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Communication

Impact of macroporosity on catalytic upgrading of fast pyrolysis bio-oil by esterification over silica sulfonic acids

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Abstract: Fast pyrolysis bio-oils possess unfavourable physicochemical properties and poor stability, due in large part to the presence of carboxylic acids, which hinders their use as biofuels. Catalytic esterification offers an atom and energy efficient route to upgrade pyrolysis bio-oils. Propyl sulfonic acid silicas are active for carboxylic acid esterification but suffer mass-transport limitations for bulky substrates. Macropore (200 nm) incorporation enhances the activity of mesoporous SBA-15 architectures (post-functionalised by hydrothermal saline promoted grafting) for the esterification of linear carboxylic acids, with the magnitude of turnover frequency (TOF) enhancement increasing with chain length from 5 % (C_3) to 110 % (C12). Macroporous-mesoporous PrSO3H/SBA-15 also offers a twofold TOF enhancement over its mesoporous analogue for the esterification of a real, thermal fast pyrolysis bio-oil derived from woodchips. The total acid number was reduced by 57 %, with GCxGC-ToFMS evidencing ester and ether formation accompanying loss of acid, phenolic, aldehyde and ketone components.

Introduction

Biofuels have an important role to play in mitigating anthropogenic climate change arising from the combustion of fossil fuels.^[1] In the context of energy, despite significant growth in fossil fuel reserves, great uncertainties remain in the economics/environmental impact of exploitation, and crucially ~65-80 % of such carbon resources cannot be burned without breaching the UNFCC targets for a 2 °C increase in mean global temperature. Biofuels will prove critical in helping many countries meet their renewable energy commitments, which for the UK are 15 % by 2020, alongside greenhouse gas (GHG) emission reductions of 34 % by 2020 and 80 % by 2050 (cf. 1990 levels). They also represent drop-in fuels able to utilise existing pipeline and filling station distribution networks.^[2] Thermochemical processing of waste biomass such as lignocellulosic materials sourced from agriculture or municipal waste offers a promising route to biofuels through pyrolysis.^[3]

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Pyrolysis is a widespread approach for bio-oil^[4] synthesis, in which biomass is thermally decomposed in an oxygen-free or oxygen-limited environment.^[5] The resulting crude bio-oil is a complex mixture of acids, alcohols, furans, aldehydes, esters, ketones, sugars and multifunctional compounds such as hydroxyacetic acid, hydroxyl-acetaldehyde and hydroxyacetone (derived from cellulose and hemicellulose), together with 3hydroxy-3-methoxy benzaldehyde, phenols, guaiacols and syringols derived from the lignin component.^[1b, 6] Pyrolysis bio-oils thus require 'upgrading' through deoxygenation and neutralisation to enhance their energy density, stability and physical properties.^[6a, 7] A range of catalytic upgrading methods are known,^[8] at least at laboratory scale, including esterification,^[12]

Carboxylic acids comprise 5-10 wt% of pyrolysis bio-oils,^[9, 13] and are largely responsible for their poor chemical stability, hence esterification (particularly employing bio-derived alcohols such as methanol, ethanol or phenols^[14]) offers an energy efficient and atom-economical route to upgrading.^[8b, 15] Homogeneous mineral acid catalysts are historically employed for esterification, however their process disadvantages and poor (environmental) E-factors are well-documented, hence strong drivers remain for the development of heterogeneous solid acid counterparts.^[11] Note that while base catalysts are widely used for the transesterification of vegetable oils (triacylglycerides) to yield biodiesel, they are unsuitable for catalytic esterification due to neutralisation/saponification.^[1d]

