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In situ upgrading of bio-oil via CaO catalyst derived from organic precursors

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Abstract

The fast pyrolysis of biomass with catalysts is a promising route for producing upgraded bio-oil as an alternative energy source. A CaO catalyst prepared from organic calcium compounds (Org-CaO) was first used to upgrade the pyrolysis oil of Jatropha curcas seeds in situ. Calcium D-gluconate monohydrate, calcium citrate tetrahydrate, and calcium acetate hydrate were employed as the organic precursors in this work. The results showed that Org-CaO exhibited better deoxygenation ability to produce more hydrocarbons than conventional CaO derived from Ca(OH)₂ (CH-CaO). Acids accounted for 83% of the oxygenated compounds in the raw bio-oil and were almost completely removed via CaO. For bio-oil catalyzed by Org-CaO, the fraction of esters in the oxygenated compounds was only \sim 9%, which was 20% less than that in CH–CaO bio-oil. The relative content of ketones and alcohols in Org-CaO bio-oil increased by 16% versus that in CH-CaO bio-oil. Org-CaO exhibited a remarkably larger pore size and much smaller particle sizes. Thus, Org-CaO entered into the fuel through the pore channels, and this promoted the formation of chemical crosslinking points between CaO and oxygenated groups. In addition, the basicity and the amount of basic sites for Org-CaO increased versus CH-CaO. Thus, the adsorption forms of oxygen-containing groups in the bio-oil on the basic sites of CaO changed: the carboxyl groups were removed from the acids and were absorbed in a stable form of unidentate carbonate on oxygen vacancies (O^{2-}) . The stable form was bidentate carbonate on $Ca^{2+}-O^{2-}$. In addition, oxygen vacancies on Org-CaO extracted more hydroxyl groups from the acids, resulting in dehydroxylation of acids to form ketones and alcohols.

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Keywords: Upgraded bio-oil; In situ catalysis; CaO; Organic precursor; Deoxygenation

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1. Introduction

The conversion of biomass to liquid fuels and value-added chemicals via thermochemical processes, such as fast pyrolysis, is an important

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