Catalysis Science & Technology

This article can be cited before page numbers have been issued, to do this please use: B. Karimi, H. Mohamad-Mirzaei, A. Mobaraki and H. Vali, *Catal. Sci. Technol.*, 2015, DOI: 10.1039/C5CY00267B.

Catalysis Science & Technology

DOI: 10.1039/C5CY00267B

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Periodic mesoporous organosilica functionalized sulfonic acid in the esterification and selective acylation reactions

Babak Karimi,*[a] Hamid M. Mirzaei[a], Akbar Mobaraki[a], and Hojatollah Vali[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

The application of sulfonic acid functionalized periodic mesoporous organosilicas (PMOs) having either phenylene (**1a**) or ethyl (**1b**) bridging groups was investigated in the esterification of a variety of alcohols and fatty acids. It was found that **1b** consistently exhibited higher catalytic performance than the **1a** in the described reaction. In particular, it was proposed that the superior catalytic activity of **1b** in esterification of fatty acids with methanol is a result of adequate hydrophobic-hydrophilic surface balance in ethyl PMO catalyst. In addition, the study of chemoselective acylation of 1,3-butandiol with dodecanoic acid with varied mesoporous solid acids including both **1a** and **1b** implies that there is a compromise between the reaction selectivity and the surface physicochemical properties of the employed catalyst. Our results clearly show that the catalyst having high surface hydrophilic nature gives high selectivity toward the formation of mono-acylated products whereas those with relatively high hydrophobic characteristics showed enhanced selectivity toward formation of di-acylated products.

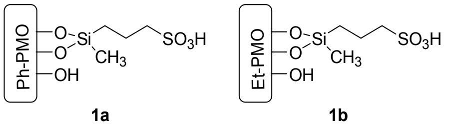
Introduction

Direct esterification of alcohols and/or acids is one of the simplest but still challenging reactions from both academic and industrial point of views.[1] Although many strong homogeneous and conventional acid catalysts can normally promote these transformations toward ester formation, there are several crucial issues that should be tackled: (1) In most cases the homogeneous catalysts are either deactivated or decomposed through the solvation with by-produced water, furnishing significant amount of acidic wastes. (2) These classified protocols require large quantities of non-recyclable homogeneous acids. (3) The selectivity of these systems is often very difficult to control especially when multi-functional alcohols or polyols are involved. Although, heterogeneous solid acids have been served to partly circumvent these issues, to date only a few solid acids are identified to exhibit acceptable performances in the reactions that water participates as by-product.[2] Moreover, the high mass transfer resistance dealing with many commercial solid acid catalysts usually gives rise to their lower catalytic performance as compared with homogeneous acid catalysts. Therefore, the search for solid acids with improved water compatibility by emphasizing the possibility to enhance both catalytic activity and reaction selectivity has become an emerging area in modern chemistry. Accordingly, the concept of acid sites isolation from water molecules by controlling the surface wettability of solid acids proposed and becomes crucial to improve their durability and catalytic performance in the presence of water.[3]

Since the discovery of ordered mesoporous silicas (OMS),[4] several types of hybrid organic-inorganic catalysts based on functionalized mesoporous silicas have been widely explored for varied important chemical transformations.[5] These materials have gradually become a promising platform for designing new fascinating catalyst since several investigations showed a clear synergistic effect between the immobilized entities and the physicochemical nature of mesoporous silica framework. Such synergy in heterogeneous catalysts consisting hybrid organic-inorganic mesoporous materials creates features that are uncommon in most conventional heterogeneous catalysts. One of the most important features is that the surface physicochemical properties of these materials could be deliberately modified in the nanospaces of mesoporous materials where the active sites are actually immobilized with the hope of improving the catalytic activity and stability and sometimes selectivity.[6] Among the hybrid organic-inorganic composites, periodic mesoporous organosilicas (PMO's)[7] which are made from direct condensation of bridge organosilanes, commonly $(R^1O)_3Si-R^2-Si(OR^1)_3$, in the presence of surfactant templates clearly provides a breakthrough in the field of mesoporous materials. PMOs featured materials with open porous structure and high loading of homogeneous distribution of organic groups covalently bonded within the siliceous framework and inside the pore walls. This allows for the easy tailoring of both the chemical and physical properties while improving hydrothermal and mechanical stability of the porous framework. Accordingly, sulfonic acid functionalized PMO's were designed and used in a variety of reactions like esterification,[8] transesterification,[9] condensation,[10] etherification,[11] rearrangement, and alkylation.[12] Sulfonic acid PMO's are mainly categorized in two groups: (1) Sulfonic acid groups tethered into organic bridges such as phenylene[13] and ethane.[14] (2) Sulfonic acid groups embedded into channel walls of

View Article Online
DOI: 10.1039/C5CY00267B

PMO through an organosilanes precursor such as 3-mercaptopropyltrimethoxusilane. Although the first group has advantages such as higher stability of sulfonic acid sites and ability of incorporating higher loading of sulfonic acid groups, the second class benefits from higher local hydrophobicity of sulfonic acid sites. In this paper, we used route 2 to investigate the support physicochemical properties in esterification and acylation reactions. Recently, we found that periodic mesoporous organosilica functionalized sulfonic acids **1b** is an active catalyst in biodiesel formation[9] and Biginelli reaction (Scheme 1).[15]



Scheme 1 Sulfonic acid based PMOs having either phenylene **1a** or ethyl **1b**.

