

Mesoporous sulfonic acid silicas for pyrolysis bio-oil upgrading via acetic acid esterification

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Catalyst characterisation

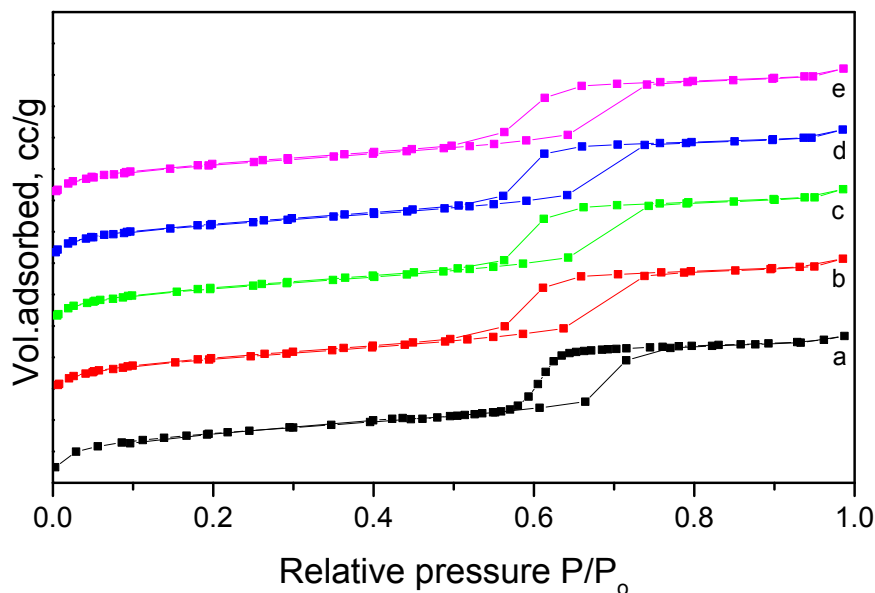


Fig. S1. Nitrogen adsorption-desorption isotherms of PrSO₃H/SBA-15 as a function of S loading: (a) SBA-15; (b) PrSO₃H(0.01ML)/SBA-15; (c) PrSO₃H(0.1ML)/SBA-15; (d) PrSO₃H(0.5ML)/SBA-15; (e) PrSO₃H(1ML)/SBA-15.

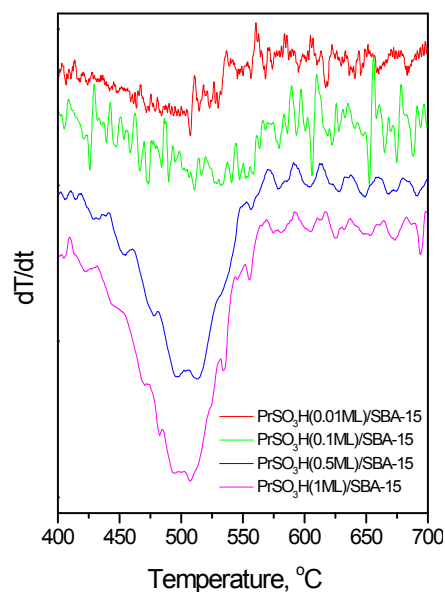


Fig. S2. Differential thermogravimetric profiles of PrSO₃H/SBA-15 as a function of S loading highlighting propylsulfonic acid decomposition between 400-600 °C.