Diverse solid acids have been explored for esterification, including zeolites,^[16], heteropolyacids, ^[17], sulfated metal oxides^[18], carbon-based acid catalysts^[19] and functionalized mesoporous silicas^[20]. Research on the latter indicates that mesoporous SBA-15^[21], KIT-6^[22], and PMO^[23] sulfonic acids, and a macro-mesoporous SBA-15 (MM-SBA-15)^[20g] analogue, are among the most promising due to their tunable pore architecture strong Brønsted acidity and hydrophobicity.^[2a, 14a, 20g, 23-24] 3-Propylsulfonic acid (PrSO₃H)/SBA-15 is reported an efficient catalyst for acetic acid esterification with methanol^[2a, 25] and other alcohols in simulated bio-oils,[26] and the most widely used sulfonic acid in solid acid catalysed esterification.[27] Such catalysts exhibit improved water tolerance during esterification when the sulfonated silica surface is co-functionalised with alkyl chains.^[2a, 5, 25b] We recently reported a post-modification Hydrothermal Saline Promoted Grafting (HSPG) route to introduce higher sulfonic acid loadings into mesoporous silicas than achievable by conventional grafting methods,^[24a] and confer stability towards leaching during the esterification of model acids.^[24b, 28] Hydrophobicity, and catalytic reactivity, can also be enhanced through incorporating organic groups into the silica framework.^[24b] Mesopore interconnectivity also plays a role in controlling esterification activity, with interconnectivity between the hexagonal cylindrical mesopores of PrSO₃H/KIT-6 offering

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superior mass transport and active site accessibility to noninterconnected PrSO₃H/SBA-15.^[20g] Mesopore expansion (from ~5 to 14 nm),^[14a] and macropore incorporation^[23] offer alternative approaches to enhance the esterification activity of PrSO₃H/SBA-15 for long chain fatty acid esterification.

With respect to bio-oil upgrading through catalytic esterification, most studies have employed only model compounds due to the complex nature of real pyrolysis bio-oils^[7a] and associated analytical challenge. We previously reported the application of PrSO₃H/SBA-15 for acetic acid esterification of model bio-oils.^[26, 28] Here, we report the synthesis and application of HSPG-derived mesoporous PrSO₃H/SBA-15, and a macroporous counterpart, for the esterification of simple carboxylic acids (C₃, C₆ and C₁₂), and the upgrading of thermal fast pyrolysis bio-oil derived from woodchips.

Results and discussion

Catalyst characterisation

Successful synthesis of an ordered mesoporous and macromesoporous (MM) skeleton for the SBA-15 and MM-SBA-15 supports was confirmed by TEM. An ordered, two dimensional hexagonal mesopore channel network was observed for the former (Fig. S1), and a well-defined interconnecting macromesopore network for the latter (with a mean macropore diameter ~200nm, close to that of the polystyrene colloidal hard template, Fig. S2). Formation of the desired p6mm pore architecture for both SBA-15 and MM-SBA-15 was confirmed by low angle X-ray diffraction (Fig S3) which revealed reflections characteristic of hexagonally ordered mesostructures. Both supports retained hexagonal close packed pore architectures following functionalisation by propylsulfonic acid in a H₂O/NaCl mixture (the HSPG method). However, a shift in diffraction peaks to higher angle is observed post-functionalisation due to mesopore contraction.^[23] Mesopore generation (and retention after sulfonation) was further evidenced by N2 porosimetry which showed type IV isotherms with H1 hysteresis loops for all materials (Fig S4). Textural properties of PrSO₃H/SBA-15 and PrSO₃H/MM-SBA-15 are summarised in Table 1. BET surface areas decreased after sulfonic acid grafting over both silicas due to micropore blockage, apparent as a dramatic drop in micropore area and pore volume. These changes are accompanied by a decrease in pore diameter and increase in wall thickness, suggesting the uniform grafting of sulfonic acid groups throughout both pore networks without distortion of their unit cells. Previous studies have shown the macropores in such hierarchical frameworks are open and interconnected by bottleneck pore openings.[23] [29]

