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Boosting the ruthenium catalyzed bio-ethanol homologation with a redox active co-catalyst

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PURPOSE OF THE ABSTRACT

Bio-ethanol refinery is a current topic due to environmental issues connected with petrochemical processes and in order to develop new economic strategies. In particular, when derived from waste or (non-food) biomass, bio-ethanol is a feedstock with a great potential for both biofuel and biochemical production.¹ An appealing pathway to upgrade the fuel properties of this bio-derived platform chemical into species with higher energy density and characteristics more similar to conventional fuel is represented by the Guerbet reaction which furnishes, in principle, an ideal mechanism for the catalytic conversion of bio-ethanol into butanol and higher alcohols. Nevertheless, although the reaction seems simple in theory, it is highly challenging especially for ethanol and particularly concerning the goal of high yields and selectivity towards butanol and higher alcohols.²

Starting from this awareness the approach to Guerbet reaction has been recently widened to homogeneous catalysis.³ Best results in terms of selectivity have been obtained by Jones et al. with a tandem catalytic approach that involves iridium and copper or nickel complexes. In this case yield reached 37% with a selectivity up to 99%.⁴ Employing a ruthenium catalyst with a tridentate ligand, the Milstein group reached the best conversion up to date of 73% in 40h.⁵

Here we describe the catalytic transformation of ethanol into butanol and higher alcohols promoted by a bi-functional ionic ruthenium based homogeneous catalyst active in hydrogenation and de-hydrogenation. Noteworthy, the catalytic activity is impressively boosted employing a redox active co-catalyst, leading to a record alcohol conversion of 74% in 4 hours, while maintaining good selectivity in 1-butanol and higher alcohols, both linear and branched (Figure 1). Linear alcohols (from n-butanol to n-octanol) are characterized by an energy density closer to gasoline and can be used directly as a blend in diesel engines (with a formulation up to 30% of alcohols in diesel fuel).⁶ However, problems can arise from their poor lubricating properties that can dilute the lubricant film on the piston wall, thus affecting engine durability.⁷ For these reasons, a mixture of linear and branched alcohols is desirable to solve these problems. Moreover, although homogeneous, the catalyst can be recovered and recycled. The reaction occurs working in ethanol without additional solvent in the presence of an

inorganic base as condensation co-catalyst (e.g. NaOEt or NaOH). It is barely affected by the presence of water and conditions can be transferred to a real matrix of wine-waste bio-ethanol, indeed employing heads and tails from ethanol distillation (supplier: CAVIRO distillery) no significant change in the final reaction mixture is observed. Mechanistic investigations will be also presented and discussed.

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FIGURES

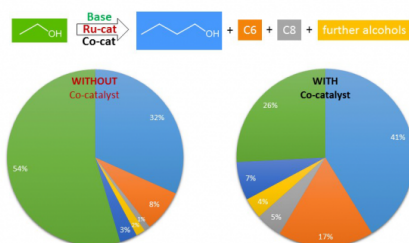


FIGURE 1

Figure 1.

Reaction mixture obtained from Guerbet reaction catalyzed by ruthenium catalyst with or without the redox active co-catalyst.

FIGURE 2

KEYWORDS

Bio-ethanol | Guerbet reaction | bio-refinery | advanced biofuel

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