 1). The amount of MSA loaded over silica ($N_{\text{MSA}}$), calculated from the sulfur content (3.2 wt %, obtained from CHNS/O elemental analysis), corresponds to 1000 µmol/g (Table 1), which is in close agreement with $W_{\text{MSA}}$.

The characterization results confirmed that a significant amount of MSA was loaded over silica by surface reaction of MSA with silanols, generating predominantly Brønsted acidity. This catalyst can be used as a solid Brønsted acid for acid-catalyzed reactions.

**Catalytic activity of SiO$_2$–MSA for the Pechmann reaction to synthesize 4-methylcoumarin derivatives and the effect of reaction parameters**

SiO$_2$–MSA catalyst was found to be active for the Pechmann reaction giving 94% yield of 7-hydroxy-4-methylcoumarin at 160 °C after 12 h (Table 1). No product formation was observed with pure silica without loading MSA. The reaction temperature was optimized by carrying out the reaction in
the range of 90–180 °C keeping all other parameters the same (see Supplementary data, Fig. S1). The maximum yield of 7-hydroxy-4-methylcoumarin (94%) was obtained after 12 h at 160 °C. The yield was observed to be slightly decreased (90% after 12 h) at 180 °C. Therefore, 160 °C was selected as the optimized reaction temperature.

To demonstrate the efficiency of the catalyst, the reaction was carried out by varying the catalyst loading (6.5, 3.9, 2.6, and 1.3 wt %) under similar reaction conditions. The yield of 7-hydroxy-4-methylcoumarin was observed to be steady (94%) up to a catalyst loading of 2.6 wt % (Fig. 5). It shows that the catalyst is very efficient and required in only a small quantity to achieve the maximum yield. However, the reaction kinetics were affected by the catalyst loading. It was...
medium has been attributed to cleavage of the product and solvent-free synthesis (Fig. 6). The lesser yield in the polar solvent, such as toluene, cumene, THF, etc., has been widely used for synthesis of 7-hydroxy-4-methylcoumarin. In nitrobenzene, the yield was significantly reduced (50% after 14 h) compared with the yield (94% after 14 h) obtained in solvent-free synthesis (Fig. 6). The lesser yield in the polar medium has been attributed to cleavage of the product and the reduction in the number of available active sites owing to bonding of nitrobenzene molecules with active sites. Non-polar solvents such as toluene, cumene, THF, etc., have been widely used for synthesis of 7-hydroxy-4-methylcoumarin and tolune has been found to be one of the best nonpolar solvents. However, toluene is a hazardous, nonseparable, nonreusable, and volatile aromatic, which limits its high-temperature applications. In the present work, higher n-alkanes were more effective than n-dodecane, n-hexadecane, and n-octadecane) were used as polar and nonpolar solvents, respectively, to study the effect of solvent on SiO2–MSA catalyzed synthesis of 7-hydroxy-4-methylcoumarin. In nitrobenzene, the yield was significantly reduced (50% after 14 h) compared with the yield (94% after 14 h) obtained in solvent-free synthesis (Fig. 6). The lesser yield in the polar medium has been attributed to cleavage of the product and the reduction in the number of available active sites owing to bonding of nitrobenzene molecules with active sites. Non-polar solvents such as toluene, cumene, THF, etc., have been widely used for synthesis of 7-hydroxy-4-methylcoumarin and tolune has been found to be one of the best nonpolar solvents. However, toluene is a hazardous, nonseparable, nonreusable, and volatile aromatic, which limits its high-temperature applications. In the present work, higher n-alkanes were more effective than n-dodecane, n-hexadecane, and n-octadecane) were used as polar and nonpolar solvents, which are nonhazardous, less volatile, and easily recoverable. The higher n-alkanes improved the activity of the catalyst by decreasing the reaction time (2–8 h) to achieve a maximum yield (>94%). n-Hexadecane and n-octadecane were more effective than n-dodecane, giving the maximum yield within 2 h. The enhanced activity of the catalyst in higher n-alkanes may be attributed to the higher nonpolar nature of the medium and the insolubility of reactant molecules in n-alkanes, which drives polar reactant molecules towards the catalyst surface for adsorption and chemical reaction. As the chain length of the n-alkane chain is increased, the reaction time to achieve maximum yield of the product was observed to be reduced as it enhances the catalytic activity of the SiO2–MSA. This effect was explained on the basis of increasing nonpolar behavior of the n-alkanes with increasing chain length. The longer chain n-alkane molecules (n-hexadecane and n-octadecane) have strong van der Waals interactions, which does not allow the polar reactant molecules to stay in the bulk of the solvent. This forces the reactant molecules to come out from the bulk of n-alkane towards the catalyst surface, facilitating the adsorption of the reactant molecules on the catalyst surface for the reaction. It appears that the bulk diffusion of the reactants from solvent to catalyst surface and the surface adsorption are made easier by higher n-alkanes. After the surface reaction, the product (7-hydroxy-4-methylcoumarin) formed on the surface is desorbed and tends to come into the n-alkane (the nonpolar solvent) as the solubility of the product is significant in the nonpolar solvent. The solubilization of product in n-alkane facilitates the removal (desorption) of the product molecules from the catalyst surface, making surface sites free, as well as the bulk diffusion of the product molecules from the catalyst surface to the bulk of the solvent. The lesser yield in the polar medium (nitrobenzene) may also be attributed to the higher solubility of the polar reactants in the solvent, which reduces the bulk diffusion rate of the reactant molecules from solvent to catalyst surface.