DRIFT spectra of the parent silicas showed bands at 700-1400 cm⁻¹ and 3000-3800 cm⁻¹ indicative of framework Si-O-Si and surface silanols respectively (Fig. S5).^[15] Additional bands appeared after sulfonation of both materials around 2960-2830 cm⁻¹, attributable to CH₂ vibrations of the propyl backbone, and a new CH₂-Si band centred at 1360 cm⁻¹. CHNS elemental analysis of the sulfonated silicas revealed that both contained ~6 wt% sulfur (Table 1) representing a five-fold increase over conventional toluene grafting, [14a, 23] in good agreement with our preliminary discovery of the HSPG method.^[24a] Sulfur 2p XP spectra of both sulfonic acid-functionalised materials in Fig S6 reveal two distinct S chemical environments; a low binding energy centred at 164.5 eV associated with unoxidised thiol, and a higher energy doublet arising from sulfonic acid groups centred at 168.9 eV.^[30] Quantitative XPS analysis (Table S4) shows that ~85 % of S was incorporated as sulfonic acid groups. Thermogravimetric analysis (Fig S7b) highlighted two major weight losses; one below 100 °C attributed to physisorbed water; and the second between 250-650 °C due to propylsulfonic acid decomposition.^[31] The bulk S content estimated from this second loss feature was ~5 wt% in accordance with elemental analysis. Acid properties of both sulfonated silica were subsequently probed through pyridine and propylamine adsorption. DRIFT spectra of pyridine titrated materials (Fig S8) evidenced only Brønsted acid sites.^[26] Temperature-programmed analysis of reactively-formed propene from chemisorbed propylamine confirmed that PrSO₃H/SBA-15 and PrSO₃H/MM-SBA-15 possessed similar acid strengths and loadings (Fig S9 and Fig S10). We can thus conclude that the incorporation of macropores into the SBA-15 architecture had minimal impact on silica functionalisation; the propylsulfonic acid functions grafted over silica surfaces in PrSO₃H/SBA-15 and PrSO₃H/MM-SBA-15 catalysts were chemically identical. Any differences in TOFs between the two catalysts must therefore arise solely from diffusion phenomena. However, despite their similar acid site loadings, the surface coverage of acid sites was higher over the macroporous material (which possessed a lower surface area). Note that the higher S loadings accessible through the HSPG method offer acid loadings around 1.5 mmol g⁻¹, approximately twice those (0.6-0.8 mmol g⁻¹) obtained through sulfonic acid grafting in toluene.^[2a] Molecular dynamics simulations and adsorption calorimetry reveal that cooperative effects between silanol and sulfonic acid functions can weaken their acidity in PrSO₃H/MCM-41 due to hydrogen bonding and associate sulfonate reorientation.^[32] However, such effects only operate for low sulfonic acid loadings, and are absent on crowded surfaces such as those employed in this work, hence cooperative effects are not expected to influence catalytic performance.

Esterification of model carboxylic acids

The catalytic performance of mesoporous and macroporous-mesoporous sulfonic acid silicas was evaluated in the esterification of propanoic (C_3), hexanoic (C_6) and lauric acids

Table 1. Physicochemical properties of mesoporous SBA-15 and macroporous-mesoporous SBA-15 and their sulfonic acid analogues.

Sample	Surface area ^a	d _p ^b	V _{total}	V _{micropore} ^c	Wall thickness	Unit cell parameter	S loading ^d	Acid loading ^e
Sample	/ m ² .g ⁻¹	/ nm	/ cc.g ⁻¹	/ cc.g ⁻¹	/ nm	/ nm	/ wt%	/ mmol.g
SBA15	879	5.5	1.17	0.08	5.5	11.0	-	-
PrSO ₃ H/SBA15	379	3.8	0.49	0.01	7.3	11.1	5.8	1.5
MM-SBA-15	357	4.5	0.55	0.02	5.9	9.0	-	-
PrSO ₃ H/MM-SBA-15	186	3.4	0.24	0.00	7.2	9.2	5.5	1.6

^a BET, ^b BJH, ^c t-plot, ^d CHNS, ^e propylamine adsorption/TGA-MS.

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(C₁₂) with methanol to explore the influence of macropores on reactivity under previously optimised conditions.^[2a] Since both catalysts possess similar acid loadings and strength, any differences in activity must arise from their pore architecture. Both sulfonic acid catalysts were active for methylic esterification of the C₃, C₆ and C₁₂ acids (**Fig S11**) which were 100 % selective to their corresponding methyl esters. The rate of esterification decreased with increasing alkyl chain length due to polar and steric effects.^[33]

The associated turnover frequencies (TOFs) for carboxylic acid esterification were similar over the both catalysts for the C_3 and C_6 acids (**Fig 1**), whereas the TOF for lauric acid over the hierarchical PrSO₃H/MM-SBA-15 was twice that observed for the purely mesoporous PrSO₃H/SBA-15 (**Fig S12**). This rate enhancement for the bulky lauric acid esterification is readily explicable in terms of improved sulfonic acid accessibility through: (i) faster in-pore diffusion of the reactant/ester product; (ii) shorter mesopore channel lengths due to truncation by macropores; and (iii) an increased number of mesopore entrances.^[23]

