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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.

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Introduction

Methanesulfonic acid (CH₃SO₃H; MSA) is a strong Brønsted acid (p $K_a = -1.9$) 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 1,1,2,2tetrafluoroethanesulfonic 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 acidcatalyzed 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 acidcatalyzed Pechmann reaction of activated phenols and a-keto esters¹³ using homogeneous Brønsted¹⁴⁻¹⁶ and Lewis^{17,18} 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 ionexchange 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 time^{20-25,27} or a higher reaction temperature^{22,24,27} 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

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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 (SiO₂–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 (~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 mLof 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 SiO₂–MSA catalyst

The catalyst was characterized by N₂ adsorption-desorption isotherm, FT-IR, FT-IR of the pyridine-adsorbed sample, potentiometric titration, thermal analysis (TGA-DTA), and CHNS/O elemental analysis. The Brunauer-Emmett-Teller (BET) surface area and average pore diameter of the samples were measured by N₂ 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 cm³/min). The amount of MSA loaded on the silica was calculated from the TGA results (W_{MSA}) using the following equation:8

$$[1] \qquad W_{\rm MSA} = (W_{\rm SiO-MSA})/{\rm FW}_{\rm MSA}$$

where $W_{\text{SiO-MSA}}$ = weight loss (mg/g) of SiO₂-MSA catalyst from 25 to 500 °C, W_{SiO} = weight loss (mg/g) of SiO₂ support from 25 to 500 °C, and FW_{MSA} = molecular weight of CH₃SO₃H. 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 SiO₂–MSA for synthesis of 4methylcoumarin derivatives by the Pechmann reaction

The derivatives of 4-methylcoumarin were synthesized by the SiO₂–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 (~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 ¹H 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. ¹H NMR spectra were determined on a NMR spectrometer (Bruker Avance DPX, 200 MHz) as dimethyl sulfoxide (DMSO-*d*₆) solutions. Chemical shifts (δ) were expressed in ppm downfield from the internal standard tetramethylsilane.



Resorcinol; $R_1=R_3=-H$, $R_2=-OH$ Phloroglucinol; $R_1=-H$, $R_2=R_3=-OH$ Pyrogallol; $R_1=R_2=-OH$, $R_3=-H$ *m*-Methoxy phenol; $R_1=R_3=-H$, $R_2=-OCH_3$ *m*-Methyl phenol; $R_1=R_3=-H$, $R_2=-CH_3$ Phenol; $R_1=R_2=R_2=H$

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

			Type of acid s	Loading of MSA e of acid site ^a (μmol/g)		f MSA		
Sample	$S_{\rm BET}$ (m ² /g)	D _P (Å)	Brønsted acidity band area (A/cm)	Lewis acidity band area (A/cm)	N _{MSA} ^b	$W_{\mathrm{MSA}}{}^{c}$	Acid site (μmol <i>n</i> -butylamine / g) ^d	Yield of 7-hydroxy- 4-methylcoumarin (wt %) ^e
SiO ₂ support SiO ₂ -MSA	373 362	31 31	5.3	 Nil	1000	1200	1200	0 94

Note: S_{BET} , BET surface area; D_{P} , 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.

^aIR study of pyridine-adsorbed sample.

^bCalculated from sulfur wt % obtained by CHNS/O analysis.

^cBy TGA analysis.

^dBy potentiometric titration with *n*-butylamine.

^eResorcinol (10 mmol), ethyl acetoacetate (20 mmol), catalyst (0.25 g), 160 °C, 12 h.

7-Hydroxy-4-methylcoumarin

mp: 185–190 °C (lit.²⁵ mp 188 °C). FT-IR (KBr, cm⁻¹): 3159 (ν_{OH}), 1674 ($\nu_{C=O}$). ¹H NMR (DMSO- d_6) 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=CH–), 2.36 (s, 3H, –CH₃).

5,7-Dihydroxy-4-methylcoumarin

mp: 283–285 °C (lit.²⁹ mp 284–285 °C). FT-IR (KBr, cm⁻¹): 3159 (ν_{OH}), 1670 ($\nu_{C=O}$). ¹H NMR (DMSO- d_6) 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=CH–), 2.5 (s, 3H, –CH₃).

7,8-Dihydroxy-4-methylcoumarin

mp: 242–245 °C (lit.³⁰ mp 242–244 °C). FT-IR (KBr, cm⁻¹): 3231 (ν_{OH}), 1648 ($\nu_{C=O}$). ¹H NMR (DMSO- d_6) 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=CH–), 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 $(373 \text{ m}^2/\text{g})$, 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 (v_{O-H}, for -OH groups of silica and adsorbed water) including small peaks at 3650 $(v_{O-H}, \text{ for free silanols } \equiv \text{Si-OH})$ and 1630 cm⁻¹ ($\delta_{O-H}, \text{ for}$ 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.⁴ The FT-IR spectrum of SiO₂-MSA shows a peak at 1337 cm⁻¹ for the $v_{S=O}$ stretching mode of the $-SO_3H$ group and a small peak at 1425 cm $^{-1}$ for the $\delta_{C\text{-H}}$ bending mode of the $-\text{CH}_3$ group.³¹ 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 Brønsted acid sites, showing the presence of a significant amount of Brønsted acidity. There is no peak in the range of 1440–1450 cm⁻¹ for adsorbed pyridine on Lewis sites. Thus, the catalyst has predominantly Brønsted 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 Scheme 2. Interaction of methanesulfonic acid (MSA) with the silanol of silica and generation of Brønsted acid sites.



