

Sulfur containing Ethene Bridged PMOs as Adsorbent and Catalyst

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Introduction – Periodic Mesoporous Organosilicas (PMOs) are ordered materials that possess large specific surface areas ($\pm 1000 \text{ m}^2/\text{g}$), contain pores around 7 nm and exhibit a narrow pore size distribution. They are synthesized with an organobisilane, for example $(\text{OEt})_3\text{-Si-CH=CH-Si(OEt)}_3$, and thus combine inorganic rigidity with chemical organic diversity. Furthermore they can be modified which leads to a fine-tuned material. They can be used in a whole range of different applications. In this study, the materials are used as a mercury(II) adsorbent^[1,2] and as a solid acid catalyst. A pure trans ethene bridged PMO (Fig. 1) is functionalized via a Grignard reaction to suit as an adsorbent via the incorporation of thiol functionalities and compared with commercially available adsorbents. The catalyst containing $-\text{SO}_3\text{H}$ groups is used in an esterification reaction.

Another method to functionalize ethene bridged PMOs has been reported very recently^[3] and describes the use of Diels Alder reactions and subsequently a sulfonation reaction to obtain solid acid catalyst (see poster NM-P-009-Mon-072).

Adsorbent – Thiol moieties are incorporated to act as a suitable adsorbent for Hg^{2+} . First of all, an adsorbent containing propylthiol groups is synthesized according to the procedure published by our group^[1] (Fig. 1 SH-PMO). This modification resulted in a ultrastable adsorbent and mercury sorption experiments showed promising results. This adsorbent was tested for adsorption in a diffusive gradient thin films application and compared with commercially (Sumichelate Q10R, Chelex-100) and non-commercial adsorbents (thiol functionalized SBA-15 and silica gel) (Fig. 2). The SH-PMO material exhibits a slightly higher mercury binding capacity in comparison with the other adsorbents which were tested.