In these studies we found that the concomitant adjustment of hydrophilic-hydrophobic balance and acidic strength in the interior of mesochannels of these PMO and functionalized ordered mesoporous materials can indeed facilitate diffusion of the reactant and products in a set of selected acid catalyzed reaction,[9, 15-16] thereby enhancing the overall catalyst performance and/or sometimes selectivity. These promising results prompted us in investigating whether the same approach would enable us to control the catalyst performance of OMS-based sulfonic acids in direct esterification of alcohols with carboxylic acids. In this context, we suspected that the use of a PMO functionalized sulfonic acid having appropriate surface wettability may provide a means of obtaining highly selective mono-acylation of diols with carboxylic acids. Herein, we wish to disclose our findings regarding the use of sulfonic acid based PMO having either phenylene **1a** or ethyl **1b** as bridge and methylpropylsulfonic acid as functionalized group in esterification of fatty acids, acylation of alcohols and chemoselective acylation of 1,3-butanediol.

Experimental Section

Characterization

Acid-functionalized mesoporous organosilicas Ph-PMO-Me-$PrSO_3H$ **(1a)** and Et-PMO-Me-$PrSO_3H$ (**1b**) and other ordered mesoporous silica supported solid acids were synthesized according to the methods mentioned previously.[9] The textural properties of the functionalized mesoporous materials were determined by nitrogen adsorption-desorption analysis at -196 °C and water sorption at 25 °C with a Belsorp-max apparatus (See ESI). The surface area and pore size distribution were calculated with the BET and BJH methods, respectively. N_2-sorption isotherms indicate that the distribution of pore diameter of all samples is in the mesoporous range (Table 1). Also, hydrophilicity indices were measured according to Thommes method using water and nitrogen sorption analyzes (See ESI for more information). Organic material present in the solids was determined by elemental analysis (Pheometric Scientific analyzer). The organic composition of the modified mesoporous materials was also determined by thermogravimetric analysis (TGA) with heating from room temperature to 800 °C under Argon flow. The ion exchange capacities of the sulfonic acid functionalized mesoporous organosilicas were determined by acid-base titration and *p*H analysis (Table 1).

Results and Discussions

To start our investigation, we first examined a set of experiments to optimize the reaction parameters in benzyl alcohol esterification with acetic acid (Table 2).

Table 1 Characterization of functionalized PMOs.

Entry	PMO	S_{BET}[a]	V_p[b]	Pore size[c]	H-index[d]	Acid capacity[e]
1	**1a**	404	0.27	2.4	0.4	0.4
2	Et-PMO-Me-PrSH	213	0.24	3.5	-	-
3	**1b**	318	0.27	3.4	0.7	0.5
4	**1b** recycled	305	0.27	3.0	-	0.4[f]
5	SBA-15-$PrSO_3H$	682	0.92	6.2	0.8	1.2
6	SBA-15-Ph-$PrSO_3H$	349	0.62	5.4	0.2	0.8

[a] BET surface area ($m^2.g^{-1}$). [b] Total pore volume ($cm^3.g^{-1}$) at $P/P_0=0.99$. [c] BJH pore size diameter (nm). [d] Hydrophilicity index (H-index)= amount of adsorbed water/amount of N_2 adsorbed at ($P/P_0\approx0.92$). [e] determined by titration after ion-exchange ($mmolH^+.g^{-1}$). The N_2 sorption and ion exchange analysis of catalyst recovered from the 10th reaction cycle of esterification of stearic acid with methanol (please Fig. 2)

In this regard, the reaction of benzyl alcohol with acetic acid with molar ratio of benzyl alcohol to acetic acid (1:10) in the presence of 5 mol% **1b** was proceeded well at even room temperature after 30 h (Table 2, entry 1). In another experiment, we have used **1a** in a similar reaction conditions and it has been declared that this reaction does not conducted well and only furnished the corresponding ester in good yield at 60 °C after 48 h (Table 2, entry 2). It was also found that the same transformation using **1b** went to completion within 6 h at 60 °C (Table 2, entry 3). To further optimise the reaction conditions, we next decreased the amount of **1b** to as low as 1 mol% under otherwise identical reaction condition. Whereas a similar quantitative yield of benzyl acetate was recovered, the reaction time was considerably increased to 16 h (Table 2, entry 4). In the next stage, the ratio of benzyl alcohol to acetic acid was decreased from 1:10 to 1:5 and it was found that the reaction still went to completion within 24 h affording quantitative yields of benzyl acetate (Table 2, entry 5). Further decreasing the benzyl alcohol/acetic acid ratio led to inferior benzyl acetate of 94% while higher loading of **1b** catalyst (3 mol%) was employed under the same reaction condition (Table 2, entry 6). In addition, **1a** comprising phenylene bridge functionality was also examined and no yield over 69% was obtained under the same conditions (Table 2, entry 7). Similarly, either strong Brønsted mineral acid H_2SO_4 or SBA-15-$PrSO_3H$ displayed a lower activity than **1b** catalyst and resulted in the benzyl acetate yield not exceeding 70% (Table 2, entry 8, 9). These later two results clearly demonstrated the crucial rule of surface physicochemical properties of **1b** in the close vicinity of sulfonic acid groups in obtaining high catalytic activity of the material in direct esterification reaction. In particular, the large differences between **1a** and **1b** catalytic systems can be also rationalized by different physicochemical properties of PMO materials as we explained in our previous publications.[9,15] Having the optimized reaction conditions, we then moved to investigate the generality and activity of **1b** catalyst in the esterification reaction of a variety of alcohols with acetic acid.

