Cross ketonization of *Cuphea* sp. oil with acetic acid over a composite oxide of Fe, Ce, and Al

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**ABSTRACT**

The objective of this work was to demonstrate the viability of the cross ketonization reaction with the triacylglycerol from *Cuphea* sp. and acetic acid in a fixed-bed plug-flow reactor. The seed oil from *Cuphea* sp. contains up to 71% decanoic acid and the reaction of this fatty acid residue with acetic acid yields the fragrance compound and insect repellent 2-undecanone. To this end, we screened several ketonization catalysts taken from the literature including CeO\(_2\), CeO\(_2\)/Al\(_2\)O\(_3\), CeO\(_2\)/ZrO\(_2\), MnO\(_x\)/Al\(_2\)O\(_3\). The catalysts were characterized by N\(_2\) adsorption/desorption, H\(_2\)-TPH, CO\(_2\)-TPD, and XRD. Each of these catalysts affected the conversion but the highest yield was found with a new coprecipitated mixed metal oxide of empirical formula Fe\(_2\)O\(_3\)Ce\(_x\)Al\(_{2-x}\)O\(_3\). In a flow reactor, Fe\(_2\)O\(_3\)Ce\(_x\)Al\(_{2-x}\)O\(_3\) gave 2-undecanone at 91% theoretical yield with reaction conditions of 400°C, weight hourly space velocity of 2, molar ratio of acetic acid to *Cuphea* oil of 23, and N\(_2\) carrier gas flow of 125 ml/min at 2.4 bar. This high yield is attributed to the low rate of coke formation on the mixed metal catalyst. In the absence of acetic acid, coupling of the decanoic acid residues gives 10-ketononadecane.

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1. Introduction

The coupling of organic acids to produce symmetrical ketones dates to the late 19th century when Squibb published the improved synthesis of acetone in which he demonstrated continuous production of acetone from acetic acid vapors in a red-hot iron tube [1]. Prior to this, acetone was prepared by the destructive decomposition of calcium acetate. Scheme 1 shows the formation of acetone from acetic acid along with the side products of water and carbon dioxide. The high conversions and selectivity of the reaction, along with water and carbon dioxide as lone side products, makes the process environmentally benign. Only the high temperatures required for conversion can detract from this portrayal.

This reaction has been further developed to include the synthesis of 3-pentanone from propionic acid [2], cyclopentanone from the cyclization of adipic acid [3], and larger ketones such as 7-tridecanone from heptanoic acid and its alkyl esters [4,5], as well as fatty acid methyl esters from rapeseed oil to give symmetrical ketones of up to 35 carbons in length [6]. Mixtures of substrates such as fermentation residue have also been upgraded to chemicals by ketonization [7]. Along with this long list of substrates, there is a list of catalysts employed in ketonizations that is even longer. At least sixteen metal oxides or carbonates including the alkaline earth metals Mg, Ca, and Ba on silica and carbon [8], the rare-earth element Ce [8–11], the actinides Th [12] and U [13], as well as the transition metals Fe [11], Cr [14], Mn [5,15,16], V [17], Ti [17,18], Zr [18,19], and Ni, Co, and Cu as composite oxides [2].

Despite the large number of substrates and catalysts used to study the ketonization reaction, mechanistic details remain elusive and it is likely that different mechanisms occur with different catalysts. The defining characteristic which may drive the different mechanisms is the presence of an abstractable α-proton. For example, the cyclization of adipic acid in the presence of BaO or KF has been suggested to occur through a rapid deprotonation of one acid group followed in turn by decarboxylation to give a carbanion which cyclizes to form the enolate anion. This then loses the hydroxide group, which combines with the acid proton to form water, and cyclopentanone [20]. This reaction also occurs, albeit at lower yields, with 2,2,5,5-tetramethylhydridic acid, which lacks an α-proton. Such a mechanism is consistent with experiments based on the decomposition of acid salts but does not describe reactions over heterogeneous catalysts, which are becoming more common.

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