Esterification of thermal pyrolysis bio-oil

The performance of both sulfonic acid silicas was also assessed for the upgrading of a bio-oil produced via thermal fast pyrolysis of oak woodchips in a bench-scale, continuous fluidised bed reactor at 500 °C. Some physicochemical properties of the parent biomass feedstock are presented in **Table S1**, and of the crude bio-oil in **Table S2**. Note that while the bio-oil possessed a similar calorific value to the woodchips, the volumetric energy density of the former is significantly higher than the original biomass whose density was only 600-900 kg.m⁻³. The bio-oil contained 23 wt% water, typical of fast pyrolysis bio-oil.^[6b, 34], although the total acid number (TAN) measured by the Modified D664A acid number titration method^[35] of 61.6 mg KOH g⁻¹ was relatively low.^[34]

Fig. 2 compares TOFs for total acid removal (as determined by KOH titration) via catalytic esterification with methanol, and the corresponding reaction profiles for total acid conversion (**Fig. 2 inset**). The PrSO₃H/MM-SBA-15 catalyst was almost three times more active in terms of TOF, and converted twice the amount of acid after 6 h, than the PrSO₃H/SBA-15. Since the pyrolysis oil contains numerous bulky compounds as described in **Tables 2-3** (and **Table S3**) we attribute the superior performance of the hierarchical catalyst to improved active site accessibility akin to that for lauric acid esterification. Note that carboxylic acid constituents of fast pyrolysis bio-oils may drive low level (<5 %) autocatalytic esterification.^[36] This was consistent with a control experiment in the absence of any sulfonic acid catalyst which revealed <8 % total acid conversion of the pyrolysis bio-oil, and hence autocatalysis exerted minimal impact on our results.

The chemical composition of the crude and upgraded biooil following catalytic treatment by PrSO₃H/MM-SBA-15 were analysed in detail by GCxGC-ToFMS, with resulting 2D chromatograms shown in **Fig. 3**. For both crude and upgraded bio-oils the chromatographic space was divided into six discreet molecular groups: acids and esters; aldehydes and ketones (including furanoics and cyclic carbonyls); hydrocarbons (saturated and unsaturated non-aromatic); aromatic hydrocarbons; phenolic compounds; and sugars. Compounds that could not be identified by the library and/or did not meet the required identification criteria (as detailed in ESI) were classified



Fig 1. TOF for esterification of various carboxylic acids over PrSO₃H/SBA-15 and PrSO₃H/MM-SBA-15 catalysts. (Reaction conditions: 25 mg catalyst, 5 mmol acid, acid:MeOH molar ratio= 1:30, 60 °C)



Fig 2. Effect of support architecture on the TOFs of sulfonic acid catalysed biooil esterification. Inset: acid conversion profiles for bio-oil esterification using sulfonic acid catalysts. (Reaction conditions: 9.2 g bio-oil ≈ 10 mmol acid, 12.1 ml MeOH (Acid:MeOH molar ratio= 1:30), 100 mg catalyst, 85 °C)

as 'unidentified'. A more detailed classification of each molecular group and their relative chromatographic area is presented in **Table 2**. Almost complete loss of organic acids (from 19.7 to 0.9 %) and a significant decrease in phenolics, ketones, aldehydes and sugars was observed following catalytic upgrading, accompanied by a significant increase in ester and alcohol components, consistent with esterification. Additional detail on the removal/formation of specific phenolics, ethers and carbonyls is presented in **Table S3**. Acetic acid was the major organic acid in both crude and upgraded bio-oils. Esters with relative areas >0.1 in the crude and upgraded bio-oils are presented in **Table 3**.





Figure 3. GCxGC-ToFMS chromatogram of a) crude thermal fast pyrolysis biooil and b) bio-oil after esterification over PrSO₃H/MM-SBA-15.

Table 2. Compositions of crude and upgraded	ed bio-oils following treatment w	vith
PrSO ₃ H/MM-SBA-15 catalyst.		

Group	Crude bio-oil / Area%	Upgraded bio-oil / Area%	
Aromatic hydrocarbons	1.8	1.9	
Aliphatic hydrocarbons	0.4	2.1	
Phenolic compounds	25.8	7.8	
Furanic compounds	0.6	1.4	
Organic acids	19.7	0.9	
Esters	1.9	11.8	
Alcohols	1.1	26.1	
Ethers	1.0	6.5	
Aldehydes	5.2	0.4	
Ketones	10.8	2.9	
Sugars and anhydro sugars	26.6	13.5	
Unidentified	5.3	24.7	

Table 3. Esters present in crude and upgraded thermal fast pyrolysis bio-oils following treatment with PrSO₃H/MM-SBA-15 catalyst.