View Article Online
DOI: 10.1039/C5CY00267B

Table 2 Esterification of benzyl alcohol with acetic acid in the presence of and Et-PMO-Me-PrSO$_3$H (**1b**)[a]

Entry	Catalyst	Catalyst (mol%)	MR	T (ºC)	Time (h)	Yield (%)[b]
1	1b	5	1:10	r.t.	30	>99
2	1a	5	1:10	60	48	>99
3	1b	5	1:10	60	6	>99
4	1b	1	1:10	60	16	>99
5	**1b**	**1**	**1:5**	**60**	**24**	**>99**
6	1b	3	1:3	60	24	94
7	1a	3	1:3	60	24	69
8	H_2SO_4	3	1:3	60	24	70
9	SBA-15 PrSO$_3$H	3	1:3	60	24	72

[a] MR is the molar ratio of benzyl alcohol to acetic acid. [b] Yields are based on isolated products using column chromatography.

As shown in Table 3, our catalyst is also quite effective for efficient reaction of aromatic alcohols as well as aliphatic alcohols, giving the corresponding ester products in excellent isolated yields. In particular, we found that even a long chain alcohol such as octadecanol gives the corresponding ester product in quantitative yield without any need for purification through column chromatography (Table 3, entry 8). In the same way, for the reaction of secondary alcohols with acetic acid in the presence of **1b**, it was possible to achieve good to excellent yield of the corresponding acetates by simply increasing the alcohol to acetic acid ratio to 1:10 (Table 3, entries 9-15). In this way, the present catalytic system was shown to be even effective for direct acetylation of relatively hindered secondary alcohols such as (-)-menthol and 2-adamantaol (Table 3, entries 14-15). However, it was unfortunately proved that **1b** was incapable in catalysing acetylation of *tert*-alcohol like 1-adamantanol even in the presence of an excess of acetic acid under reflux condition (Table 3, entry 16). From the data embodied in the Table 3, primary fatty alcohols were particularly found to effectively undergo the direct acetylation with acetic acid and consequently the corresponding fatty acetates were formed in good to quantitative yields (Table 3, entries 5-8).

Table 3 Acylation of a variety of alcohols with acetic acid in the presence of **1b**[a]

Entry	alcohol	MR	Yield (%)[b]
1	benzyl alcohol	1:5	>99
2	2-phenylethanol	1:5	92
3	3-phenylpropan-1-ol	1:5	94
4	4-nitrobenzyl alcohol	1:5	76
5	1-octanol	1:5	89
6	1-nonanol	1:5	86
7	1-decanol	1:5	90
8	1-octadecanol	1:5	>99
9	2-octanol	1:10	78
10	cyclohexanol	1:10	79
11	1-cyclohexylethanol	1:10	79
12	cycloheptanol	1:10	90
13	cyclooctanol	1:10	86
14	menthol	1:10	85
15	2-adamantanol	1:10	95
16[c]	1-adamantanol	-	40

[a] Alcohols (1 mmol) were reacted in the presence of 1 mol% **1b** catalyst for 24 h, MR is the molar ratio of alcohol to acetic acid. [b] Yields are based on isolated product using column chromatography by a solvent mixture of ethyl acetate:*n*-hexane (1:10). [c] Acetic acid (2.5 ml) was used in reflux condition for 24 h.

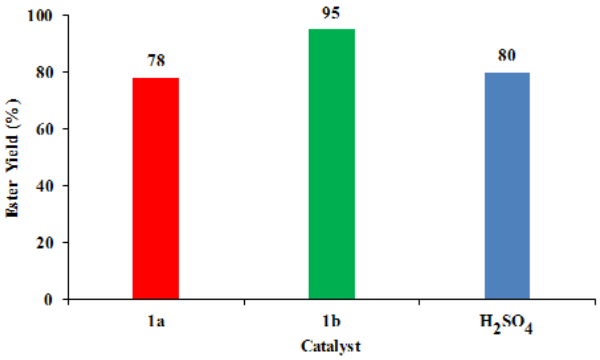
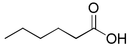
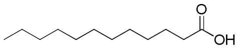
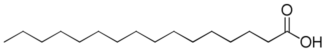
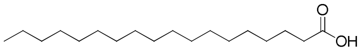


Fig. 1 Activity of **1a**, **1b** and **H_2SO_4** in the esterification of dodecanoic acid with methanol: dodecanoic acid (1mmol), methanol (10 mmol), catalyst (3 mol%), 60 °C for 30 h. Products are separated by column chromatography.

These initial interesting results stimulated our attention to also investigate the esterification of free fatty acids (FFA) with methanol, a reaction which is highly desirable in biodiesel formation (Table 4). For this reason, the esterification of dodecanoic acid (1 mmol) and methanol (10 mmol) was carried out over both mesoporous **1a** and **1b** catalysts, and also sulfuric acid using 3 mol% mesoporous catalysts and equivalent amount of sulfuric acid (Fig. 1). The reaction mixture was heated at 60 °C for 30 h and subsequently was filtered and washed with 20 ml dichloromethane to recover the catalyst. The dichloromethane and unreacted methanol were evaporated off and the corresponding methyl ester product was isolated by column chromatography.