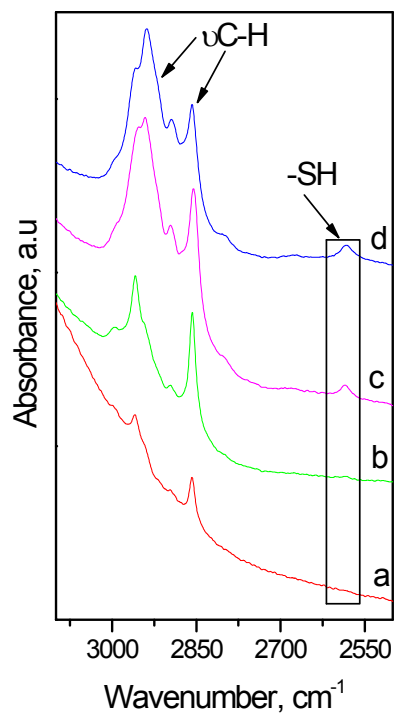


Fig. S3. DRIFT spectra of MPTMS functionalised SBA-15 as a function of S loading: (a) $\text{PrSO}_3\text{H}(0.01\text{ML})/\text{SBA-15}$, (b) $\text{PrSO}_3\text{H}(0.1\text{ML})/\text{SBA-15}$, (c) $\text{PrSO}_3\text{H}(0.5\text{ML})/\text{SBA-15}$, (d) $\text{PrSO}_3\text{H}(1\text{ML})/\text{SBA-15}$.

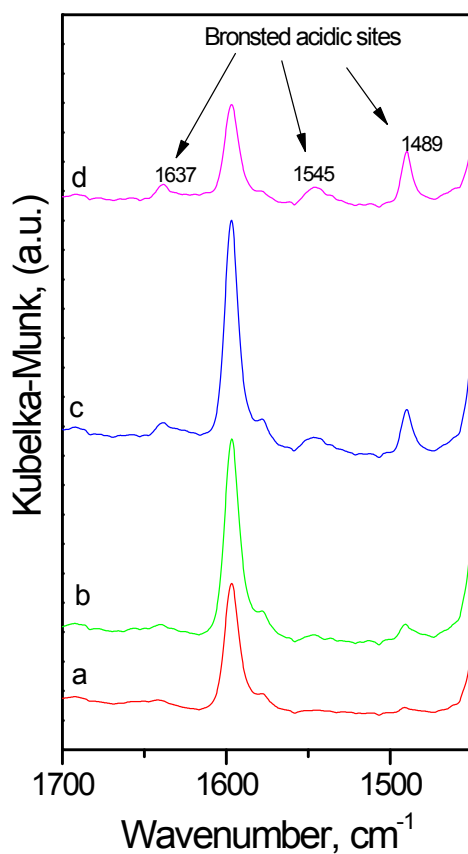


Fig. S4. DRIFT spectra of pyridine titrated $\text{PrSO}_3\text{H}/\text{SBA-15}$ as a function of S loading: (a) $\text{PrSO}_3\text{H}(0.01\text{ML})/\text{SBA-15}$, (b) $\text{PrSO}_3\text{H}(0.1\text{ML})/\text{SBA-15}$, (c) $\text{PrSO}_3\text{H}(0.5\text{ML})/\text{SBA-15}$, (d) $\text{PrSO}_3\text{H}(1\text{ML})/\text{SBA-15}$.

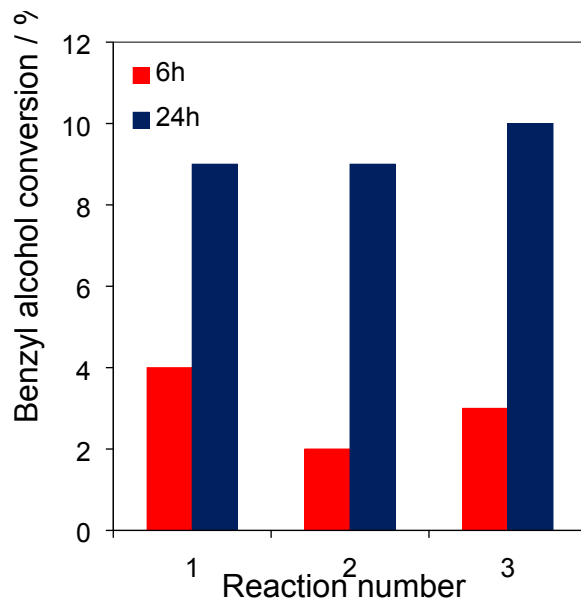


Fig. S5. Control reactions for acetic acid esterification with benzyl alcohol in the absence of catalyst. Reaction conditions: 100 °C, acid:alcohol = 2:1, toluene solvent.