Crude bio-oil	Esterified bio-oil	
Acetic acid, methyl ester	Acetic acid, methyl ester	
Formic acid, 2-propenyl ester	Butanedioic acid, dimethyl ester	
Ethanedioic acid, diethyl ester	Hexanoic acid, methyl ester	
Propanoic acid, ethenyl ester	9-Octadecenoic acid (Z)-, methyl ester	
Ethyl homovanillate	Butanedioic acid, methyl-, dimethyl ester	
	Methyl propionate	
	Octanoic acid, methyl ester	
	Levulinic acid, methyl ester	
	Nonanoic acid, methyl ester	

Methyl acetate accounts for 10.8 % of the total chromatographic area of the esterified bio-oil, as compared to only 1.4 % of the crude bio-oil, alongside a range of methyl and dimethyl esters from C₃-C₁₁ compounds. Identifiable ethers were mainly C₃-C₆ methoxy-compounds, with 1,1,2,2-tetramethoxyethane predominant. Considering phenolics, upgrading principally removed methoxy-phenols, whereas cresol and catechol derivatives were recalcitrant. The increase in alcohols appears to arise from glycolaldehyde dimethyl acetal (GDA) formation from levoglucosan.^[37] Previous studies reveal that levoglucosan can be transformed in alcohol media by acid catalysts to methyl levulinate through intermediate glycolaldehyde (GA) formation^[38] (which may itself form glycolaldehyde dimethyl acetal). GA and GDA were detected in the upgraded bio-oil, supporting this proposed reaction pathway. Future work will address the recyclability of PrSO₃H/MM-SBA-15 for the esterification of real bio-oils, wherein we expect strong adsorption of organics that will require the development of low temperature regeneration protocols that avoid decomposition of the grafted sulfonate.

In summary, GCxGC-ToFMS analysis confirmed that $PrSO_3H/MM$ -SBA-15 was an effective catalyst for the esterification of a real thermal pyrolysis bio-oil, significantly reducing the bio-oil acidity through esterification of organic acids under mild reaction conditions.

Conclusions

Mesoporous and hierarchical macroporous-mesoporous propyl sulfonic acid silicas were synthesised by hydrothermal saline promoted grafting of the pre-formed architectures. Textural properties of the parent silicas were unperturbed by sulfonation, which resulted in similar sulfonic acid loadings and strengths for both pore networks. Turnover frequencies for catalytic esterification of model C3-C12 carboxylic acids with methanol decreased with alkyl chain length over both materials, however the introduction of 200 nm macropores into the SBA-15 framework doubled the activity per acid site for the bulkiest lauric acid, attributed to enhanced mass transport and active site access, and a higher -PrSO₃H surface density. Macropore incorporation also enhanced esterification activity for the upgrading of a real bio-oil derived from thermal fast pyrolysis of oak woodchips; the TOF for total organic acid removal increased three-fold relative to the mesoporous sulfonic acid silica, again attributed to superior in-pore mass transport and active site accessibility. The total acid number was reduced by 57 % over 6 h reaction at 85 °C using the hierarchical PrSO₃H/MM-SBA-15 catalyst. GCxGC-ToFMS confirmed that catalytic upgrading removed almost all organic

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acids, and significantly lowered the concentration of reactive, phenolic, aldehyde and ketone components, accompanied by the formation of carboxylic acids methyl esters and ethers.

Experimental

Full details of the catalyst synthesis, bulk and surface characterisation (TEM, XRD, N₂ porosimetry, DRIFTS, XPS, TGA, pyridine adsorption/DRIFTS, propylamine adsorption/TGA-MS), and catalytic esterification and bio-oil analysis protocols are provided in the ESI.

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Keywords: mesoporous silica • sulfonic acid • esterification • bio-oil • acidity • pore architecture

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Catalytic Bio-oil Upgrade esterification

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Impact of macroporosity on catalytic upgrading of fast pyrolysis bio-oil by esterification over silica sulfonic acids