Table 4 Direct esterification of carboxylic acids with methanol in the presence of **1b**[a]

Entry	Carboxylic acid	Yield (%)[b]
1		85
2		95
3		95
4		100

[a] 1 mmol carboxylic acid, 10 mmol methanol, 3 mol% **1b** catalyst at 60 °C for 30 h. [b] Isolated yield after column chromatography by solvent mixture (ethyl acetate:*n*-hexane in 1:10 volume ratio).

Figure 1 obviously demonstrated that **1b** catalyst has superior activity compared to **1a** and H_2SO_4. Once again these results confirmed the high activity of **1b** catalyst in esterification of free fatty acids. To examine and screen the ability of **1b** catalyst, fatty acids with varied chain length were used in this reaction. As summarized in Table 4, **1b** catalyst is also quite effective for efficient reaction of fatty acids and in this way the longest chain fatty acid gave the highest isolated yield (Table 3, entries 1-4), a similar behavior which was declared in the esterification of long chain alcohols (Table 3, entries 5-8). To provide an initial assessment on the recyclability of **1b** catalyst, a recovery investigation was conducted in which the esterification of stearic acid with methanol was studied over 10 cycles under the conditions summarized in Table 4.

View Article Online
DOI: 10.1039/C5CY00267B

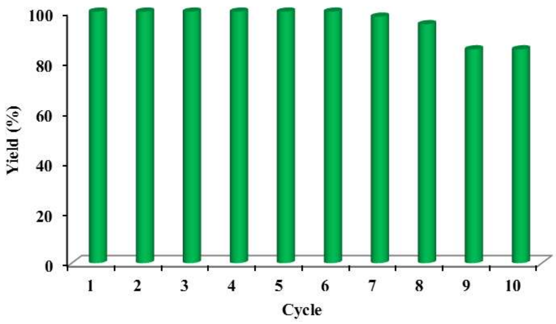
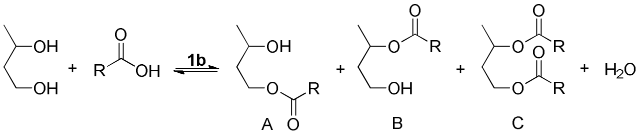


Fig. 2 Recyclability of **1b** catalyst in the esterification of stearic acid with methanol (1 mmol stearic acid, 10 mmol methanol, 3 mol% catalyst at 60 $^{\circ}$C for 30 h**.**

In each reaction run, the catalyst **1b** was easily separated from the reaction mixture, washed with dichloromethane and subsequently oven dried at 70 $^{\circ}$C before another reaction was performed. The recovered material could be added to the fresh substrate giving almost identical behavior (for at least 6 recycles) and then maintained approximately 85% of the original activity 4 additional cycles, demonstrating its high stability and durability under the present reaction conditions (Fig. 2). Further evidence for the stability and robustness of **1b** was obtained from TEM and *N₂* sorption analysis of catalyst recovered from the final cycle (Fig. 3). As illustrated in Figure 3 the majority of textural as well as structural characteristics of the recovered **1b** were largely retained. In the last run, titration of ion-exchanged catalysts shows that there is indeed a negligible decrease in the proton capacity of the recycled catalyst from 0.5 mmol H^+ g^{-1} for fresh catalyst to 0.4 mmol H^+ g^{-1} for the recycled catalyst from the 10th run (Table 1, entry 4). This result clearly shows the high stability of our catalyst under the described reaction condition and recycling experiments.

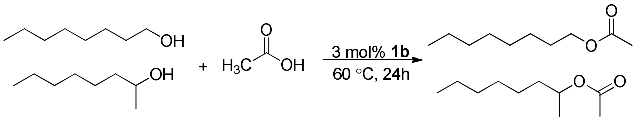
Study of selective acylation of 1,3-butanediol

To further investigate the utility of **1b** in the esterification reaction, we then chose to evaluate the ability of this catalyst in chemoselective acylation of an unsymmetrical diol such as 1,3-butanediol with some selected carboxylic acids (Scheme 2).



Scheme 2 Chemoselective acylation reaction of 1,3-butanediol with carboxylic acids in the presence of **1b** catalyst.

For the purpose of comparison, we started our investigation with comparing esterification of a primary alcohol with a secondary one having similar carbon number in a one-pot reaction to find whether primary or secondary acetate might be selectively formed (Scheme 3). In this way, a competitive acylation reaction between 1-octanol (1 mmol) and 2-octanol (1 mmol) with acetic acid (1 mmol) was conducted in the presence of **1b** catalyst at 60 $^{\circ}$C for 24 h. Subsequently, the corresponding ester products were isolated by column chromatography. The reaction gave 49% isolated yield and NMR spectroscopy revealed that there is a mixture of both 1-octyl acetate and 2-octyl acetate in ratio of 5:1 (~83% selectivity for primary alcohol esterification), respectively.



Scheme 3 Selective acylation reaction of primary and secondary alcohols

Following this result, we next managed to conduct the esterification reaction of 1,3-butanediol (1 mmol) with acetic acid (1 mmol) at 60 $^{\circ}$C in the presence of **1b** catalyst. After 24 h, the products were isolated through column chromatography and it was found in addition to the corresponding mono esters A and B mixture, diacylated product C were also obtained in 53% and 14% isolated yields, respectively (Table 5, entry 1).

