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Products of Homogeneous Two-Stage Oxidation of 1-Butene to Butanone with O₂ Over the Catalyst Pd + Heteropoly Acid

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Oxidation of 1-butene to butanone in the presence of homogeneous catalyst Pd + HPA ($H_{12}P_3Mo_{18}V_7O_{85}$) followed by regeneration of the catalyst with O₂ proceeds with selectivity 97.5 %. Side products of the process are acetic acid (1.4 %) and condensed compounds C₇H₁₂O₂, C₈H₁₄O₂, C₆H₆O₂, and C₈H₁₀O₂ (total 1.1 %). In the course of the catalyst regeneration at 170 °C under O₂ pressure, the compounds C₆–C₈ are completely oxidized to CO₂ and acetic acid. n-Butanal is absent in the reaction products, that permits readily to separate butanone as a water azeotrope from the reduced catalyst.

Keywords: *Oxidation of 1-butene to butanone, homogeneous catalyst Pd + HPA, reaction products.*

Introduction

The processes of oxidation of lower alkenes C₂–C₄ to carbonyl compounds with dioxygen by reaction (1) are of great practical importance:



Here R = H, CH₃, or C₂H₅. In the late 1950s the Wacker company had suggested for such processes a homogeneous catalyst, which was an aqueous solution of PdCl₂ + CuCl₂ [1, 2]. CuCl₂ here is a reversible oxidant, which reduced form is readily oxidized with dioxygen. Such catalyst had a high concentration of chlorides (up to 2 M), that led to formation of toxic chloroorganic side products. Their amount strongly increased in the series C₂ (ca. 2 % [3]) < C₃ (ca. 4 %) < C₄ (> 6 %) [2, 4]. Amount of chloroorganics strongly increased also at elevated temperature [4] but decreased after dehydrochlorination (see later). Besides, various amounts of aldehydes, RCH₂CHO, were formed together with ketones, CH₃COR. When propene or 1-butene were oxidized, yield of RCH₂CHO varied from 3 to 18 % [2, 5]. Only in oxidation of 2-butene, butanone was the single reaction product [1]. Now

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