Ligand functionalized UiO-66 (Zr) for the catalytic transfer hydrogenation of levulinic acid: influence of hydrophilicity

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Introduction

With the depletion of fossil fuels and the rising concerns on environmental protection, there is strong demand in the development of sustainable alternatives to chemicals and fuels from the petroleum refineries. In this regard, the development of biorefineries that use the widely available and low-cost lignocellulosic biomass as feedstocks has received massive attention. Transformation of biomass to high value-added chemicals and fuels is a promising solution to ensure energy and materials supply, stepping forward towards a low-carbon society. A wide range of platform molecules have been obtained from decomposition of lignocellulosic biomass by various strategies, among which levulinic acid (LA) is highly attractive and is listed as one of the top 12 priority platform chemicals, illustrating the great potential in upgrading LA into valuable products.[1] γ-valerolactone (GVL) is an attractive molecule derived from the hydrogenation of LA which finds a wide range of applications, such as solvent, fuel additive, and liquid fuel, as well as precursor for valuable chemicals (e.g., olefins, polymers, 5-nanonone).[2]

Catalyst design plays an essential role in the efficient transformation of LA to GVL. Zirconium-based catalysts have been reported to be highly effective in this process via catalytic transfer hydrogenation (CTH) pathway using secondary alcohols as hydrogen donor.[3, 4] Benefiting from excellent physico-chemical properties (e.g. large surface area, tunable structure, and functionality of metal ions and organic ligands), zirconium-based metal organic frameworks are particularly attractive.[5, 6] In this work, UiO-66 was functionalized with organic linkers with different functional groups to tune the hydrophilicity of UiO-66 and the effect on the transformation of LA to GVL is investigated.

Materials and Methods

750 mg $ZrCl_4$ (3.22 mmol) and 6 mL HCl 37% HCl were added to 30 mL dimethyl formamide (DMF), following by 20 minutes sonication. Subsequently, 3 mmol terephthalic acid or its functionalized derivates were added to the above solution. The mixture was sonicated for 20 minutes and then heated at 120 °C for 24 hours in a Teflon bottle. The generated solids were filtered and washed with 120 mL DMF and 120 mL methanol, then dried in vacuum at 180 °C for overnight. The catalytic reaction was performed in the following conditions: 50 mg catalyst and 30 mL 0.6 mol/L LA in 2-propanol were introduced into a 50 mL Teflon lined batch reactor which was heated to 180 °C for 24 hours. The collected samples were analyzed in a GC equipped with DB-5 column, while n-heptane was used as internal standard.

Results and Discussion

The XRD patterns of the synthesized samples are shown in Figure 1 (left), in which the peaks at $2\theta = 7.43°$ and $8.58°$ are two characteristic peaks of UiO-66, indicate the successful synthesis of the UiO-66 structure. The functionalization of UiO-66 was assessed by IR spectroscopy and their hydrophilicity was measured by water sorption measurements. The catalytic performance of the materials is shown in Figure 1. Full conversion of LA was achieved with all catalysts. The reaction catalyzed by UiO-66 showed the highest selectivity (46%) towards GVL suggesting a beneficial role of hydrophobicity among the five materials. It is followed by the UiO-66-Br with 42% selectivity. The hydrophilicity of UiO-66-NH_2 and UiO-66-NO_2 are very similar, resulting in similar selectivity (around 35 %) to GVL. UiO-66-2,5-OH showed the lowest selectivity among the materials due to its most hydrophilic nature.

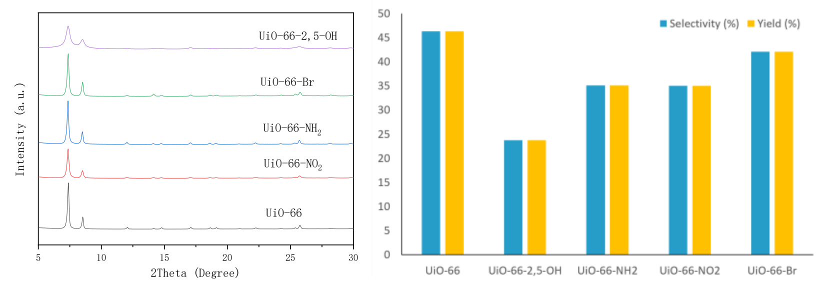

Figure 1. XRD patterns of UiO-66 functionalized with different ligands (left); catalytic performance of UiO-66 and its functionalized derivates in hydrogenation of LA.

Significance

Ligand functionalized UiO-66 were synthesized and applied in the catalytic transformation of LA to GVL by CTH. The catalytic results indicate that the selectivity to GVL is affected by the hydrophilicity/hydrophobicity balance in these materials. This will be significant to optimize UiO-66 catalysts and possibly other effective catalysts in the perspective of establishing an effective integrated biorefinery for renewable and sustainable chemicals and fuels.

References

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