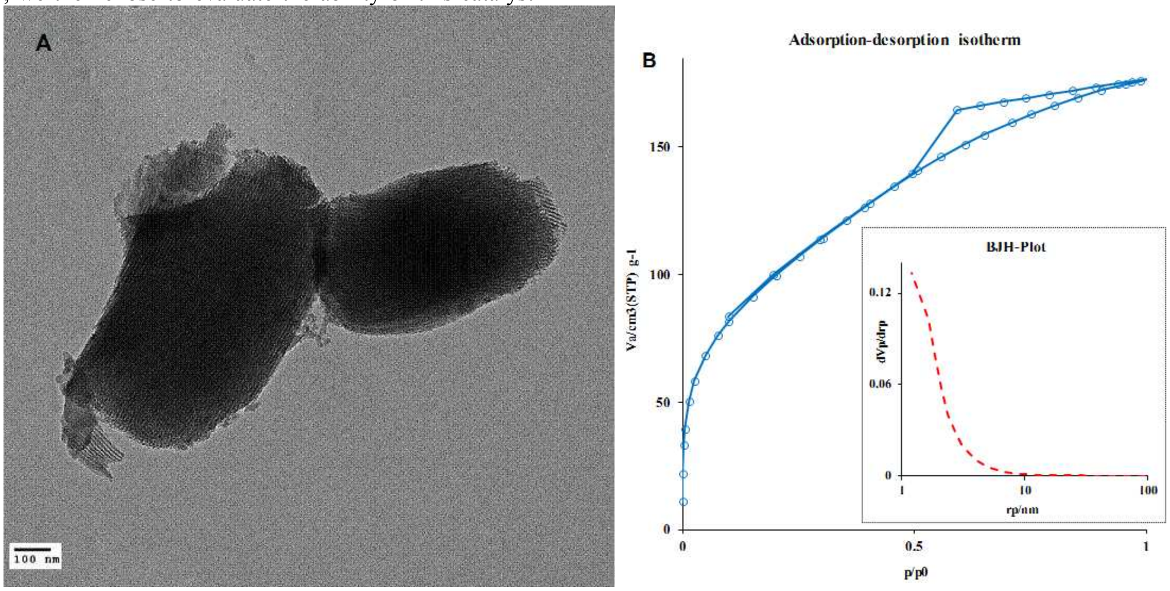


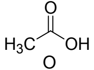
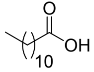
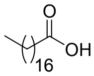
Fig. 3 TEM (A) and N_2 adsorption-desorption isotherm (B) of **1b** catalyst (the inset is BJH pore size distribution plot) after 10 times recycling from the esterification reaction of stearic acid with methanol.

Dynamic Article Links ►
View Article Online
DOI: 10.1039/C5CY00267B

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Table 5 Chemoselectivity of 1,3-butanediol in the reaction with carboxylic acids in the presence of **1b**[a]

Entry	Carboxylic acid	Yield (%)[b]	S_{mono} (%)[c]	S_{di} (%)[c]
1		67	79	21
2		56	72	28
3		64	87	13

[a] 1 mmol carboxylic acid, 1 mmol 1,3-butanediol, 3 mol% catalyst (0.060 g), 60 °C, 24 h. [b] products were isolated by column chromatography and reported yield is total isolated yield. [c] S_{mono} and S_{di} are selectivity of mono-acylated and di-acylated products, respectively.

Moreover, ^{1}HNMR spectroscopy revealed that products A and B are a mixture with ratio of (2.5:1). Thus, to collect more information about the nature of chemoselectivity in our catalytic system, other carboxylic acids such as dodecanoic acid and stearic acid were employed under the same reaction conditions in the presence of **1b** catalyst (Table 5, entries 2-3). Once again, the products were isolated and the corresponding A, B, and C product yields were determined using column chromatography and NMR spectroscopy. Interestingly, these reactions also resulted in the same ratio of mono-acylated products A and B (2.5:1). Moreover, these experiments demonstrated regardless to the hydrophobic nature of the employed carboxylic acid a more or less the same reaction selectivity toward mono-acylated formation over **1b** catalyst was attained (Table 5, entries 1-3).

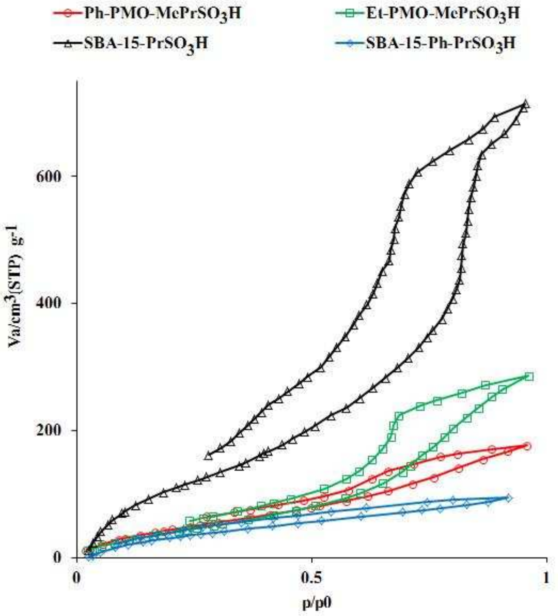


Fig. 4 Water sorption analysis for mesoporous solid acids.

