Preparation of Higher Fatty Acids by Catalytic Hydrocarboxylation of Olefin-Paraffin Mixtures

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Carboxylic acids and their derivatives (anhydrides, esters, amides, metal salts) are valuable products of chemical industry. They find wide application as detergents, emulsifiers, softeners, greases and so on. Among several known routs to higher saturated carboxylic acids olefin hydroformylation followed by aldehyde oxidation, Koch synthesis and partial oxidation of paraffins are of commercial importance. Transition metal catalysed hydrocarboxylation of olefins is rarely applied:

$R–CH=CH–R' + CO + H_2O \rightarrow R–CH(COOH)–CH_2–R' + R–CH_2–CH(COOH)–R'$

R, R' = H, alkyl

However, this reaction provides some important advantages such as high total selectivity, relatively mild conditions for Pd-based catalysts, absence of by-products (so-called “atom economy principle”).

From technological point of view, hydrocarboxylation of olefin-paraffin mixtures from dehydrogenation units looks attractive because eliminates such expensive preliminary operation as separation olefins from paraffins. Resulted fatty acids have much higher boiling points than initial hydrocarbons and therefore could be easily separated by distillation. Chemical separation via water-soluble salts is also possible.

We studied Pd-catalysed synthesis of saturated carboxylic acids by hydrocarboxylation of both artificial olefin-paraffin mixtures and olefinic fractions obtained from industrial units of paraffin dehydrogenation. Reaction mixtures were biphasic and acetone, formic acid, water or molten salts were applied as polar phases. Catalytic systems containing no phosphine ligands were proposed to perform the reaction. Effects of acidic promoter, reagents ratio, temperature and pressure on catalyst activity and regioselectivity were studied in detail. Biphasic conditions of the reaction allow to perform multiple reuse of catalytic system with minimum loss of palladium.