COMMUNICATIONS TO THE EDITOR

ANION EXCHANGE STUDIES. XIX. ANION EXCHANGE PROPERTIES OF HYDROUS ZIRCONIUM OXIDE[1,2]

Sir:

In a search for inorganic materials which might exhibit anion exchange properties, investigation of hydrous zirconium oxide appeared particularly attractive. It is extremely insoluble and is expected to be insensitive to attack by acids, bases, oxidizing and reducing agents. Some adsorption properties of "zirconium hydroxide" have been described.[3] Anion exchange properties might be anticipated if one visualizes it to be formed from positively charged zirconium polymers, known to occur in solution,[4] which are partially cross-linked into a network during hydroxide precipitation or subsequent drying. Further, some hydroxides (or oxides) such as aluminum oxide or ferric hydroxide[5] have long been known to be good adsorbents for a number of materials.

"Zirconium hydroxide" was precipitated from recrystallized zirconium oxychloride with ammonia, centrifuged off, dried (room temperature to 800°), ground and sized. The materials, of indefinite composition, contained small amounts of water and chloride ions. They showed good adsorption in acidic solutions for negative ions, *e.g.*, Cl^-, Br^-, NO_3^-, and particularly sulfate and chromate and some, though small, selectivity for complex anions. At low drying temperatures they showed good uptake of negative ions from acidic solutions, *e.g.*, if dried at 32° apparent capacity for chromate was *ca.* 1.4 moles per kg. Though adsorptive capacity decreases with firing temperature, this does not become excessive below *ca.* 300°. Adsorption on the materials can be described in terms of ion exchange terminology. The materials show typical anion exchange displacement reactions and, at least at low loading, exchange is essentially ideal, *e.g.*, in tracer Br^-–NO_3^- exchange experiments the distribution coefficients D of Br^- (amount per kg. adsorber/amount per liter solution) were inversely proportional to M NO_3^-.

The materials should be classed as weak-base exchangers, since even in strongly acidic solutions apparent capacity is dependent on acidity. Although studies of rates of adsorption are not available, in adsorption–elution experiments the exchangers respond readily to changes in conditions, and elution bands showed at reasonable flow rates (*e.g.*, 1 cm. per minute) the expected Gaussian distributions. In view of their high chemical stability, high adsorptive capacities, rapid response, and reasonable selectivities, the hydrous zirconium oxides appear to be promising new materials for anion exchange applications.

Many insoluble "hydroxides" appear to have anion exchange properties. This was demonstrated, for example, for Sn(IV), Th(IV), Ti(IV), Cr(III), in addition to Fe(III) and Al(III). Precipitates of molybdic and tungstic acid, however, showed negligible anion exchange properties, even in strongly acidic solutions. Instead, they showed cation exchange properties. The hydrous zirconium oxides in basic solutions (*e.g.*, 0.01 or 1 M NaOH) lose their anion exchange properties but adsorb positive ions, *i.e.*, they become cation exchangers. Presumably the hydroxides and hydrous oxides in general may exhibit either anion exchange or cation exchange properties, depending on the acidity of the solutions and the tendency of the solids toward amphoteric character.

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(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous paper: F. Nelson and K. A. Kraus, THIS JOURNAL, **77**, 4508 (1955).

(3) E. Wedekind and H. Wilke, *Kolloid-Z.*, **34**, 83, 283 (1924); **35**, 23 (1924).

(4) See, *e.g.*, J. S. Johnson and K. A. Kraus, *J. Am. Chem. Soc.*, in press.

(5) See *e.g.*, F. Nydahl and L. A. Gustafsson, *Acta Chem. Scand.*, **7**, 143 (1953).

CONTINUOUS RECORDING OF ELECTRON DENSITY IN A FUNCTIONING NICKEL CATALYST

Sir:

The decrease of magnetization occurring when supported nickel chemisorbs hydrogen[1] may be recorded by modifying standard gas adsorption apparatus.

The adsorption apparatus is the familiar purification train, gas buret, manometer, sample chamber, McLeod gage, and vacuum pumps.

Magnetization is determined by adapting an old method: the change of induced e.m.f. in a secondary coil surrounding the sample and energized by a primary solenoid producing about 1000 oersteds.[2] The secondary, of 50 turns, is connected in opposition through a similar, standard coil to a vacuum tube voltmeter. The primary, of 3100 turns, carries 1 ampere at 230 volts stabilized a.c. The output from the voltmeter amplifier circuit is isolated by a 1:1 transformer, then passed through a full-wave rectifier to a recorder.

A 7.66-g. sample of U.O.P. nickel hydrogenation catalyst, containing 52.8% nickel, was reduced for 12 hours at 350°, evacuated 2 hours at 350°, then cooled under vacuum to 25°. Hydrogen was then flushed on to the sample, up to atmospheric pressure. This caused an instantaneous decrease of magnetization, part of which was related to warming of the nickel by the heat of chemisorption. After 10 minutes the sample had cooled to a steady state in which the e.m.f. from the secondary before amplification was 0.40 millivolt less than initially, corresponding to a decrease in magnetization of 11.3%. The corrected volume of hydrogen ad-

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(1) P. W. Selwood, S. Adler and T. R. Phillips, THIS JOURNAL, **77**, 1462 (1955).

(2) S. J. Barnett, *J. Applied Phys.*, **23**, 975 (1952).