Fig. 1. FT-IR spectra of silica support and SiO₂ – methanesulfonic acid (MSA) catalyst.



Fig. 2. FT-IR spectrum of pyridine adsorbed SiO₂ – methanesulfonic acid (MSA) catalyst.



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 ($E_i = 612 \text{ mV}$)²⁵ 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 SiO₂ support and SiO₂–MSA catalyst are given in Figs. 4*a* and 4*b* showing two-stage weight loss in SiO₂–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_{MSA}) ,⁸ was 1200 µmol/g (Table 1). The amount of MSA

loaded over silica (N_{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_{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 **Fig. 3.** Potentiometric titration curves of SiO_2 – methanesulfonic acid (MSA) catalyst and SiO_2 support.



Fig. 4. TGA-DTA profile of (*a*) silica support and (*b*) SiO_2 – methanesulfonic acid (MSA) catalyst.





Fig. 5. Yield (wt %) of 7-hydroxy-4-methylcoumarin at different

catalyst loading (6.5-1.3 wt %). (Reaction conditions: resorcinol -

Fig. 6. Yield (wt %) of 7-hydroxy-4-methylcoumarin with time in solvent-free conditions and in the presence of various solvents. (Reaction conditions: 10 mmol resorcinol, 20 mmol ethyl acetoacetate, 3 mL solvent, 0.25 g catalyst, 160 °C)



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

Sample			Reaction		Yield	
No.	Solid acid	Reaction temp. (°C)	time (h)	Solvent	(wt %)	Ref.
1	Amberlyst ion-exchange resins	Reflux temp.	2	Toluene	95	19
2	Zeolite	120/Reflux temp.	4	None/toluene	77-80	20
3	Montmorillonite				96	21
	K-10	150	4	None		
	K-10	Reflux temp.	8	Toluene	94	
	KSF	150	5	None	88	
	KSF	Reflux temp.	10	Toluene	90	
4	SO_4/ZrO_2	170	3–24	None	91	22
5	Benzylsulfonic acid functionalized mesoporous Zr–TMS	150	20	None	86	23
6	Metal (Ga ³⁺ , In ³⁺ , La ³⁺ , and Ce ³⁺) ion-exchanged ZAPO-5	175	6	None	90	24
7	W/ZrO ₂	Reflux temp.	6	Toluene	80	25
8	Nafion resin/silica nanocomposites	Reflux temp.	2	Toluene	80–97	26
9	Polyaniline sulfate salt	150/170	6	None	72	27
10	SiO ₂ –MSA catalyst	160	2	<i>n</i> -Hexadecane/ <i>n</i> -octadecane	99	

Table 2. The reaction conditions and yield of 7-hydroxy-4-methylcoumarin reported with various solid acid catalysts and SiO_2 – methanesulfonic acid (MSA) catalyst.

also observed that the higher the catalyst amount, the faster the initial rate (see Supplementary data, Fig. S2.

Nitrobenzene and higher n-alkanes (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 product¹⁹ and the reduction in the number of available active sites owing to bonding of nitrobenzene molecules with active sites.²² Nonpolar solvents such as toluene, cumene, THF, etc., 19,20 have been widely used for synthesis of 7-hydroxy-4-methylcoumarin and toluene has been found to be one of the best nonpolar solvents.¹⁹ However, toluene is a hazardous, nonseparable, nonreusable, and volatile aromatic, which limits its hightemperature applications. In the present work, higher *n*-alkanes (n-dodecane, n-hexadecane, and n-octadecane) were used as 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 noctadecane 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.¹²

Regeneration study of spent SiO₂-MSA

The spent catalyst, recovered from the reaction mixture (in *n*-octadecane) was regenerated by washing with methanol



Table 3. Yield (wt %) of 4-methylcoumarin derivatives synthesized by the Pechmann reaction using SiO_2 – methanesulfonic acid (MSA) catalyst.

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

 $(2 \times 10 \text{ mL})$ 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 SiO_2 -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 4. Regeneration study of spent SiO_2 – methanesulfonic acid (MSA) catalyst.

Reaction cycle	Yield (wt %) of 7-hydroxy- 4-methylcoumarin ^{<i>a</i>}	Amount of MSA $(N_{MSA}, \mu mol/g)^b$
Fresh catalyst	99	1000
I	97	_
II	96	_
III	94	984

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

^bCalculated 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).

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