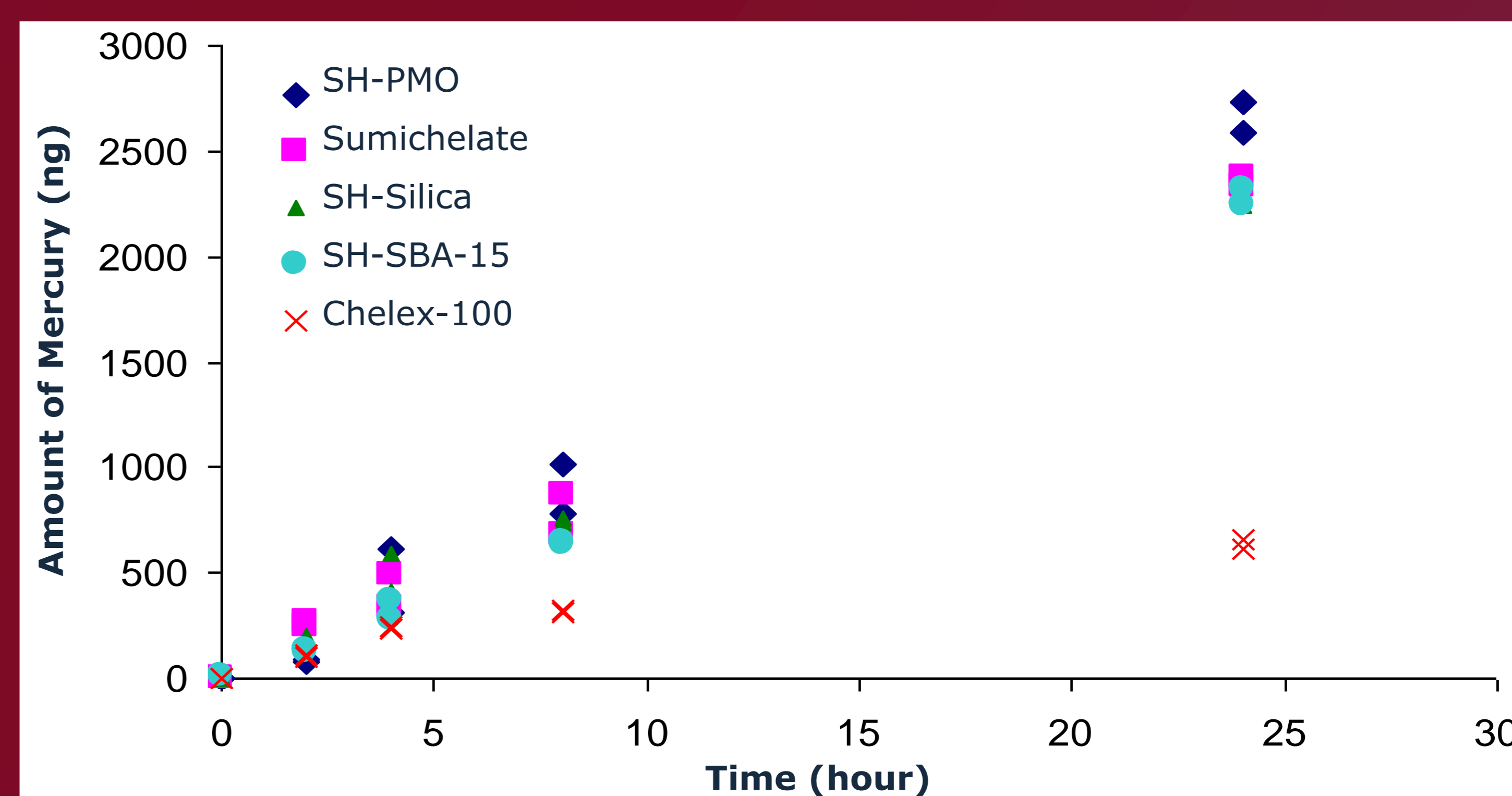


Fig. 2: Mercury binding capacity of the different adsorbents.

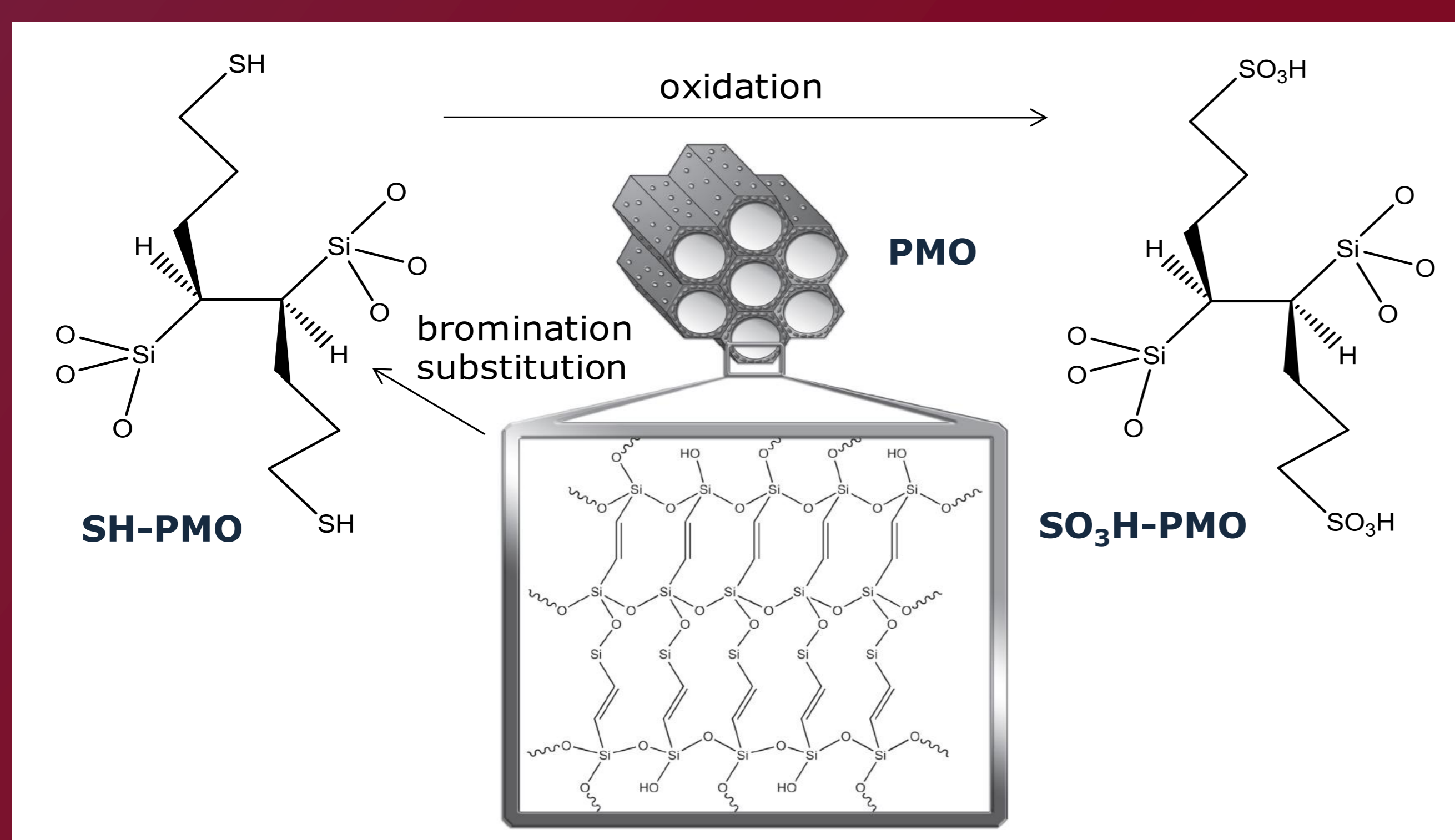


Fig. 1: Overview of synthesized materials PMO, SH-PMO and $\text{SO}_3\text{H-PMO}$.

