Oxidation of Some Unsaturated Hydrocarbons Over Copper Catalysts

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An investigation was made of the kinetics of oxidation of isobutylene, piperylene and isoprene over copper catalysts.

It was established that the rates of formation of unsaturated aldehydes and of carbon dioxide depend upon peculiarities of the structures of hydrocarbons to be oxidized and upon reactivity of the aldehydes formed.

Catalytic Oxidation of Propylene into Acrolein in Presence of Selenium

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The results are summarized for a study covering air oxidation of propylene into acrolein over $CuSO_4$, CuO, $CuSeO_3$ on active aluminum oxide, $CuSiO_3$, silica gel, etc.—as the carriers. The function of selenium is explained as follows: due to chemisorbtion it blocks the active centers essential for complete oxidation of propylene; in addition, during formation of acrolein, selenium participates in the transfer of oxygen to the propylene molecules.

Formation of acrolein takes place over a very wide temperature range of 220° to 360°C. The reaction occurs in the kinetic region and approximates a first order reaction with respect to propylene. The activation energy is 14,000 cals/mole. At a temperature of 325° and apparent contact times of 2.0–2.5 secs the yields of acrolein reach 81–82% and conversion of propylene per pass amounts to 90–95%. The optimum content of copper in the catalyst is 12–16% by weight.

Catalytic Oxidation of Propylene into Acrolein In Presence of Inert Diluting Substances

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A study was made of the process of oxidation of propylene to acrolein in presence of water vapor. It was demonstrated that, unlike the case of oxidation of propylene into acrolein without the inert diluent, selectivity of this process improves but the catalyst lacks stability. Use of nitrogen or of carbon dioxide lowers reaction selectivity. At temperatures of 340°–400° the optimum concentration of diluent water vapor is 40%. Addition of promoters to copper catalysts stabilizes their activity and increases cycle-life. For a 500-hour run over a promoted catalyst, the average yield of acrolein was 285 grams/liter hour; the yields for acrolein were 82% and 53.3% based on propylene and oxygen reacted, and the corresponding conversions of the two reactants were 4.95% and 48.2%.

Catalytic Oxidation of Propylene into Acrolein in Presence of Water Vapor

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A study was made of the specific function of water vapor which raises selectivity of conversion of propylene into acrolein. Both selectivity and stability of the catalyst are improved when dilution of the reaction mixture with water vapor is accompanied by introduction into the gaseous phase of trace amounts of halogen derivatives. The process conditions were determined for a 6% conversion of propylene at a 70% selectivity.

Kinetics of Catalytic Oxidation of Benzene into Maleic Anhydride

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An investigation was made of the kinetics of catalytic oxidation of benzene into maleic anhydride over a vanadium-molybdenum catalyst over a broad range of concentrations of charge stocks and products.

It was established that the reaction rates for catalytic oxidation of benzene can be calculated by use of Equations (9) through (18). At low oxygen partial pressures the order of this reaction was found to be anomalously high with respect to this gas.

The effect of temperature on the reaction rate constants, k_1, k_2 and k_3, and the apparent activation energy were determined. It was demonstrated that the empirical kinetic equations describing the processes of this type are explainable in the light of the processes accounting for the phase changes within the catalyst crystals.