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Some of the Problems of Kinetics and Reaction Mechanism in Heterogeneous Catalytic Oxidation of Organic Compounds

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The kinetics and reaction mechanism were investigated for the process of heterogeneous catalytic oxidation of organic substances. The effects of the following processing variables were determined:

(1) Manner of initial attack of a molecule;

(2) Relationship between the reaction and the desorption rates;

(3) Phase changes in the catalyst.

The possibility to carry out heterogeneous reactions of this type in liquid phase is also noted.

Modification of Catalysts for Oxidation of Hydrocarbons

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An investigation was made of the effects of great many additives upon the working process yields and activity of metal and semiconductor catalysts (silver and copper oxide). The modifying additives with electronegative values, ϵ, greater than the ϵ value of the catalyst decrease its activity and, at the same time, increase the work function, and selectivity of oxidation of ethylene and propylene. It was demonstrated that for mixed catalysts, MnO_3-Bi_2O_3 and WO_3-Bi_2O_3, the selectivity and the electronic work function correlate with catalyst composition.

Modifying Effect of Additives on Performance of Ethylene Oxidation Catalysts

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A study was made of the modifying effect of S, Se, Te and Cl on a silver catalyst for oxidation of ethylene, using a radiochemical method. In each case the optimum activity was found to lie in the modifier concentration range which corresponds to small coverages of the catalyst surface. Data were obtained on the modifier distribution within the catalyst and on its surface and on their volatility to the gaseous phase.

The changes in activity of the catalyst due to the added modifiers are attributed to a change in the bond energy of adsorbed oxygen.

Investigation of Phase Composition of Mixed Vanadium Catalysts for Oxidation of Aromatic Hydrocarbons

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This investigation covered a study of phase compositions of fresh and spent catalysts, comprising mixtures of oxides of vanadium and molybdenum and of vanadium and chromium, and of their activity for oxidation of benzene to maleic anhydride. It was demonstrated that the composition of a vanadium-molybdenum catalyst of optimum activity approaches that corresponding to the limiting solubility value of MnO_3 in V_2O_5 in solid solution. In a number of cases spent catalysts were found to have formed two-phase oxide systems. The effect of the additives on the rate of catalyst regeneration by the reaction media was also determined.

Effect of Method of Preparation of Silver on Its Specific Activity in Oxidation of Ethylene

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An investigation was made of the effect of method of preparation of silver on its specific catalytic activity for oxidation of ethylene. It was demonstrated that the instability in specific activity of silver which occurs when recovering this metal by various methods, is caused by a change in chemical composition of the catalyst surface as a result of contamination with microimpurities. It was also established that pure silver has approximately the same activity, regardless of the method of its preparation.

Kinetics of Catalytic Oxidation of Ethylene

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A study was made of the kinetics of oxidation of ethylene over a silver catalyst into ethylene oxide and into carbon dioxide and water, using a recycle-continuous process. A detailed study was made of the retarding effect of the reaction products. Based on a concept of the mechanism of this catalytic process, new kinetic equations were developed which satisfactorily agree with the experimental data for a wide range of changes in the concentrations of charge stocks and of reaction products. The kinetic equations developed are also in agreement with the results obtained by other investigators.

Oxidation of Ethylene in a Pseudo-Liquefied Catalyst Layer

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A catalyst was developed for production of ethylene oxide in a pseudo-liquefied layer. An investigation of the kinetics of the process was carried out at high concentrations of ethylene in the reaction mixture at constant concentrations of promoters in the gaseous phase. It was demonstrated that the reaction rate of the process is proportional to the oxygen concentration and that the reaction is retarded by the reaction products. The hydrodynamics of pseudo-liquefaction were also investigated.

Kinetics of Oxidation of Propylene into Acrolein Over a Copper Catalyst

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A study was made of the kinetics of oxidation of propylene into acrolein over a copper oxide catalyst in a recycle-continuous operation. It was shown that increasing propylene concentration improves selectivity of the process. The kinetic equations for oxidation of propylene to acrolein and carbon dioxide are as follows:

$$W_1 = \frac{k_1[O_2][C_3H_6]^0}{1 + b(\text{Product})}; \quad W_2 = \frac{k_2[O_2]}{[C_3H_4O]^{0.7}[C_3H_6]^{0.2}}.$$

Under normal operating conditions the activation energies of formation of acrolein, E_{acr}, and of carbon dioxide, E_{CO_2}, were found to be 30 ± 2 and 36 ± 2 kcals/mole, respectively. On the other hand, in absence of the retarding effect of the reaction products the activation energy values for acrolein and carbon dioxide were determined to be $E_{acr} = 20 \pm 1$ and $E_{CO_2} = 26 \pm 1$ kcals/mole.

A parallel-series scheme of operation for catalytic oxidation of propylene was also found workable.

Transfer Processes in Catalytic Oxidation of Propylene

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An investigation was made of the effects of heat and material transfer stages both to the outer and to the inner surfaces of catalyst granules. It was demonstrated that the processes of mass- and heat transfer to the outer surfaces have no effect on the overall reaction rate of the process. The effect of the two transfer processes within the granules depends upon porosity of the catalyst and concentration of copper in it. In a majority of cases, the difficulty to recover the acrolein from the interior of the pores accounts for a decrease in selectivity.

Oxidation of Propylene to Acrolein Over Cu-on-Al_2O_3 Catalysts Modified by Molybdenum Oxides

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Active aluminum oxide-based catalysts were prepared for oxidation of propylene into acrolein.

A study was also made of the kinetics of oxidation of propylene over Cu-on-Al_2O_3 catalysts, using oxides of molybdenum and of tungsten as modifiers.