Acid Catalysts – Oxidation of the thiol group results in a sulfonic acid group which can be used as an acid catalyst for esterification reactions (Fig. 1). In this study, the catalytic performance of $\text{SO}_3\text{H-PMO}$ in the esterification of acetic acid and glycerol is evaluated (Fig. 3). Approximately 95% of acetic acid conversion was observed. The heterogeneous catalyst was used in several catalytic runs and even after 4 runs a good catalytic performance was still observed.

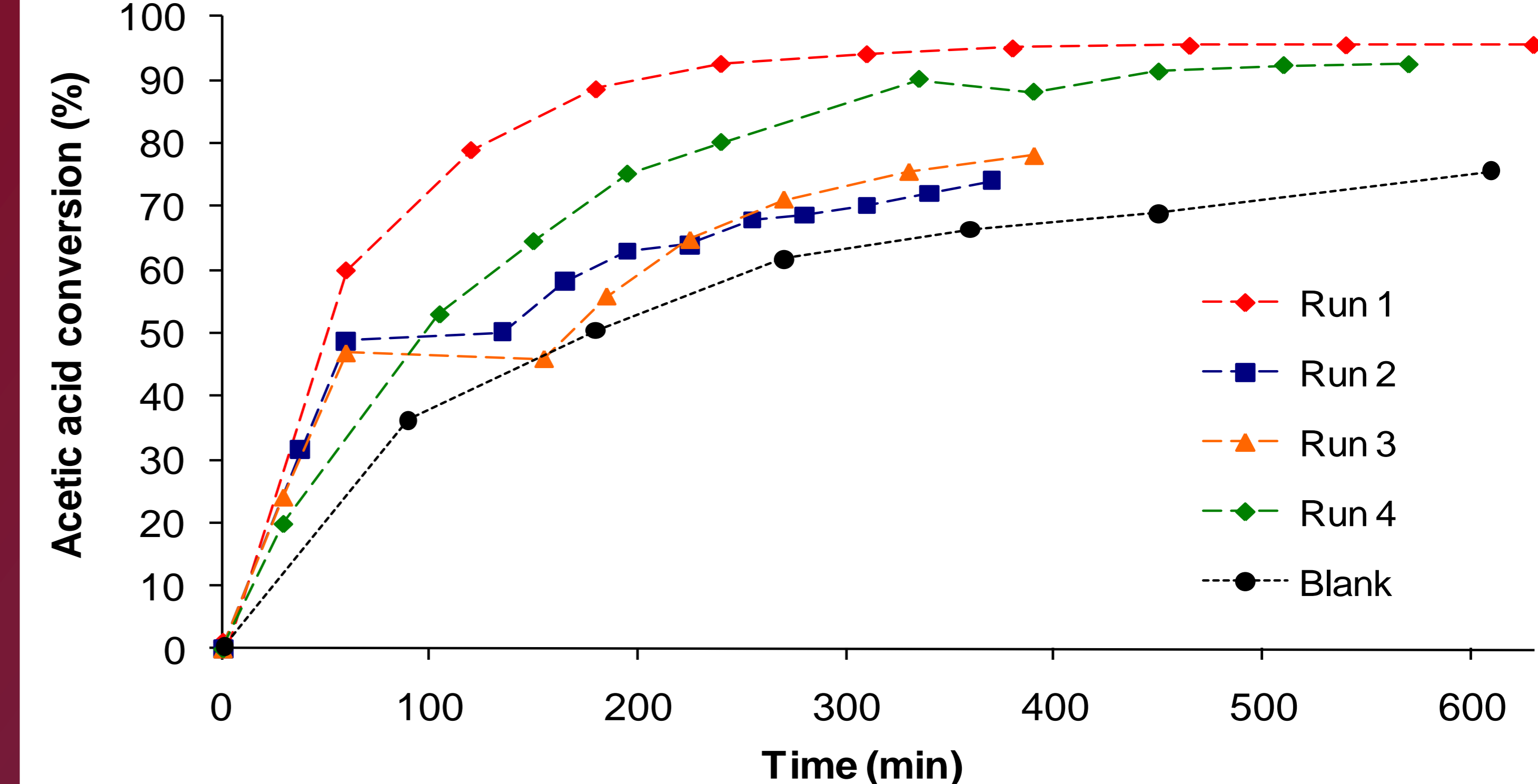


Fig. 3: Recyclability test of $\text{SO}_3\text{H-PMO}$ in the esterification reaction of acetic acid and glycerol.

Conclusions – The ethene bridged PMO is a versatile and stable material which can be used as an adsorbent or catalyst with the proper modification. Promising results were obtained as adsorbent and catalyst. Other synthetic routes are now being investigated.

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