

ing kinetic equations. The experimental data are utilized to evaluate the kinetic constants used in these equations.

#### An Extensive Investigation of Iron Catalysts for Use in Ammonia Synthesis

By S. S. LACHEENOV, A. M. ROBEENSHTEIN, V. M. AKEEMOV, A. N. KL'YATCHKO-GORVEECH, I. N. KON'YUKHOVA, L. D. KOZNI'YETZOV, T. T. LEVEETZKAYA, N. A. PREEBITKOVA, A. A. SLEENKEEN, AND R. V. CHESNOKOVA

*Institute of Chemical Physics of the Academy of Sciences of USSR  
State Institute for Nitrogen Industry*

A study was made of the effect of concentration (0-88 wt. %) of aluminum oxide in CO-precipitated iron catalysts—for use in high pressure ammonia syntheses—upon their phase composition, texture, catalytic activity, and magnetic properties. The structure, texture, composition, and activity of the catalysts were determined, using both the oxidized fresh- and the reduced used catalysts. The effects of these properties and of the reaction temperature upon specific catalytic activity were determined. Also investigated was the relationship between the reducing characteristics of the catalysts and their phase compositions.

#### Investigation of Catalytic Dehydrogenation of n-Butylenes at Pulsed Flow Conditions

By E. I. SEEM'YEN'YENKO, S. Z. ROG'EENSKY, AND M. I. YANOVSKY

*Institute of Chemical Physics of the Academy of Sciences of USSR*

Catalytic dehydrogenation of n-butylenes to divinyl was studied by a pulsed chromatographic technique, using an aluminum-chromium catalyst. Consecutive contacting of the test samples with the catalyst gradually changes the character of the resulting chromatograms: initially only pure divinyl is present; subsequently, along with divinyl, there gradually appear  $\alpha$ -butylene,  $\beta$ -cis-, and  $\beta$ -trans-butylenes; later, the character of the chromatograms changes but little.

At low reaction temperatures (85°-200°) the actual yields of divinyl are 1.5-2.0 times greater than the equilibrium yields calculated for the conditions employed. The heats of adsorption of the butylenes and of divinyl on the aluminum-chromium catalyst were determined chromatographically. The feasibility of evaluating activated adsorption processes by chromatographic techniques is pointed out.

#### Study of Ammonia Oxidation Over a Platinum Catalyst by a Secondary Ion Emission Method

By YA. M. FOGEL, B. T. NADIKTO, V. F. RIBALKO, V. I. SHVACHKO, AND I. E. KOROBCHANSKAYA

*A. M. Gorky State University in Kharkov*

A new method was developed by the authors to study heterogeneous catalytic reactions. Its effectiveness in studying catalytic oxidation of ammonia over a platinum catalyst is described. The new method involves running cross-comparisons of the slopes of the I(T) curves (I, intensity of a certain line in the mass-spectrum; T, catalyst temperature) for the secondary ions, displaced from the catalyst surface by the primary ion beams, and for the ions formed by ionization of the gaseous media around the catalysts. The nature of some of the elementary processes occurring in catalytic oxidation of ammonia are described. Some of the phenomena resulting from poisoning of the platinum catalyst by hydrogen sulfide are also described.

#### Determination of Surface Areas of Supported Silver Catalysts by Chemisorption

By K. M. KHOL'YAV'YENKO, M. YU. ROOBANEK, AND N. A. CHERNOOKHEENA

*L. V. Peesarijevsky Institute of Physical Chemistry of the Academy of Sciences of Ukrainian SSR*

Chemisorption of oxygen by catalytic substances was investigated at a temperature of 200° and pressures of 0.1-5 mm Hg. The catalysts studied were tableted silver, silver deposited on fragments of porcelain and on corundum, and silver with added Be(OH)<sub>2</sub>. The results show that the chemisorbed oxygen reaches saturation at pressures of 2-3 mm Hg.

Based on the results of chemisorption of oxygen and physical adsorption of krypton, the calculated surface areas of the various tableted silver catalysts were found to be nearly equal. This finding formed the basis upon which the method for determination of the surface areas of complex silver catalysts was developed.

