

Oxidation of some oxygen containing C₂ – C₄ Intermediates of the Oxidation of 1-Butene over VO_x containing Catalysts

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Introduction:

The cracking of butane/butene mixtures on VO_x containing catalysts is a promising process for the production of acetic and formic acid [1]. According to literature [2,3] the formation of acetic and formic acid takes place via the intermediate products (IP's) 2-butanol (2-BuOH), methyl ethyl ketone (MEK), propionaldehyd (PrAld) and acetaldehyde (AcAld). The aim of this work was the elucidation of the influence of reaction conditions on product formation during the oxidation of the above mentioned IP's on a VO_x-TiO₂ and a VO_x/SbO_y-TiO₂ catalyst.

Experimental:

The catalysts were produced by spray drying an aqueous suspension of the corresponding metal oxides with subsequent calcination in air. The catalysts were characterized by surface area, TPR, TPD and XRD [4]. The catalytic oxidation of the IP's was accomplished in a integral flow reactor with oxygen in presence of water in the temperature range from 390 to 550 K. The products of the reactions were analysed by a mass spectrometer and an IR gas analyzer.

Results and Discussion:

The yields of acetic and formic acid depended on reaction temperature. The highest yield of acetic acid was observed during the oxidation of 2-BuOH on VO_x/SbO_y-TiO₂ (Y: 63 %; T: 473 K). For both catalysts used, the total oxidation to CO and CO₂ increased with increasing reaction temperature. During the oxidation of 2-BuOH, 1-butene, MEK, methyl vinyl ketone (MVK), propionic acid (PrA), diacetyl (DA), and furan could be detected. The yields of MEK, MVK, PrA, and DA decreased with increasing temperature. Though DA and crotonic acid possess the same mass fragment 86 it can be concluded [5] that the detected compound is DA because crotonic acid is formed at high temperatures whereas DA is formed at low temperatures. During oxidation of MEK the yields of MVK, PrA, and DA decreased with increasing temperature. According to literature [5,6] crotonic acid is not formed from MEK. During oxidation of PrAld and AcAld at low temperatures the corresponding carboxylic acids were formed and with increasing temperature the yields of CO and CO₂ increased.

Literature:

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