Altogether, these results roughly point to the fact that both hydrophobic and hydrophilic starting materials can similarly penetrate into the nanospaces of **1b**, and a surface hydrophilic/hydrophobic balance in **1b** might be the major reason for the observed more or less similar chemoselectivity. To get insight into whether the surface physicochemical properties in acid catalyst could influence (change) the mode of the described chemoselectivity, we repeated the esterification of 1,3-butanediol with dodecanoic acid in the presence of SBA-15-PrSO_3H, SBA-15-Ph-PrSO_3H, and **1a** catalysts under the same reaction conditions. These catalysts differ from the standpoint of surface polarity as evidenced by their water adsorption-desorption isotherm in the gas phase and we suspect that a change in surface polarity of a catalyst might result in a change in its product selectivity. As it can be clearly seen in Figure 4, Among the described solid sulfonic acid catalysts, SBA-15-PrSO_3H exhibited the highest water uptake at relative $>P/P_o \approx 0.7$-0.8 due to capillary condensation of water and thus can be considered as the most hydrophilic catalyst. In contrast, SBA-15-Ph-PrSO_3H showed the lowest water condensation in the above-mentioned relative pressure range, demonstrating that its mesopores are highly hydrophobic in nature. On the other hand, the total amounts of water uptake in the mesopores of either ethyl or phenylene PMO supported sulfonic acids are located within these two limits that is most likely owing to a more or less hydrophilic-hydrophobic balance in their nanospaces. Having characterized the surface physicochemical properties of the catalyst, the catalytic activity of these catalysts (3 mol%) was then individually examined in the esterification of 1,3-butanediol (1 mmol) with dodecanoic acid (1 mmol) under otherwise optimized reaction condition demonstrated in Table 5. From the results demonstrated in Table 6, it appeared that while SBA-15-PrSO_3H (most hydrophilic catalyst) exhibited excellent selectivity toward the formation of mono-acylated product A, SBA-15-Ph-PrSO_3H (most hydrophobic catalyst) resulted in the highest selectivity in di-acylated product C production (Table 6, entries 1, 2). Under similar reaction condition, **1a** also exhibited a considerable selectivity toward di-acylated product C but the value is lower than that of SBA-15-Ph-PrSO_3H whereas it is still higher than that of **1b** (Table 6, entries 2-4). Taking into consideration the different surface physicochemical properties of the described catalysts (Fig. 4) and the results in Table 6, it is obviously clear the catalyst with more hydrophobic character gave more di-acylated product and the catalyst with hydrophilic character will result in more mono-acylated product. To quantify the hydrophobic-hydrophilic nature of the catalysts, we also used H-index which shows differences in surface chemistry between porous materials regardless to their chemical composition.[17] To measure this index, water and nitrogen adsorption analyzes were performed for all catalysts and the amount of water and nitrogen gas adsorbed at P/P_0~0.92 were converted from gas volume into liquid volume using Gurvich rule assuming that all pores were filled at this point.

View Article Online
DOI: 10.1039/C5CY00267B

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

Table 6 Chemoselectivity of 1,3-butanediol in the reaction with dodecanoic acid in the presence of various mesoporous sulfonic acids[a]

Entry	Catalyst	H-index	MR	Yield (%)	mono-acylated yield (%)[b]	S_{mono} (%)[c]	di-acylated yield (%)[b]	S_{di} (%)[c]
1	SBA-15-$PrSO_3H$	0.8	1:1	59	57	97	2	3
2	SBA-15-Ph-$PrSO_3H$	0.2	1:1	60	25	42	35	58
3	**1b**	0.7	1:1	56	40	72	16	28
4	**1a**	0.4	1:1	41	24	58	18	44
5	SBA-15-Ph-$PrSO_3H$	0.2	1:2	90	29	32	61	68

[a] 1 mmol 1,3-butanediol, 3 mol% catalyst, 60 °C, 24 h. [b] products were isolated by column chromatography. [b] S_{mono} and S_{di} are selectivity of mono-acylated and di-acylated products, respectively.

These indices can be measured according to formula [H-index=$V_{p(water)}/V_{p(Nitrogen)}$] where $V_{p(water)}$ and $V_{p(Nitrogen)}$ are, respectively, the volume of water and nitrogen in liquid form at a P/P_o=0.92. In this context, higher H-index value of a catalyst is an indication for its higher surface hydrophilicity. After calculating this parameter for all catalysts, a diagram of their individual relative product selectivities either toward mono- or di-acylated products was depicted against the respected H-indices (Fig. 5). As the H-index increased from 0.2 to 0.8 the selectivity for mono-acylated products enhanced markedly. This diagram also highlights the notion that decreasing the H-index value of the employed catalysts would gradually result in a selectivity changeover toward the formation of di-acylated product, reaching to a maximum value of 58% in the case of SBA-15-Ph-$PrSO_3H$ catalyst which has the lowest H-index ≈ 0.2 (Fig. 5, black dash plot). This diagram accompanied with the data embodied in Table 6 implies that the high surface hydrophobicity of the catalyst in close vicinity of the active sites is indispensable in attaining high selectivity toward di-acylated product. It is clear that the esterification of 1,3-butanediol with fatty acids like dodecanoic acid would first result in monoester, which is more hydrophobic than the starting diol. Therefore, it is reasonable to speculate that high affinity of silica framework in SBA-15-$PrSO_3H$ (H-index ≈ 0.8) for polar 1,3-butanediol provides a driving force for rapid departure of monoester form the relatively hydrophilic catalyst surface, thus suppressing to a great extent the formation of diester C.

