



Photoreforming of biomass in metal salt hydrate solutions†‡

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Metal salt hydrate (MSH) solutions allow for the complete solubilisation of biomass and we demonstrate its use as a reaction medium for the photocatalytic reforming of lignocellulose. Different types of photocatalysts such as TiO₂ and carbon nitride can be employed in MSH to produce H₂ and organic products under more benign conditions than the commonly required extreme pH aqueous solutions.

Photoreforming (PR) allows for the simultaneous production of H₂ gas and organic products from the sunlight-driven conversion of waste polymeric substrates such as biomass and plastics in aqueous medium under ambient temperature and pressure.^{1–6} TiO₂ is the archetypical photocatalyst for this process, and CdS quantum dots and carbon nitride (CN_x) have recently been reported as visible-light absorbing alternatives.^{7–11}

Efficient PR requires the substrate to easily access the photocatalyst, which poses a challenge for an insoluble polymeric substrate in combination with a heterogeneous photocatalyst.^{4,12} Lignocellulose is a highly desirable substrate for the PR process due to its abundance as inedible biomass waste and potentially interesting reaction products.¹³ However, its recalcitrance demands harsh reaction conditions such as extremely alkaline or acidic media for complete solubilisation.

Employing PR under more benign conditions has the potential to improve the sustainability and efficiency of the process. Lignocellulosic biomass can be solubilised at relatively mild conditions in metal salt hydrate (MSH) solutions.^{14–16} Very high concentrations of inorganic salts such as LiBr with low acid concentrations in water can be used to depolymerise lignocellulosic biomass into soluble sugars.^{17–19} Li⁺ coordinates water molecules strongly and thereby generates acidity that aids cellulose depolymerisation. The presence of Br[−] exhibits favourable hydrogen bonding interactions with the cellulose chain.^{14,19} The majority of studies in MSH have so far

solely focussed on the dissolution process of cellulose. Investigations into the chemical conversion of depolymerised cellulose in MSH solutions are rare,^{20,21} and PR in MSH solutions has not yet been explored.

Here, we report PR of cellulose and real-world lignocellulosic biomass in MSH solutions for the co-production of H₂ gas and soluble organic products (Fig. 1). We show the depolymerisation of cellulosic substrates in LiBr MSH solutions, followed by PR of the solubilised sugars with photocatalyst suspension systems based on different TiO₂ and CN_x particles. The influence of LiBr concentration and pH value on PR performance is also investigated.

First, the dissolution of microcrystalline cellulose (100 mg) in a LiBr MSH solution (2 mL of 62.5 wt% LiBr in aqueous 0.1 M H₂SO₄) at 90 °C open to air was studied. The cellulose was completely dissolved after 30 min and the dissolved products were analysed by high performance liquid chromatography (HPLC) after

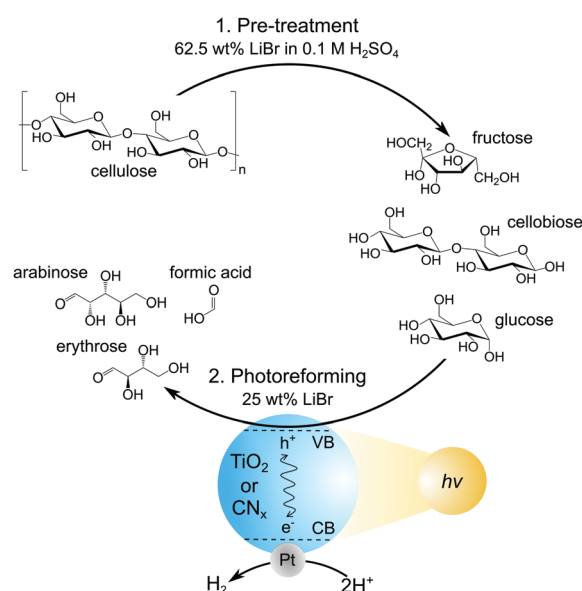


Fig. 1 Schematic overview of the PR process in MSH solution.

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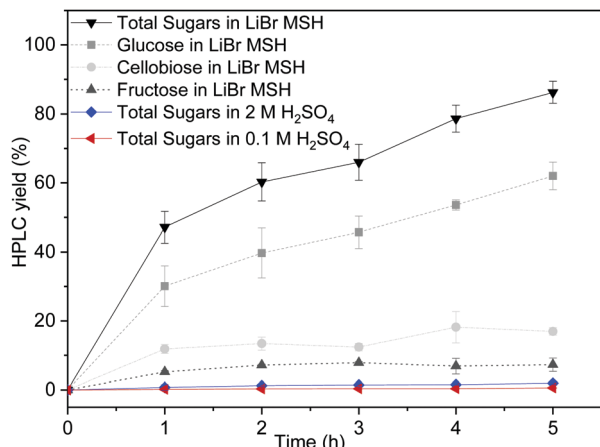


Fig. 2 Yield of soluble products from dissolution of microcrystalline cellulose (100 mg) in 2 mL LiBr MSH (62.5 wt% LiBr in 0.1 M H₂SO₄), 0.1 M H₂SO₄ (no LiBr) and 2 M H₂SO₄ (no LiBr) at 90 °C. The yield of total sugars is the sum of glucose, fructose and cellobiose. Error bars indicate standard deviation.

regular time intervals. Gradual depolymerisation of the cellulose chains into low molecular sugars is observed, with more than 90% of cellulose being converted into glucose, cellobiose and fructose after 5 h (Fig. 2). The concentration of cellobiose remains at approximately 20% in the course of the hydrolysis reaction and fructose results from acid-catalysed isomerisation of glucose.

