

of radicals in these systems, and give data on the yield of radicals (G_R) for various percentages of coverage of the zeolite surface. It is shown that radical accumulation in these systems proceeds somewhat differently than during irradiation of free water or methanol at 77°K.

Further, the authors studied the behavior of the radicals when the temperature was raised above 77°K, and found that their stability depends on the structure of the zeolite and the mobility of the adsorbed molecules. The $\dot{O}H$ and $\dot{C}H_2OH$ species recombine via a stepwise mechanism. The annihilation of the \dot{H} radicals is a bimolecular process whose $k_n = 4.2 \times 10^{-16} \text{ Exp} - [(4600 \pm 800)/RT] \text{ cm}^3/\text{sec}$.

Thermal Decomposition of Silver Permanganate in the Presence of Metal Oxides

V. F. KOMAROV, A. A. KABANOV,
AND V. T. SHIPATOV

The Nuclear Physics Institute of the Polytechnic Institute of Tomsk, and the Tomsk Institute of Electronic Physics and Technology

The authors decomposed silver permanganate at 115°C and showed that ZnO and ThO₂ promote the reaction, that Co₃O₄ and NiO are inert, and that TiO₂ inhibits the process (as do the products of degradation of the silver permanganate itself). The results are explained by assuming an electron exchange between the reactant and the oxide via a layer of reaction product.

The authors have found that $\varphi_1 > \varphi_2 \leq \varphi_3$ in the system ZnO-decomposition product-AgMnO₄, and that the electrons are transferred from the decomposition product to ZnO and AgMnO₄.

An Explanation of the "Distribution Function" in the Theory of Adsorption on Nonuniform Surfaces

F. F. VOLKENSHEIN AND O. PESHEV

*Institute of Physical Chemistry,
Academy of Sciences, USSR*

The authors discuss a semiconductor doped with an impurity which does not directly participate in chemisorption, and which is nonuniformly distributed throughout the matrix or on the surface of the semiconductor. It is shown that in this case the Fermi level in the forbidden zone between the energy bands (and, consequently, the chemisorptive properties of the surface) vary in the different areas of the surface. Under these conditions, the surface exhibits unequal heats of adsorption from point to point. The pattern of this nonuniformity depends on the distribution pattern of the impurity. There exists a relationship between the concentration gradient of the

impurity and the "distribution function" of the heats of adsorption.

Liquid-Phase Oxidation of Hydrocarbons over Solid Catalysts. I. Paraffins and Cycloparaffins

N. V. KLIMOVA AND I. I. IOFFE

Institute of Organic Intermediates and Dyes

Both metals and metal oxides catalyze the partial liquid-phase oxidation of paraffins, aromatics, and cycloparaffins. The activity of oxides is promoted by additives. The authors postulate a heterogeneous-homogeneous mechanism. They also report a new method for control of liquid-phase oxidation (by proper combination of solid catalysts and inhibitors).

Selective Hydrogenation of Crotonaldehyde (to Butyraldehyde)

S. D. RAZUMOVSKIY, V. S. LEVCHUK,
AND E. B. RUDOVSKAYA

All-Union Institute of Petrochemical Processes

Crotonaldehyde was hydrogenated at 100°–180°C at various H₂:C₃H₅CHO ratios and space velocities ranging from 0.2 to 2.2 hr⁻¹. The selectivity with which butyraldehyde is produced is $S_{\text{overall}} = 190.2 + 40V - 0.73T - 46/x$. The optimum industrial conditions are 150°C, $V = 1\text{--}1.5 \text{ hr}^{-1}$, and a C₃H₅CHO:H₂ ratio of 1.

Shift of the Catalyst Potential as a Function of the Rate of Liquid-Phase Hydrogenation. IV. Comparison of Activities of Raney Nickel, and Platinum and Palladium Blacks

V. A. DRUZ' AND L. N. SADCHIKOVA

The S. M. Kirov Kazakh State University

The activities of Raney nickel, and platinum and palladium blacks in liquid-phase hydrogenation were compared in terms of productivity per unit active surface (as referred to hydrogen) and in terms of active surfaces. The productivity factor is specific to each catalyst (and, all other conditions being equal, is determined by the nature of that catalyst).