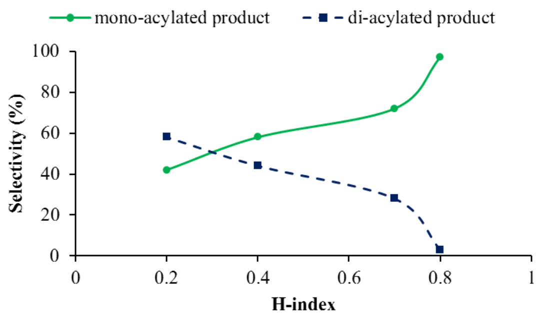


Fig. 5 Product selectivity dependence for the reaction of 1,3-butanediol and dodecanoic acid with H-index.

On the other hand, when the catalyst surface becomes more hydrophobic as in the case for SBA-15-Ph-$PrSO_3H$ (H-index ≈ 0.2), the resulting monoesters A and B would tend to reside inside the system pore of the catalyst to a greater extend. This allows monoesters to undergo further esterification at the available catalyst active sites, thus increasing the corresponding diester C products. Based on this model, it is thereby expected that any increasing the in the amount of starting dodecanoic acid should improve the selectivity of the process toward diester formation. In fact, we found that by increasing dodecanoic acid:1,3-butanediol ratio from 1:1 to 2:1 in the presence of SBA-15-Ph-$PrSO_3H$, the selectivity toward the formation of diester was increased from 58% to 68%, further verifying the validity of this model. Altogether the results demonstrated in Table 6 offer the possibility of achieving significant degree of chemoselectivity toward either mono-acylated or di-acylated products by adjusting the surface hydrophobicity of the employed solid acids.

In a similar way, the lower selectivity of either **1a** or **1b** compared to SBA-based sulfonic acids might be most likely attributed to hydrophilic-hydrophobic balance in the system pores of these PMO-based catalyst, which inevitably allowed both hydrophobic (monoester and/or dodecanoic acid) and hydrophilic (1,3-butanediol) materials to favourably reach at their available active site, thus causing significant drop in selective formation of either mono- or diacylated products. This hydrophilic-hydrophobic balance inside the nanospaces of **1b** may also account for its enhanced catalytic performance in the esterification of fatty acids with methanol (Table 4), where a fast mass transfer of both hydrophobic and hydrophilic starting materials to the active sites located inside the nanospaces of the catalyst is prerequisite to ensuring the observed high product yields.

Conclusions

Sulfonic acid functionalized Periodic Mesoporous Organosilicas (PMOs) having ethyl or phenylene bridging groups were employed in the esterification reaction. It has been shown that catalyst bearing ethyl bridging group consistently exhibited higher catalytic performance rather phenylene PMO counterpart. In particular, it was proposed that the superior catalytic activity of **1b** in esterification of fatty acids with methanol is a result of adequate hydrophobic-hydrophilic surface balance in ethyl PMO

View Article Online
DOI: 10.1039/C5CY00267B

catalyst. In addition, the study of chemoselective acylation of 1,3-butandiol with dodecanoic acid with varied mesoporous solid acids including both **1a** and **1b** implies that there is a compromise between the reaction selectivity and the surface physicochemical properties of the employed catalyst. Our results clearly show that the catalyst having high surface hydrophilic nature gives high selectivity toward the formation of mono-acylated products whereas those with relatively high hydrophobic characteristics showed enhanced selectivity toward formation of di-acylated products. We speculate the results of this study would provide more information in designing novel types of sophisticated hybrid solid acid catalysts with tuneable selectivity in the described reaction by just adjusting their surface physicochemical Properties of the employed catalyst.

Notes and references

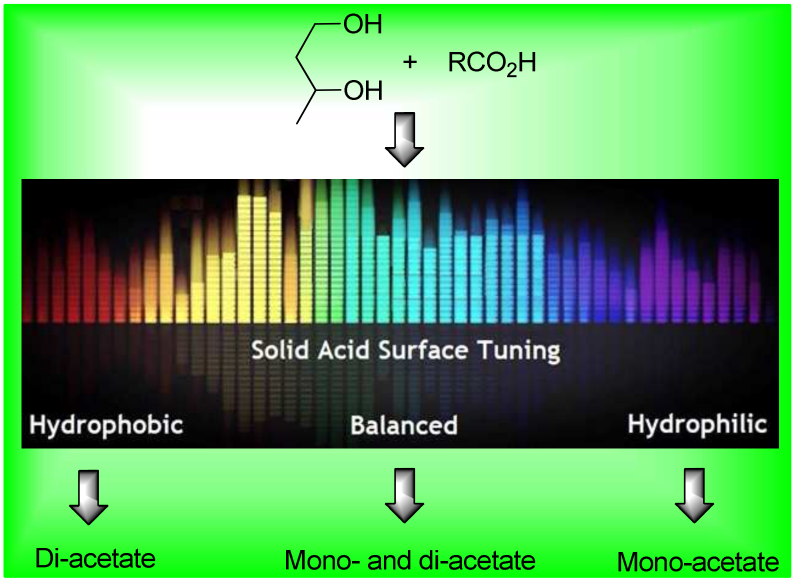
[a] *Prof. Dr. Babak Karimi, Hamid M. Mirzaei, and Akbar Mobaraki*
Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS),Zanjan 45137-6731 (Iran)
Fax: (+98)-241-415-3232
E-mail:karimi@iasbs.ac.ir
[b] *Prof. Hojatollah Vali*
Department of Anatomy and Cell Biology and Facility for Electron Microscopy Research, McGill University, Montreal, Quebec, H3A 2A7 Canada.