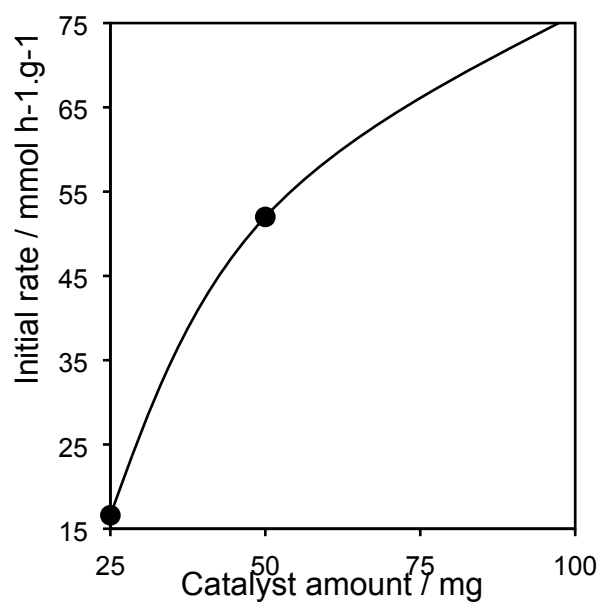


Fig. S6. Dependence of acetic acid esterification with benzyl alcohol on catalyst charge over PrSO₃H(1ML)/SBA-15. Reaction conditions: 100 °C, acid:alcohol = 2:1, toluene solvent.

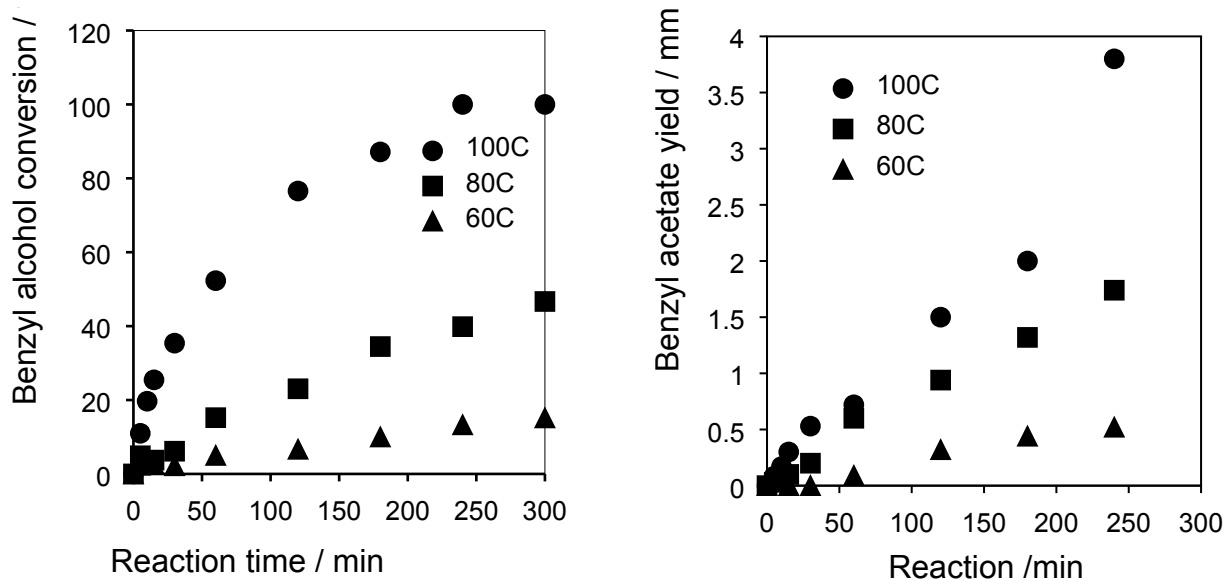


Fig. S7. Dependence of acetic acid esterification with benzyl alcohol over PrSO₃H(1ML)/SBA-15 on reaction temperature. Reaction conditions: 50 mg catalyst, acid:alcohol = 2:1, toluene solvent.

