Selective hydroconversion of coconut oil-derived lauric acid to alcohol and aliphatic alkane over MoOₓ-modified Ru catalysts under mild conditions†

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Molybdenum oxide-modified ruthenium on titanium oxide (Ru–(y)MoOₓ/TiO₂; y is the loading amount of Mo) catalysts show high activity for the hydroconversion of carboxylic acids to the corresponding alcohols (fatty alcohols) and aliphatic alkanes (biofuels) in 2-propanol/water (4.0/1.0 v/v) solvent in a batch reactor under mild reaction conditions. Among the Ru–(y)MoOₓ/TiO₂ catalysts tested, the Ru–(0.026)MoOₓ/TiO₂ (Mo loading amount of 0.026 mmol g⁻¹) catalyst shows the highest yield of aliphatic n-alkanes from hydroconversion of coconut oil derived lauric acid and various aliphatic fatty acid C6–C18 precursors at 170–230 °C, 30–40 bar for 7–20 h. Over Ru–(0.026)MoOₓ/TiO₂, as the best catalyst, the hydroconversion of lauric acid at lower reaction temperatures (130 ≥ T ≤ 150 °C) produced dodecane-1-ol and dodecyl dodecanoate as the result of further esterification of lauric acid and the corresponding alcohols. An increase in reaction temperature up to 230 °C significantly enhanced the degree of hydrodeoxygenation of lauric acid and produced n-dodecane with maximum yield (up to 80%) at 230 °C, H₂ 40 bar for 7 h. Notably, the reusability of the Ru–(0.026)MoOₓ/TiO₂ catalyst is slightly limited by the aggregation of Ru nanoparticles and the collapse of the catalyst structure.

Introduction

The catalytic hydroconversion of fatty acids and their esters into fatty alcohols and aliphatic alkanes is receiving increased attention in the context of upgrading of bio-based feedstocks by using heterogeneous mono- or bi-metallic catalysts.[1–4] Both fatty alcohols and aliphatic alkanes are basic building blocks in organic synthesis, living organisms, energy, fuels, surfactants, lubricants, plasticizers, coatings, polymers, and the materials industry.[5,6] The catalytic hydroconversion of fatty acids can be classified into three reactions: hydrodeoxygenation (HDO), hydrodecarbonylation (HDCO), and hydrodecarboxylation (HDCO₂), and a number of comprehensive reviews have been

reported in the last decade.[7–12] HDCO and HDCO₂ yield hydrocarbons with one carbon atom less than the fatty acid precursor, while HDO gives hydrocarbons with the same chain length as the starting compounds.[13] Among these hydroconversion approaches, HDO, producing hydrocarbons without C–C bond cleavage of fatty acids, is more atom-efficient than the other methods (HDCO and HDCO₂) with C–C bond cleavage of the fatty acids. Moreover, the reaction rate of HDCO or HDCO₂ is slow and needs to be carried out at higher reaction temperatures.[14]

The development of effective heterogeneous catalyst systems (in the form of supported reduced or sulfided metals or bimetallic) for the hydroconversion of fatty acids has been longstanding industrial target by researchers.[15–18] The literature shows that heterogeneous supported platinum group metals (PGM) (e.g., Pt, Pd, Rh, Ru, Ni) catalysts showed high selectivity toward HDCO or HDCO₂ rather than HDO products even under H₂ atmosphere.[19–23] To improve the HDO activity rather than HDCO and HDCO₂ of fatty acids, the modification of those PGM-based catalysts is necessary, i.e., the addition of more electropositive metals[24,25] or the use of oxide supports that strongly interact with the active metals,[26–28] or direct modification with the metal oxide species.[29] The addition of second metals (e.g., Sn and B) to Ru enhanced the dispersion of Ru and improved the electron density of Ru. The change of electron

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