Activity of Platinum Catalysts. V. Effect of KOH on the Activity of Platinized Carbon

K. H. SCHNABEL

Institute of Inorganic Catalysis, The Academy of Sciences, Berlin, East Germany

Catalysts produced by reduction of H₂PtCl₆ with aqueous formaldehyde and KOH (the Zelin-sky method) are more active in C₂ dehydro-

cyclization than analogous compounds obtained by reduction with hydrogen at 330°C. KOH affects both catalysts in an identical manner. Thus, small additions of KOH promote the activity, but large ones poison the catalyst. The ring expansion in 1,1,3-trimethylcyclopentane is gradually inhibited by higher base concentrations. The activation energies for dehydrocyclization on catalysts containing different amounts of KOH differ substantially. It would appear that small amounts of KOH promote the active sites on platinum. It is shown that the surface of platinized carbon contains several different types of active sites and that dehydrocyclization proceeds differently on every one of these.

The Activities of Phthalocyanins of Platinum Group Metals

B. D. BEREZIN AND A. V. LOSHCHELOVA

The Ivanovo Chemical Engineering Institute

Osmium and ruthenium phthalocyanins (Pc) exhibit very high oxidizing activity, but the other phthalocyanins of this group are inactive. The activity of $(\text{HSO}_4)_2\text{OsPc}$ is higher than that of $(\text{HSO}_4)_2\text{RuPc}$; either of these is much more active than iron phthalocyanin. The authors have investigated the catalyst-poisoning effects of N_2F , HCN, and NH_3 , and have determined the kinetics of homogeneous and heterogeneous reactions involving these catalysts, as well as the kinetic equation, rate constants, and activation energies. They postulate a mechanism for catalysis by phthalocyanins.

Oxygen-Initiated Heterogeneous Catalytic Polymerization of Olefins in the Presence of Hydrogen

N. I. ERSHOV, YA. T. EYDUS,

AND V. P. EROKHINA

The Zelinsky Institute of Organic Chemistry, Academy of Sciences, USSR

The authors investigated the behavior of 1-hexene-hydrogen mixtures (1.3-1.5:1) over clay-supported Co at 100°C and atmospheric pressure. Under these conditions, 1-hexene undergoes hydro-polymerization to higher hydrocarbons. The yield is 7.5%. Addition of 1.3% O_2 increases the yield to 22%, while adding the oxygen and raising the temperature to 140°C raises it to 25%. It appears that no catalyst break-in period is necessary. At 190°C the oxygen ceases to promote the reaction.

Nonstoichiometric Sulfur in WS_2 Catalysts

I. V. KALECHITS AND E. N. DERYAGINA

Institute of Petro- and Coal Chemistry, Irkutsk State University

Nonstoichiometric amounts of sulfur are incorporated into the WS_2 catalyst during its preparation. This sulfur appears to account for the isomerizing and cracking activity of this catalyst. It is suggested that the sulfur is incorporated into the WS_2 lattice during formation.

Kinetics of Dehydrogenation of Cyclohexane over Chromium Oxide in a Nongradient System. II.

V. S. GADZI-KASUMOV, S. L. KIPERMAN,

G. V. ISAGULYANTS, AND

A. A. BALADIN (deceased)

The Zelinsky Institute of Organic Chemistry, Academy of Sciences, USSR

The authors have studied the kinetics of dehydrogenation of cyclohexane over various chromium oxide catalysts in a circulatory-flow unit. The reaction rate may be described by $\omega = kP_{\text{C}_6\text{H}_{12}}$. The activation energies vary between 31 and 42 kcal/mole, depending on the catalyst. Comparison of the rates with the rate of the *para-ortho* conversion in hydrogen showed that under these conditions hydrogen desorption cannot be the controlling stage.

Gas-Chromatographic Studies on the Kinetics of Cumene Cracking over Modified Silica-Alumina Catalysts

A. A. SPOZHAKINA, I. F. MOSKOVSKAYA,

AND K. V. TOPCHIEVA

Department of Chemistry, University of Moscow

Pulse gas chromatography was used to determine the activity of a series of silica-alumina catalysts in cracking of cumene. The activities of amorphous silica-alumina catalysts are compared with those of Y-type zeolites of the same cationic forms.

Hydrogenation of Glucose on Raney Nickel. I.

F. B. BIZHANOV, D. V. SOKOLSKIY,

N. I. POPOV, N. YA. MALKINA,

AND A. M. KHISAMETDINOV

The Kazakh Chemical Engineering Institute

The authors studied the hydrogenation of glucose over Raney-type nickel-palladium and nickel-ruthenium catalysts at above-atmospheric pressure and with intensive mixing of the medium. Palladium or ruthenium are promoters of Raney nickel and can raise its activity by as much as 30% (0.1-0.5% ruthenium or 5% palladium). The controlling step is hydrogen activation ($E_{\text{act}} = 12-$