#### Adsorption of Hydrogen on the Oxygen-Covered Surface of Tungsten

By YU. G. POOSHEENSKY AND B. A. CHOIIKOV

*Institute of Physics of the Academy of Sciences of Ukrainian SSR*

A study was made of the effect of preadsorbing oxygen on a tungsten surface upon the condensa-

tion coefficient, limiting concentration, and heat of adsorption of hydrogen on this metal. The results show that increasing the coverage with preadsorbed oxygen from 0 to  $\sim 1.5 \times 10^{14}$  molecules/cm<sup>2</sup> decreases the initial value of the condensation coefficient by about 50%. Also, the limiting concentration of hydrogen decreases with increasing concentration of the preadsorbed oxygen. At the oxygen concentration of  $\sim 1.6 \times 10^{14}$  molecules/cm<sup>2</sup>, adsorption of hydrogen by tungsten at a room temperature practically ceases. Oxygen preadsorbed on tungsten surface also decreases the heat of hydrogen adsorption by this metal.

**Determination of Heats of Hydrocarbon Adsorption on Aluminum Oxide by Gas Chromatography**

By A. A. KOBASOV, I. V. SMEERNOV,  
AND K. V. TOPCHEEYEV

*Chemistry Department of M. V. Lomonosov  
State University in Moscow*

The effect of desorption temperatures on the volumes of cyclohexane, cyclohexene, methyl cyclohexane, methyl cyclohexenes, toluene, and n-heptane retained by aluminum oxide was studied with the aid of gas adsorption chromatography. For the ring hydrocarbons, the retention volumes decrease with the type in the following order: aromatics, cycloolefins, cycloparaffins. The heats of adsorption were calculated using these tempera-

ture-volume retention data. The relatively small values of the heats of adsorption of cycloolefins are apparently the result of specificity of orientation of their molecules on the aluminum oxide surface. The greatest activity exhibited by cycloolefins on this adsorbent tends to substantiate the validity of these values.

Addition of methyl radical to cyclic hydrocarbons increases their retention volume and heat of adsorption characteristics.

**Gas-Chromatographic Characterization Factors of Unit Surfaces of Adsorbents**

By A. V. KEES'YEL'YOV, R. S. P'YETROVA,  
AND K. D. TSHCHERBAKOVA

*Chemistry Department of M. V. Lomonosov  
State University in Moscow*

Using normal alkanes and silica gels of broad ranges of porosity, the authors develop a correlation between the relative values of specific retention volumes (cc/g of an adsorbent tested)—as determined experimentally by gas chromatography, and the absolute retention values (volume per unit of adsorbent surface) which are independent of the magnitude of specific surface of an adsorbent. These absolute values are physicochemical constants which define the nature of any adsorbate-adsorbent system. The absolute retention volumes so evaluated, facilitate rapid determination by gas chromatography of specific surfaces of silica gels with wide ranges of pore sizes.

## Abstracts from *Shokubai (Catalyst)*

*Shokubai (Catalyst)* publishes both original articles and reviews or translations of articles appearing originally in languages other than Japanese. The following abstracts are of original Japanese language articles only.

**Catalysts for Complete Oxidation of Hydrocarbons**

By NAUYUKI TODO, TOSHIO SATO,  
AND MINORU YANAGI

*From the Government Chemical Industrial Research  
Institute, Tokyo, Meguro-ku, Tokyo, Japan*

In order to select a suitable oxidation catalyst for automotive exhausts, the ability of a variety of catalysts under the wide range of conditions encountered with exhaust systems has been in-

vestigated. The mixtures of Mn<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>, with a weight ratio of 40-20 to 60-80, are active at lower temperatures and have marked resistance to poisoning by lead compounds. The loss in the activity by heat treatment of catalysts at 700°C for 3 hours are the least of investigated catalysts.

The effect of Fe<sub>2</sub>O<sub>3</sub> as an additive to Mn<sub>2</sub>O<sub>3</sub> is to protect the crystal growth of catalysts by the formation of substituted solid solution.

Received October 1, 1964.