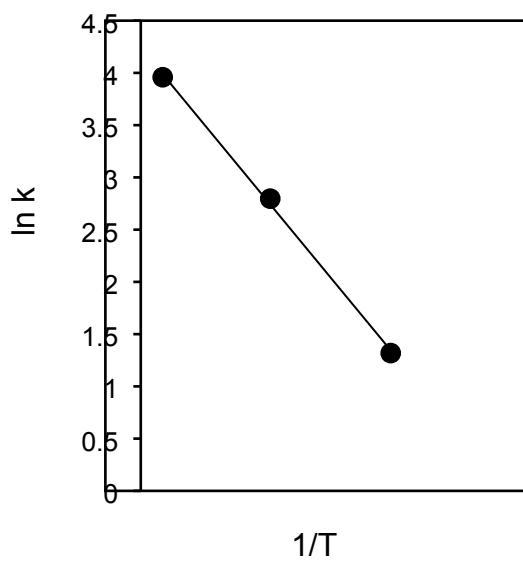


Fig. S8. Arrhenius plot for acetic acid esterification with benzyl alcohol over PrSO₃H(1ML)/SBA-15. Reaction conditions: 50 mg catalyst, acid:alcohol = 2:1, toluene solvent.

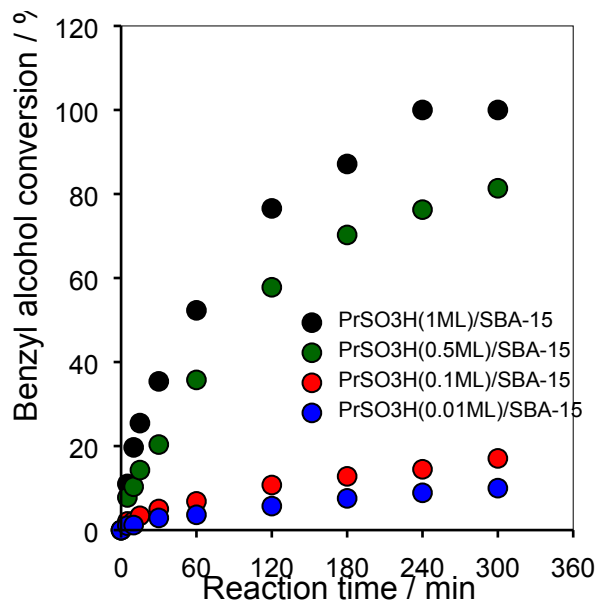


Fig. S9. Acetic acid esterification with benzyl alcohol over PrSO₃H/SBA-15 as a function of S loading. Reaction conditions: 100 °C, 50 mg catalyst, acid:alcohol = 2:1, toluene solvent.