The yield of 7-hydroxy-4-methylcoumarin and the reaction conditions reported with the other solid acid catalysts were compared with the SiO2–MSA catalyst (Table 2). It can be observed that SiO2–MSA in the presence of higher n-alkanes as solvents gives the highest yield (99%) in the shortest time (2 h) at relatively lower temperature in comparison with the other catalysts.

The SiO2–SA catalyst showed significant activity for the synthesis of derivatives of 4-methylcoumarin (Table 3). However, the activated phenols (resorcinol, phloroglucinol, and pyrogallol) were found to be more reactive, giving 99%, 78%, and 70% yields of the corresponding coumarin derivatives. No product formation was observed under the given reaction conditions with less reactive phenols (m-methoxyphenol, m-methylphenol, and phenol). The reactivity of various phenols for the Pechmann reaction has already been reported.

**Regeneration study of spent SiO2–MSA**

The spent catalyst, recovered from the reaction mixture (in n-octadecane) was regenerated by washing with methanol.
(2 × 10 mL) then with petroleum ether (10 mL), followed by drying at 120 °C for 2 h (see Supplementary data, Fig. S3). The regenerated catalyst was reused for three cycles under similar reaction conditions as with fresh catalyst. The regenerated catalysts showed similar activity to fresh catalyst giving 94%–96% yield (Table 4). The CHNS/O elemental analysis of regenerated catalyst showed a slight loss of MSA, giving 984 µmol MSA/g catalyst (Table 4).

In conclusion, a cost-effective, efficient, and reusable SiO₂–methanesulfonic acid (MSA) solid acid catalyst was synthesized and used for the synthesis of 4-methylcoumarin derivatives by the Pechmann reaction. The higher n-alkanes were used as nonpolar solvents for the Pechmann reaction and found to be the best alternative to conventional nonpolar solvents.

### Table 3. Yield (wt %) of 4-methylcoumarin derivatives synthesized by the Pechmann reaction using SiO₂–methanesulfonic acid (MSA) catalyst.

<table>
<thead>
<tr>
<th>Phenol</th>
<th>4-Methyl coumarin derivative</th>
<th>Isolated yield (wt%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resorcinol</td>
<td><img src="image" alt="Resorcinol" /></td>
<td><img src="image" alt="7-hydroxy 4-methyl coumarin" /></td>
</tr>
<tr>
<td>Phloroglucinol</td>
<td><img src="image" alt="Phloroglucinol" /></td>
<td><img src="image" alt="5,7-dihydroxy-4-methyl coumarin" /></td>
</tr>
<tr>
<td>Pyrogallol</td>
<td><img src="image" alt="Pyrogallol" /></td>
<td><img src="image" alt="7,8-dihydroxy-4-methyl coumarin" /></td>
</tr>
<tr>
<td>m-methoxy phenol</td>
<td><img src="image" alt="m-methoxy phenol" /></td>
<td>Not obtained</td>
</tr>
<tr>
<td>m-methyl phenol</td>
<td><img src="image" alt="m-methyl phenol" /></td>
<td>Not obtained</td>
</tr>
<tr>
<td>Phenol</td>
<td><img src="image" alt="Phenol" /></td>
<td>Not obtained</td>
</tr>
</tbody>
</table>

<sup>a</sup>Phenol substrate (10 mmol), ethyl acetoacetate (20 mmol), n-octadecane (3 mL; solvent), catalyst (0.25 g), 160 °C, 2 h.

### Table 4. Regeneration study of spent SiO₂–methanesulfonic acid (MSA) catalyst.

<table>
<thead>
<tr>
<th>Reaction cycle</th>
<th>Yield (wt %) of 7-hydroxy-4-methylcoumarin&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Amount of MSA (N&lt;sub&gt;MSA&lt;/sub&gt;, µmol/g)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>99</td>
<td>1000</td>
</tr>
<tr>
<td>I</td>
<td>97</td>
<td>—</td>
</tr>
<tr>
<td>II</td>
<td>96</td>
<td>—</td>
</tr>
<tr>
<td>III</td>
<td>94</td>
<td>984</td>
</tr>
</tbody>
</table>

<sup>a</sup>Phenol substrate (10 mmol), ethyl acetoacetate (20 mmol), n-octadecane (3 mL; solvent), catalyst (0.25 g), 160 °C, 2 h.

<sup>b</sup>Calculated from sulfur wt % obtained by CHNS/O analysis.
Supplementary data

Supplementary data are available with the article through the journal Web site (www.nrcresearchpress.com/cjc).

Acknowledgement

The authors are thankful to H.M. Desai, Vice-Chancellor, Dharmsinh Desai University (DDU), Gujarat, India, for providing necessary facilities and Professor D.O. Shah, Founding Director, Shah-Schulman Center for Surface Science and Nanotechnology (SSCSSN), DDU, for valuable technical discussions. They are also thankful to Shimadzu Application Director, Shah-Schulman Center for Surface Science and Dharmsinh Desai University (DDU), Gujarat, India, for providing necessary facilities and Professor D.O. Shah, Founding Director, Shah-Schulman Center for Surface Science and Nanotechnology (SSCSSN), DDU, for valuable technical discussions. They are also thankful to Shimadzu Application Director, Shah-Schulman Center for Surface Science and Nanotechnology (SSCSSN), DDU, for valuable technical discussions. They are also thankful to Shimadzu Application}

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