

Hydrodeoxygenation of biomass-derived polyols to green butadiene over Rhenium modified supported catalysts

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ABSTRACT

1,3-butadiene (BD), an important petrochemical intermediate to produce synthetic rubbers is currently manufactured from fossil-based processes. As its demand continues to grow the development of sustainable processes has become imperative^[1,2]. Biomass-derived polyol, such as erythritol (an industrially fermentation product) is a sustainable resource to produce hydrocarbons. Catalytic hydrodeoxygenation (HDO) of erythritol, yet a challenging and not an extensively studied path, is an alternative to produce BD. This study aims at the development of suitable catalytic material for the effective erythritol HDO to BD. Considering that catalysts commonly used in similar processes could potentially exhibit notable performance^[2,3], a series of Re, Mo and mixed Re-M (M:Mo, Ag) supported on black carbon (BC) were synthesized and evaluated under batch conditions in liquid phase, at specified reaction conditions (T: 140°C, P_{H₂, initial}: 60 bar, catalyst/substrate: 0.56, t: 5 h). The results indicated that Re/BC catalysts with low loadings (2-5%) are very active towards butenes (the hydrogenation product of BD), while high loadings (20%) favor both conversion and BD production. This is attributed to the different structure of the materials, as according to XRD, Re is fully crystallized as Re₃O₁₀ in the case of 20% Re/BC, while over low loadings it appears as broad peaks resembling an amorphous material. To avoid using high Re loadings owing to its high cost, the catalysts were modified by impregnating Mo at low loadings. The latter is a well-known catalyst for its mild hydrogenation activity^[3,4]. Indeed, BD selectivity was improved in addition to erythritol conversion. The effect of reaction time was further studied over 5% Mo-10% Re/BC and as it was expected, short reaction times favor the formation of butenediol (the main intermediate towards BD). Maximum BD selectivity (93%) was achieved at 5 h, while after 7 h its formation is restricted in favor of butenes/butane. The effect of key reaction parameters was further studied at t=5 h and it was found that increased temperature and H₂ pressure enhance both conversion and BD selectivity by eliminating the production of butenediol. A maximum 93% BD selectivity was achieved for 51.5% conversion at 140°C, P_{H₂, initial}=60 bar and 5 h. XPS measurements confirmed the presence of fully oxidized Mo-Re species (Mo⁶⁺, Re⁶⁺, Re⁷⁺), while CH₃OH-TPSR indicated that the surface of Re-Mo catalysts host both redox and acid sites. HDO experiments under continuous flow conditions are in progress.

KEYWORDS: Hydrodeoxygenation, 1,3-butadiene, erythritol, rhenium-molybdenum-catalysts,

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