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Immobilised Heteropolyacids as catalysts for the valorisation of cellulose and hemicellulose

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PURPOSE OF THE ABSTRACT

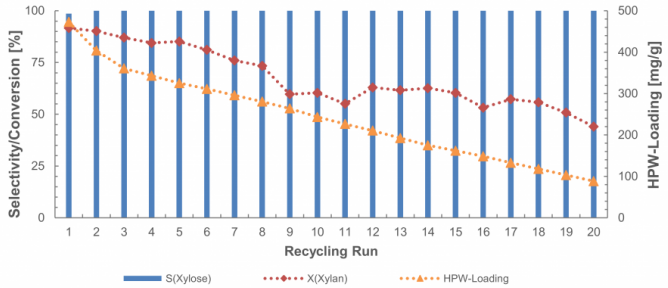
Heteropolyacids (HPAs) have been identified as promising catalysts for hydration and dehydration reactions, which play an important role in the valorization of cellulose and hemicellulose.[1] HPAs exhibit adaptable Brønsted acidity and show a redox multi-functionality depending on the transitions metals they are composed of. Due to the very good solubility of HPAs in water and various organic solvents, their immobilisation is highly interesting for green chemistry applications.

In our research, we have developed different immobilized HPA catalysts: On the one hand, we have supported $H_3PW_{12}O_{40}$ on activated carbon and applied the catalyst in the hydrolysis of xylan (hemicellulose) to xylose. After the optimisation of the impregnation procedure, the prepared solid acid catalyst HPA/AC was characterized by N2-physisorption, ICP-MS, NH3-TPD and FT-IR. Compared to the parent AC the specific surface area decreased to 1219 m2/g, while the number of acidic sites increased. A high HPW-loading of 473 mg/g was realised and the structural form of the $H_3PW_{12}O_{40}$ (the Keggin structure) was kept intact. In the hydrolysis of xylan to xylose, HPA/AC showed a high activity (91% conversion) and selectivity to xylose (98%). Furthermore, the long-term stability of the catalyst was demonstrated in batch recycling experiments over 20 runs (Figure 1). The activity decreases linearly over the runs to conversion of 44% after 20 recycling runs. This loss in activity correlates with a moderate HPW-leaching, which is high at the beginning, but then levels off to a constant value of 3 to 4%. Activated carbon is therefore a promising support material for HPAs, allowing high recyclability in aqueous reaction medium. Further investigation of the HPW-carbon interaction as well as the implementation of a continuous set-up is currently in progress.

On the other hand, we have prepared an assembly catalyst of $H_3PMo_{12}O_{40}$ and the ionic liquid 1 methyl-3-(3-sulfopropyl)-1H-imidazol-3-ium (MIMPS). This catalyst shows a thermo-responsive behaviour, i.e. the catalyst is immiscible with water at RT, but dissolves completely in water at reaction temperature (> 60°C), resulting in a monophasic system. The MIMPS-HPA catalyst was successfully applied in the aerobic conversion of cellulose to glycolic acid (GA). Compared to the completely homogeneous $H_3PMo_{12}O_{40}$, a similar activity and selectivity was found for MIMPS-HPA (Figure 2). The main product GA was formed with a yield of 51% and a conversion of 82% was reached. Side products of the conversion are formic acid (FA), C6 sugars and 5-hydroxymethylfurfural (HMF). The ionic liquid MIMPS itself was also moderately active in the conversion, which can be explained by its minor Brønsted acidity.

All in all, our research contributes to the efforts of immobilization of HPAs so that they can be more easily separated from the reaction solution. We not only demonstrate the applicability of our catalysts in the conversion of biomass, but also contribute to the understanding of the catalysts and thus to further improvement beyond the current state-of-the-art.

FIGURES



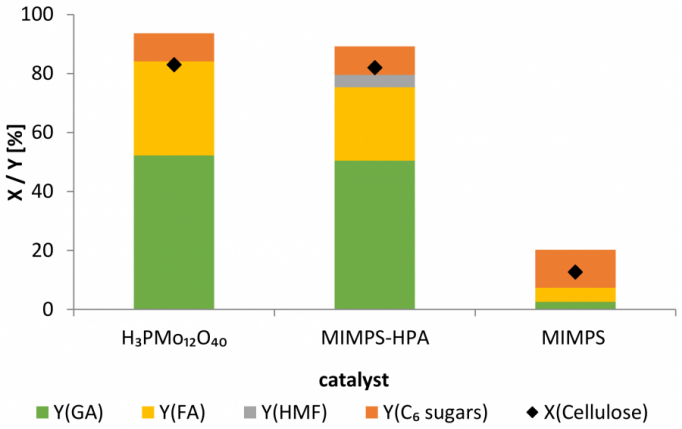


FIGURE 1

Catalyst recycling of HPW/AC in the hydrolysis of xylan

(conditions: T = 130 °C, t = 2 h, 750 rpm, m(Xylan) = 0.345 g, m(HPW/AC) = 0.391 g, V(H2O) = 15 mL).

FIGURE 2

HPMo, MIMPS-HPA and MIMPS as catalysts for the aerobic conversion of cellulose

(conditions: T = 150 °C, t = 8 h, p(O2) = 10 bar, m(cellulose) = 0.1 g, n(catalyst) = 0.06 mmol).

KEYWORDS

heteropolyacid | immobilisation | cellulose | hemicellulose

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