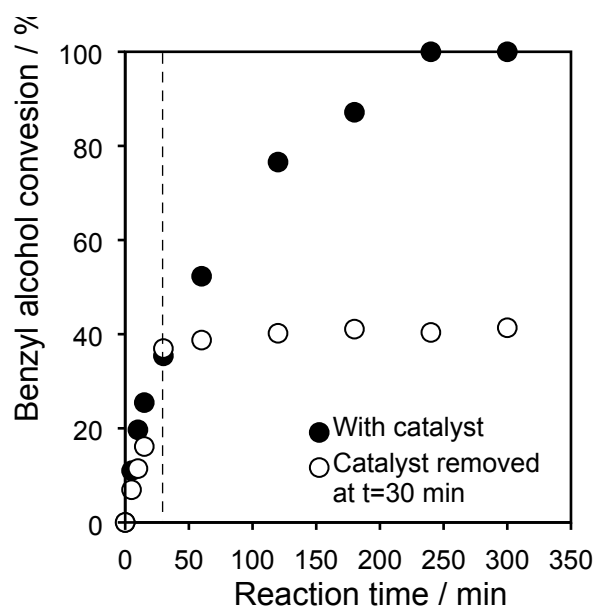


Fig. S10. Acetic acid esterification with benzyl alcohol with and without PrSO₃H(1ML)/SBA-15 removal. Reaction conditions: 100 °C, 50 mg catalyst, acid:alcohol = 2:1, toluene solvent.

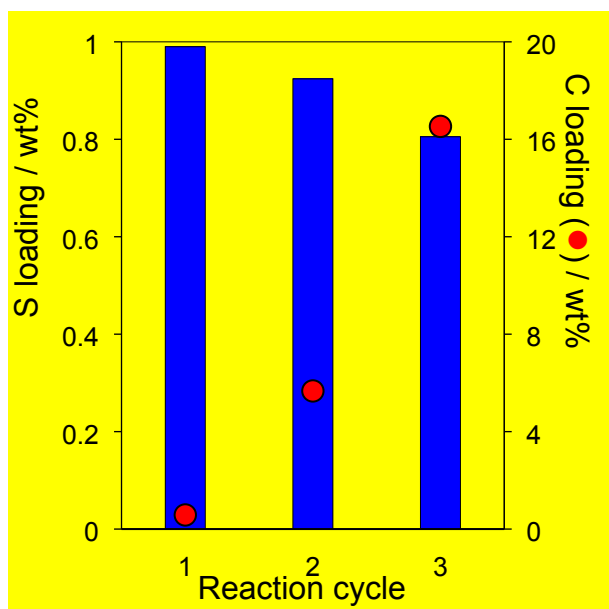


Fig. S11. Impact of acetic acid esterification with benzyl alcohol over $\text{PrSO}_3\text{H(1ML)/SBA-15}$ on catalyst composition as a function of re-use. Reaction conditions: 100 °C, 50 mg catalyst, acid:alcohol = 2:1, toluene solvent; spent catalysts washed with cold toluene and subsequently methanol between each cycle to remove weakly bound adsorbates.

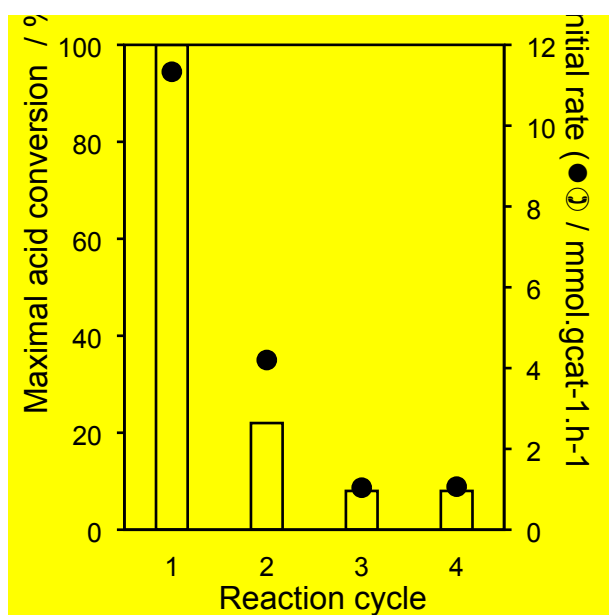


Fig. S12. Impact of catalyst re-use on acid esterification with benzyl alcohol over $\text{PrSO}_3\text{H(1ML)/SBA-15}$. Reaction conditions: 100 °C, 50 mg catalyst, acid:alcohol = 2:1, toluene solvent; spent catalysts washed with cold toluene and subsequently methanol between each cycle to remove weakly bound adsorbates.