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Sn-Al-containing Beta and USY zeolites for the one pot transformation of glucose into methyl lactate

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PURPOSE OF THE ABSTRACT

Poly(lactic acid) (PLA) is a biomass-derived polymer linked to expensive fermentative production processes, whose industrial demand exponentially increases every year. Chemocatalysis offers interesting and efficient alternatives for the production of lactic acid, such as the retro-aldol condensation of sugar monosaccharides in the presence of heterogeneous zeolite catalysts [1]. Within this context, tin functionalized zeolites have revealed as excellent catalysts for the transformation of a wide variety of biomass-derived substrates, including glycerol, dihydroxyacetone, fructose and glucose [2], into lactic acid derivatives. BEA and Faujasite-type zeolites offer a superior catalytic activity than other structures, owed to their relative larger pore size, and resistance against deactivation [3]. Nevertheless, crystallization of Sn-containing zeolites is not easy, as it usually requires complicate, long synthesis procedures. Zeolite post-synthetic metalation strategies offer simple and fast alternatives for preparing tin-functionalized zeolites. Within the present study, we have applied one of these strategies to the synthesis of Sn-Al-containing beta and USY zeolites to be used in the direct transformation of glucose into methyl lactate.

Sn-Al-containing zeolites were prepared through a two-steps procedure [3]. Dealumination was performed by treating commercial beta (Zeolyst, CP814C) & USY zeolites (Zeolyst, CBV712) with aqueous HNO₃ solutions (1-10 mol/L; 20 mL/g) during 1 h at 25°C. The zeolite framework vacancies were occupied with tin atoms by refluxing iPrOH solutions of SnCl₄ in the presence of previously dealuminated zeolites (0.075 mol Sn/L; 15 mmol Sn/g zeolite). Materials characterization revealed that up to 90% of the starting aluminium can be extracted from the zeolite framework -in both beta & USY zeolites-, while preserving a large fraction of the starting crystallinity, even in those where the aluminium removal was more intense. On the contrary, tin incorporation was much more effective in the case of USY as compared to beta zeolite, probably because the larger pore sizes of the faujasite structure better accommodate large tin atoms within the created framework vacancies. XRD revealed that no large domains of SnO₂ were present in the final samples, and DR UV-Vis (Figure 1) demonstrated that most of the tin species showed a low coordination number -tetrahedral and penta-coordinated Sn- but also the presence of some domains of octahedral Sn.

Catalytic tests were performed in a batch reactor, treating methanolic solutions of glucose (0.27 mol·L⁻¹; 100 mL) in presence of Sn-Al-zeolite (10 g·L⁻¹) for 6 h at 170°C. Reaction was monitored by GC analysis using a CPSil 52CB column.

Both types of zeolites promoted two types of reaction pathways under the tested reaction conditions: the dehydration of glucose to HMF, followed by alcoholysis to methyl levulinate, and the retro-aldol condensation of the starting monosaccharide, either symmetrically to trioses and its sequential transformation to methyl lactate, or asymmetrically to eritritose. The promotion of both reaction cascades require both Brønsted and Lewis acidity, but its prevalence depend on the dominant catalytic acid sites present in the zeolites. Thus, Brønsted-type acidity, provided by the AlO₂-H⁺ sites, promote sugar dehydration, whereas Lewis acidity associated to Sn species, lead

to reatro-aldol condensation. Increasing the Sn/Al ratio within the catalysts provides higher yields to retro-aldol condensation products. Under the tested conditions, results suggested negligible influence of the zeolite structure on the catalytic performance or prevalence of the reaction pathway. However, since tin incorporation within the beta zeolite framework is limited, higher methyl lactate yields -up to 32% in 6 h- were obtained in the presence of the Sn-Al-USY zeolites (Figure 2). Optimization of the catalyst synthesis and reaction conditions are in progress.

FIGURES

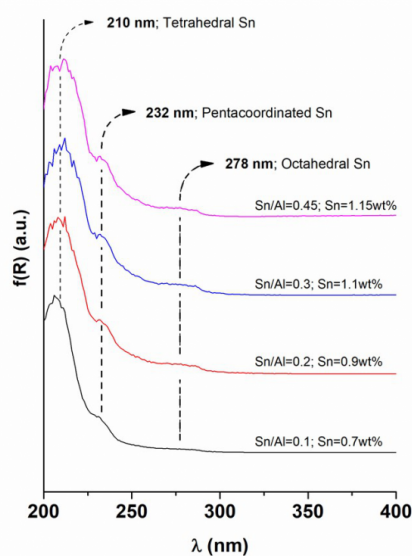


FIGURE 1

DR UV-Vis spectra recorded for Sn-Al-USY zeolites showing different Sn/Al molar ratios
Spectra comparison

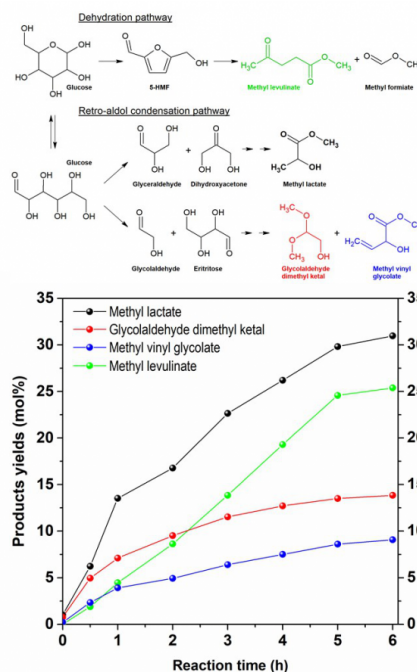


FIGURE 2

Reaction scheme and products distribution achieved from the catalytic test performed in presence of Sn-Al-USY zeolite
(Sn/Al=0.45; Sn=1.15wt%)

KEYWORDS

Zeolites | Retro-aldol condensation | Methyl lactate | Bifunctional catalysts

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