† Electronic Supplementary Information (ESI) available: [procedures for catalysts preparation, porosimetry data, TG analysis, TEM, ^{1}HNMR, ^{13}CNMR]. See DOI: 10.1039/b000000x/

1 J. Otera, Esterification: Methods, Reactions and Applications, Wiley-VCH Verlag GmbH &Co. KGaA, Weinheim, 1st edn, 2003.
2 a) T. Okuhara, *Chem. Rev.*, 2002, **102**, 3641; b) K. Inumaru, T. Ishihara, Y. Kamiya, T. Okuhara, and S. Yamanaka, *Angew.Chem. Int. Ed.* 2007, **46**, 7625; c) A. Corma, and M. Renz, *Angew. Chem. Int. Ed*. 2007, **46**, 298; d) C. Tsai, H. Chen, S. M. Althaus, K. Mao, T. Kobayashi, M. Pruski, and V. S. –Y, Lin, *ACS Catal*. 2011, **1**, 729; e) Q. Yang, S. Ma, J. Li, F. Xiao, and H. Xiong, *Chem. Commun*. 2006, 2495;
3 a) I. K. Mbaraka and B. H. Shanks, *J. Catal*., 2005, **229**, 365; b) I. K. Mbaraka and B. H. Shanks, *J. Catal*., 2006, **244**, 78; c) L. Sherry and J. A. Sullivan, *Catal. Today*, 2011, **175**, 471; d) P. L. Dhepe, M. Ohashi, S. Inagaki, M. Ichikawa and A. Fukuoka, *Catal. Lett.,* 2005, **102**, 163; e) A. Karam, J. C. Alonso, T. I. Gerganova, P. Ferreira, N. Bion, J. Barrault and F. Jérôme, *Chem. Commun.*, 2009, 7000; f) M. H. Tucker, A. J. Crisci, B. N. Wigington, N. Phadke, R. Alamillo, J. Zhang, S. L. Scott and J. A. Dumesic, *ACS Catal.*, 2012, **2**, 1865.
4 a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710; b) D. Zhao, J. N. Feng, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.
5 a) A. P. Wight and M. E. Davis, *Chem. Rev.*, 2002, **102**, 3589; b) Z.-L. Lu, E. Lindner and H. A. Mayer, *Chem. Rev.*, 2002, **102**, 3543; c) J. A. Melero, R. van Grieken and G. Morales, *Chem. Rev.*, 2006, **106**, 3790.
6 K. Inumaru, T. Ishihara, Y. Kamiya, T. Okuhara and S. Yamanaka, *Angew. Chem., Int. Ed.*, 2007, **46**, 7625.
7 a) S. Inagaki, S. Gouan, Y. Fukushima, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 1999, **121**, 9611; b) B. J. Melde, B. T. Holland, C. F. Blanford and A. Stein, *Chem. Mater.*, 1999, **11**, 3302; c) C. Ishii, T. Asefa, N. Coombs, M. J. MacLachlan and G. A. Ozin, *Chem. Commun.*, 1999, 2539.
8 a) Q. Yang, M. P. Kapoor and S. Inagaki, *J. Am. Chem. Soc.*, 2002, **124**, 9694; b) Q. Yang, M. P. Kapoor, N. Shirokura, M. Ohashi, S. Inagaki, J. N. Kondo and K. Domen, *J. Mater. Chem.*, 2005, **15**, 666; c) D. Elhamifar, B. Karimi, A. Moradi and J. Rastegar, *ChemPlusChem*, 2014, **79**, 1147.
9 B. Karimi, H. M. Mirzaei and A. Mobaraki, *Catal. Sci. Technol.*, 2012, **2**, 828.
10 V. Dufaud and M. E. Davis, *J. Am. Chem. Soc*., 2003, **125**, 9403.
11 a) J. G. C. Shen, R. G. Herman and K. Klier, *J. Phys. Chem. B*, 2002, **106**, 9975; b) B. Sow, S. Hamoudi, M. H. Zahedi-Niaki and S. Kaliaguine, *Microporous Mesoporous Mater.*, 2005, **79**, 129.
12 B. Rác, P. Hegyes, P. Forgo and A. Molnár, *Applied Catalysis A: Gen*., 2006, **299**, 193.
13 a) K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen and J. N. Kondo, *Adv. Mater.*, 2005, **17**, 1839; b) K. Nakajima, I. Tomita, M. Hara, S. Hayashi, K. Domen and J. N. Kondo, *Catal. Today*, 2006, **116**, 151; c) D. Esquivel, E. De Canck, C. Jimenez-Sanchidrian, P. Van Der Voort and F. J. Romero-Salguero, *J. Mater. Chem.*, 2011, **21**, 10990.
14 D. Esquivel, O. van den Berg, F. J. Romero-Salguero, F. Du Prez, and P. Van Der Voort, *Chem. Commun.,* 2013, **49**, 2344.
15 B. Karimi, A. Mobaraki, H. M. Mirzaei, D. Zareyee and H. Vali, *ChemCatChem*, 2014, **6**, 212.
16 a) B. Karimi and D. Zareyee, *Org. Lett.*, 2008, **10**, 3989; b) B. Karimi and D. Zareyee, *J. Mater. Chem.*, 2009, **19**, 8665.
17 M. Thommes, S. Mitchell and J. Pérez-Ramírez, *J. Phys. Chem. C*, 2012, **116**, 18816.

View Article Online
DOI: 10.1039/C5CY00267B

Graphical Abstract



A simple adjusting of surface physicochemical Properties of the solid acid catalyst would provide selective formation of the desired product.