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Reactivity of Sugars over Homogenous Tungsten- and Molybdenum-Based Catalysts

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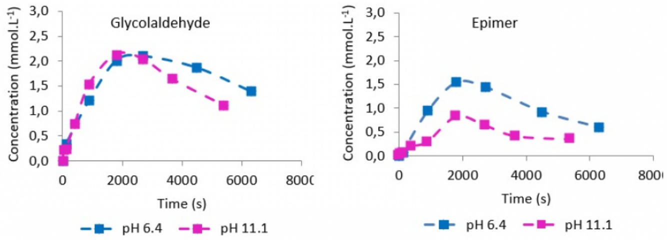
PURPOSE OF THE ABSTRACT

The production of ethylene glycol, from biomass-abundant glucose is possible through a Retro-aldol Condensation reaction (RAC) towards the key intermediate glycolaldehyde (GA).[1] The reaction medium is complex as many side reactions can potentially occur. Undesired C3 species (glyceraldehyde or dihydroxyacetone, precursors of 1,2-propanediol) are likely to be formed due to the formation of fructose in the reaction medium,[1] via an essential side reaction to avoid, the isomerization of glucose.[2] The epimerization of glucose to mannose forms another secondary transformation.[1] Homogenous tungsten and molybdenum salts thereof sodium tungstate and molybdate (Na2WO4 and Na2MoO4) or homopolyanions such as ammonium metatungstate (AMT) and ammonium heptamolybdate (HMA) are active catalysts for the RAC of sugars, but are less active in glucose interconversion to fructose, leading to higher C2 selectivity.[3-5] These species are also catalytically active for epimerization.[1,6] RAC and epimerization were supposed to have common mechanistic steps and possibly same active species. A clear understanding of the reaction mechanism at a molecular scale have not been yet reached.

The main goal of our research work is to discover the genuine active species controlling the selectivity towards the production of C2 intermediates using a combined spectroscopic study including XAS and NMR techniques, together with theoretical computational approach at the density functional theory level. A first study aimed at probing the possible metal-carbohydrate complexes in aqueous solutions by means of ex-situ NMR and XAS measurements. The solutions were prepared by mixing the sugars involved in the process (glucose, mannose and erythrose) with the metallic salts (Na2WO4, Na2MoO4, AMT and HMA). Various molybdate and tungstate complexes of the sugars were modeled and optimized using Gaussian 09 suite for which 1H and 13C NMR chemical shifts were theoretically computed. The calculations were done at B3LYP level of theory using tzvp basis set for C, H and O atoms and def2-tzvp for W and Mo atoms. A parametric study considering the catalytic activity of the metals, the initial form of the metal precursor and the various operating conditions (pH, temperature, ?) were investigated. The kinetic curves of the different products concentrations were plotted. In parallel, the optimized complexes were used as starting points for the DFT calculation of the reaction pathways for the formation of the different possible products. Theoretical activation barriers are compared to each other and to the experimental activation energies to allow finding the active species promoting the reaction.

Ex-situ NMR measurements showed that all the detected species are complexes involving a sugar ligand chelating a ditungstate or a dimolybdate ion. These complexes have pH dependent behavior. According to the catalytic tests, tungsten-based catalysts are more active to promote the RAC while molybdenum is more efficient to catalyze the epimerization of the sugars. Both W and Mo catalyze RAC of the sugars regardless the pH of the reaction medium while the epimerization was influenced by the variation of the pH (Figure 1) indicating that both reactions are not promoted by the same active species. In this context, we proposed the dinuclear complex involving the acyclic hydrated form of the sugar as an active species exclusively for epimerization. Moreover, the theoretically computed activation barriers for sugar's epimerization using this complex model are in full agreement with the experimental observations.(Figure 2)

FIGURES



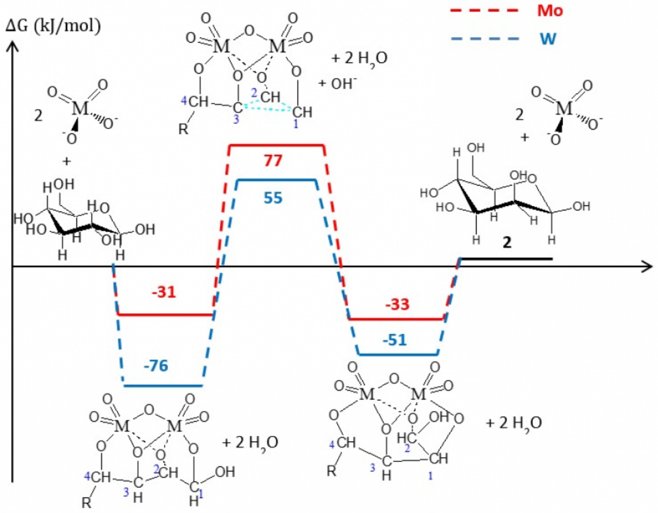


FIGURE 1

Glycolaldehyde and epimer concentrations as function of reaction time and pH of the reaction medium for the conversion of mannose over AMT catalyst. The reaction was performed at 423 K, under 40 bar N2 pressure, mannose concentration of 5 mmol.L-1 and tun

FIGURE 2

Theoretical calculation for the M-catalyzed (M= Mo or W) epimerization of glucose to mannose. Calculated Gibbs energy profiles are reported in kJ/mol at 298,15 K and optimized structures of the species involved in the process, including active species and

KEYWORDS

Biomass-based sugars | Retro-aldol condensation | epimerization | Tungsten and Molybdenum-based homogenous salts

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