Abstract

The valorisation of lignocellulosic biomass and its derivatives has become a sustainable alternative to the use of fossil sources for the production of fuels and chemicals. In this context, the conversion of light oxygenated compounds present in aqueous effluents derived from primary treatments of biomass (i.e. fast pyrolysis), after a phase separation process via water addition is a key step in the actual biorefinery scheme processes. The strategy is based on the transformation of these low-value water-soluble oxygenated compounds into a mixture of hydrocarbons and aromatics useful for blending with automotive fuels. In general, the activity of the catalysts employed in these processes is based on their bifunctional character. Nonetheless, their activity in complex aqueous mixtures and their stability under faithful operating conditions close to industrial scenarios are critical challenges to be further applied.

This thesis comprises a detailed work in the design of new solid catalysts with high activity and stability in consecutive aqueous-phase condensation reactions of light oxygenated compounds (C$_1$-C$_4$) mixtures under moderated process conditions. In this sense, this work differs from usual probe molecules studies performed even in the absence of water.

Firstly, mixed oxides (including Ce$_x$Zr$_{1-x}$O and hydrotalcite-derived materials) were employed as they have been widely studied in condensation and ketonization reactions. These materials show good catalytic results in the liquid-phase condensation of light oxygenates, but strong catalysts deactivation was observed due to the active phase partial leaching. Therefore, new heterogeneous acid catalysts must be developed in order to meet these new process requirements: complex aqueous
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environments with high contents of organic acids and moderated reaction conditions.

In this sense, the addition of aqueous HF during TiO$_2$ catalysts synthesis is essential to selectively control the preferential growth of catalytic more reactive {001} TiO$_2$ facets. Moreover, Lewis acid sites on faceted TiO$_2$ materials have great stability in condensation reactions, especially in the presence of organic acids and high water contents. Thus, this strategy allows obtaining materials that show better catalytic results and stability than other commercial titanium oxides.

Moreover, hydrothermal synthesized Nb- and WNb-mixed oxides have shown the advantage of having crystalline structure, area and acid properties modified by tailoring their composition and post-synthesis heat-treatments conditions. Optimized NbO$_x$ and WNbO materials show higher activity and stability in the aqueous-phase condensation of oxygenated compounds than other commercial samples, commonly employed in literature.

Finally, new acid catalysts prepared via co-precipitation based on tin, titanium and niobium (Sn$_x$Ti$_y$Nb$_z$O) mixed oxides have been developed. These materials mainly present SnO$_2$ rutile-phase crystalline structure, which has been claimed to have interesting hydrophobic characteristics. Tailoring of composition and calcination conditions allows obtaining mixed oxides with uniform crystalline structures, enhanced surface areas and a higher concentration of Lewis acid sites compared to analogous commercial catalysts. These materials show high activity and stability in the valorisation of oxygenated compounds present in aqueous effluents derived from different biomass processes.