

ity of the semiconductor and the intensity of its electrical surface charge.

### Catalytic Properties of Metal Oxides of the IV-th Period of the Periodic Table in Oxidation Reactions: Oxidation of Methane

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Catalytic activity of  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$ ,  $\text{CuO}$ , and  $\text{ZnO}$  was determined in complete oxidation of methane in a recycle-continuous system. A temperature-reaction rate correlation and the order of the reaction with respect to methane were determined.

### Study of Chromium Oxide—Oxygen System by Infrared Spectroscopy

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A study of the infrared spectra of a chromium oxide-oxygen system at different temperatures shows that interaction of the oxide with oxygen leads to formation of individual compounds on the surface and in the adjacent underlying layers. Chromic anhydride and a product of its thermal decomposition were identified. Based on the spectral analyses, thermal preactivation with hydrogen does not result in formation of a new solid phase on the chromium oxide surface.

### Kinetics of Dehydrogenation of Cyclohexane in a Non-Gradient System

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Using a recycle-continuous unit, kinetic data were obtained in dehydrogenation of cyclohexane over a nickel catalyst on zinc oxide carrier at the far-from-equilibrium conditions. At partial pressures of cyclohexane of over 100 mm Hg, the reaction rates conform to the equation of the zero order reactions; at partial pressures below 100 mm Hg, the rates are described by the equation,  $\omega = kP_{\text{C}_6\text{H}_{12}}^{0.5}$ . Activation energy of the reaction is 14.2 kcal/mol. The results obtained are interpreted by assuming that the reaction has no limiting stage at high and moderate surface coverages and the far-from-equilibrium conditions. Transition from a high to a moderate surface coverage changes the (observed) order of the reaction.

### Bismuth-Molybdenum-Phosphorus Catalysts for Oxidation and Oxidative Ammonolysis of Propylene

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A study was made of the effect of phosphorus addition on the structure and catalytic properties of bismuth molybdates differing in structure and having the following compositions:  $\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3$  ( $\alpha$ );  $\text{Bi}_2\text{O}_3 \cdot 2\text{MoO}_3$  ( $\beta$ );  $\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$  ( $\gamma$ ). The results show that introduction of 0.2–0.8% of phosphorus at the conditions to form the  $\alpha$ -phase, produces structural and phase changes in the  $\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3$ . Here, the  $\alpha$ -phase is partially transformed into the  $\beta$ -phase, which is characterized by the greatest catalytic activity. Addition of phosphorus in amounts greater than 4% (wt), leads to formation of the compound,  $2\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot \text{P}_2\text{O}_5$ . This substance has lower catalytic activity than either the  $\text{Bi}_2\text{O}_3 \cdot 3\text{MoO}_3$  or the  $\text{Bi}_2\text{O}_3 \cdot 2\text{MoO}_3$  forms.

### Oxidation of Methanol to Formaldehyde Over a Silver Catalyst: Properties of the Process

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Air-oxidation of methanol was studied over a silver-on corundum catalyst at temperatures of 510°–920°K. At temperatures of 510°–570°K and 750°–850°K, the respective activation energies are 21–22 and 2–3 kcal/mol. At temperatures of 570°–650°K, the process is unstable and the reaction temperature spontaneously increases or decreases, reaching the temperature values outside the interval of unstable conditions. Qualitatively, the kinetic correlations for the process in the high temperature range differ from those in the low range. It is concluded that at temperatures above 650°K, the reaction is not diffusion-limited. Calculation of surface temperature of the catalyst qualitatively supports this conclusion.

### Kinetics of Ethylene Polymerization to a Crystalline Polymer Over a Chromium Oxide Catalyst

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A study of ethylene polymerization kinetics was carried out at temperatures below 90°, using suspensions of a chromium oxide in cyclohexane as the catalyst. The reaction rate-on-stream time

dependence is clearly demonstrated during the induction period, in the course of which the rate of polymerization increases from zero to a fixed value.

After a period of polymerization at a constant rate, the rate decreases. Below a certain minimum concentration of the catalyst, the polymerization reaction does not occur. The results show that at fixed system pressures of 3-40 atm (abs), the polymerization rate varies very nearly as the square of the ethylene partial pressure.

The experimental information shows that accurate picture of the kinetics of ethylene polymerization over the chromium oxide catalyst can be obtained only by taking into account the effect of different additives in the reaction system.

#### Chemisorption of Hydrogen by $\gamma$ - $\text{Al}_2\text{O}_3$

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A reaction mechanism is proposed which is based on the experimental data of the kinetics of chemisorption of hydrogen by  $\gamma$ - $\text{Al}_2\text{O}_3$ . This assumes that surface migration of atomic hydrogen from the active centers of one type to those of another type is the reaction limiting step.

#### Structure of Silica-Titania Catalysts

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Binary  $\text{SiO}_2$ - $\text{TiO}_2$  catalysts form a specific amorphous (X-ray analysis) silicate structure, with the atoms of titanium being present in the lowered (quaternary) coordination relative to the oxygen. Replacement of silicon in the silicate structure by titanium atoms is accompanied by depolarization of the silicate skeleton. Formation of the specific silica-titania structure occurs in the source of preparation of the catalyst. In silica-titania catalyst, the strongly-bound water is primarily attached to the surface atoms of the silicon.

#### Mathematical Model and Kinetics of Polymerization of Ethylene in Presence of Suspended Chromium Oxide Catalyst

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A mathematical model is described for polymerization of ethylene over a chromium oxide cata-

lyst in suspension. The model was designed with the aid of Analogue Computer MN-14. The mathematical description of the process elucidates the experimentally-determined kinetic correlations.

#### Kinetics Scheme to Optimize Ethylene Yields in Pyrolysis of Ethane

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A kinetic scheme was constructed to optimize yields of ethylene in high-temperature pyrolysis of ethane. The scheme is based on the results of a detailed study, utilizing tagged atoms in the experimental determination of the kinetics and products formation mechanism in a high temperature (800°-900°) decomposition of ethane.

#### Thermometric Study of Kinetics of Reactions in Liquid Phase

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An apparatus is described for thermometric determination of the reaction rates in exothermal and endothermal reactions in liquid phase. The method used is based on quantitatively measuring the heat losses. The equipment is useful in studying reactions of 3 minutes to 5 hours duration and the average rate of heat release of not less than 7-10 kcal/hr. The method and equipment were proven in polycondensation of terephthalyl chloride with ethylene glycol, using dioxane as the solvent. The thermal effect of the reaction,  $Q$ , is 14.2 kcal/mol and the reaction constant,  $k$ , at a temperature of 65° is  $4.1 \times 10^{-4}$  l/mol-sec.

#### BRIEF COMMUNICATIONS:

##### Initiation Mechanism in Thermal Decomposition of Ethane

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The results of theoretical calculations of the variation of constants,  $k_0$  and  $k_1$ , with pressure are compared with published experimental data for thermal decomposition of ethane. The calculated constants satisfactorily agree with those based on the experimental results.