For comparison, dissolution of cellulose in aqueous 0.1 M and 2 M H₂SO₄ without LiBr was also studied under the otherwise same experimental conditions (90 °C). The cellulose remains mostly insoluble in the absence of LiBr-based MSH. Only minor amounts of dissolved sugars are formed by the depolymerisation of the cellulose chains: ~2% total molecular sugars in 2 M H₂SO₄ and <1% in 0.1 M H₂SO₄. The LiBr MSH is therefore crucial for effective cellulose dissolution and depolymerisation.

The cellulose solutions after 5 h MSH treatment were subsequently used for PR with a variety of photocatalyst particles. The photocatalysts were prepared by loading 1 wt% Pt onto different types of TiO₂ (P25, anatase and rutile) nanoparticles and cyanamide-functionalised carbon nitride (^{NCN}CN_x) powder (see ESI† for experimental procedures and materials characterisation and Fig. S1 and S2, Pt particle size 5–15 nm for TiO₂ supports and 3–8 nm for ^{NCN}CN_x).^{2,3,22} The latter was employed due to its visible light absorbing properties and high activity to oxidise alcohols, including sugars, over its cyanamide functionality.^{7,8,23–25}

To prepare the standard PR solution, 1 mL of the cellulose lysate in LiBr MSH solution (62.5 wt% LiBr in 0.1 M H₂SO₄) was added to 1.5 mL H₂O containing 4 mg dispersed photocatalyst (final LiBr concentration: 25 wt%; see Fig. 1). This solution was then used for PR under simulated solar light irradiation (AM1.5G at 100 mW cm⁻²) for 24 h at 25 °C. The amount of H₂ produced from PR was quantified by gas chromatography and the oxidation products by HPLC (dilution of reaction solution 10:1 with H₂O for analysis, Fig. 3). PR activities in MSH-free solutions using aqueous H₂SO₄ (2 M) are also shown for comparison. In this case cellulose was pre-treated for 5 h at 90 °C in 2 M H₂SO₄, where only 2% of cellulose are converted into soluble sugars (Fig. 2). 1 mL of this solution was diluted with 1.5 mL H₂O and subjected to PR.

The three TiO₂ photocatalysts show a far higher rate of H₂ production in LiBr MSH treated cellulose compared to a control experiment in 2 M H₂SO₄. This result demonstrates the benefit of dissolution and depolymerisation of cellulose in LiBr MSH solution and the compatibility with the PR process. The lower available amount of soluble sugars from the H₂SO₄ treatment results in a lower H₂ yield. The formation rates of oxidation products in Fig. 3 for rutile are twice than for P25 and anatase nanoparticles, although the difference in H₂ yield is only around 20%. This may be explained by the different reaction mechanisms of the catalysts,²⁶ as rutile forms surface bound

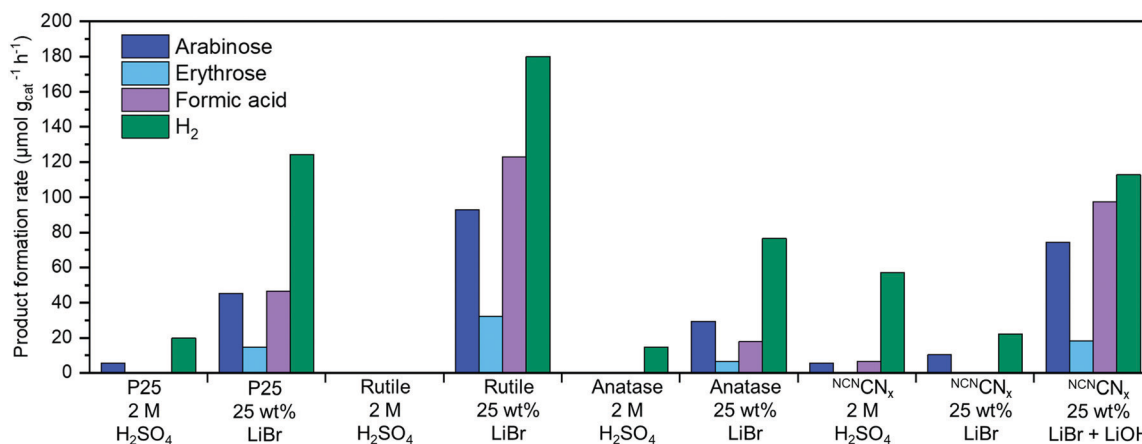


Fig. 3 Photoreforming results after 24 h using different photocatalysts and conditions using AM 1.5G, 100 mW cm⁻² irradiation at 25 °C. Cellulose (50 mg) in 1 mL of 62.5 wt% LiBr in 0.1 M H₂SO₄ is added to 1.5 mL aqueous solution containing 4 mg photocatalyst to give 2.5 mL of 25 wt% LiBr. Note that organic products originating from alkaline degradation in the dark were subtracted from the values obtained during PR with ^{NCN}CN_x in 25 wt% LiBr with LiOH (see ESI† for details). Standard deviations for H₂ yields can be found in Table S1 (ESI†) (between 5–20%). Taking these deviations and the error for the HPLC analysis into account, standard deviation for the organic products can be estimated to be around 20%.



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