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Surface Area of UO_2 Powder
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Abstract

Applicability of the surface-exchange method to determination of surface area of UO_2 powder has been investigated. Preliminary results indicate that the method offers a rapid and easy determination of surface area with a precision of $\sim 10\%$.

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Introduction

There has been considerable interest in developing a rapid method for determination of surface area of uranium-oxide powders which is capable of reasonable accuracy. Probably the most accurate surface determinations have been made by the nitrogen adsorption technique (BET method). However, this method is rather difficult and could require several hours to complete. Since other methods of surface determination also possess more or less serious disadvantages (see Orr and Dalla Valle⁽¹⁾ for a comprehensive review of surface area methods) evaluation of the surface-exchange method was considered desirable.

The only special requirements of the method are availability of a suitable radioisotope tracer and radiation detection equipment. Advantages are the speed and simplicity with which determinations are made (~ 2 hours for four samples). Also the surface area indicated includes the area due to pores and cracks greater than a few atomic diameters in width (5-10 Å).

Principles

The surface-exchange method for determination of surface area has been reviewed by Orr and Dalla Valle⁽¹⁾ and by Wang.⁽²⁾ The method was introduced in 1922 by Paneth and coworkers and has since been used rather extensively by Kolthoff and coworkers and by others.* Surface determinations of barium, strontium, calcium, lead, and thorium salts, chromates, glass, and metals have been made and are generally in fair agreement with results obtained by other methods.

The basis of the method is the heterogeneous exchange reaction between ions on the surface of a solid and ions in solution. If a saturated

*For bibliographies of these papers see References 1 and 2.

solution of a solid whose total surface area is to be determined is tagged with a radioactive, isotopic tracer, the radioactivity of the solution being mixed with the solid decreases with time. The initial fairly rapid decrease is due to an exchange reaction between the tracer atoms (or ions) in solution and the non-radioactive atoms (or ions) in the surface of the solid. After the initial, rapid decrease, the radioactivity of the solution slowly approaches an equilibrium value due to incorporation of the tracer atoms within the solid particles. The amount of radioactivity adsorbed in the initial surface exchange gives a measure of the surface area of the solid adsorbent. The specific surface of the solid is calculated as follows (taken from Wang⁽²⁾):

When surface-exchange equilibrium is established

$$\frac{N'_S}{N_S} = \frac{N'_L}{N_L}$$

or

$$N_S = \frac{N'_S}{N'_L} N_L$$

where N'_L = number of tracer atoms on the surface,

N_S = total number of this species of atoms on the surface,

N'_S = number of tracer atoms in the bulk of the solution,

N_L = total number of this species of atoms in the bulk of solution.

The ratio N'_S/N'_L is determined from the observed counting rates of the tagged solution before and after surface exchange, R_B and R_A respectively.

$$\frac{N'_S}{N'_L} = \frac{R_B - R_A}{R_A}$$

N_L is found by conventional analysis of the exchange solution or by a radio-metric method. If the radioisotope used to tag the exchange solution is incorporated homogeneously into a solid of the same chemical form as the unknown solid (whose surface is to be determined), the tagged solid can be used to saturate the exchange solution and simultaneously to tag it. The total number of tagged atoms in solution (both radioactive and non-radioactive) can then be determined by counting an aliquot of the saturated solution before any exchange occurs and comparing its count rate to that of a weighed quantity of the tagged solid counted under identical conditions. Thus

$$N_L = \frac{W_c N R_B f}{M_c R_c}$$

where W_c = weight of tagged solid taken for comparison,

N = Avagadro's number,

R_B = count rate of aliquot of exchange solution,

f = total volume of exchange solution/volume of aliquot counted,

M_c = molecular weight of tagged solid,

R_c = count rate of tagged solid taken for comparison.

The specific surface S can be obtained from the relation

$$S = \frac{N l^2}{w}$$

where w is the weight of the unknown solid sample and l^2 , the effective area of a tagged atom on the surface, is given by

$$l^2 = \left(\frac{M_u}{a N \rho} \right)^{2/3}$$

Here, M_u = molecular weight of unknown solid,

a = number of gram-atoms of the tagged species of atoms per mole of unknown solid,

ρ = density of unknown solid.

Experimental and Results

Tracer Preparation

For these experiments uranium oxide tagged with U-237 (6.75 day half-life) was prepared by irradiation of uranium oxide in the hydraulic tube facility of the Oak Ridge Research Reactor for ~ 24 hours. The principal nuclear reaction leading to U-237 was $U^{238}(n,2n)U^{237}$ induced by neutrons of energy > 6 Mev. Uranium was separated from fission products and neptunium by the procedure of Moore and Reynolds.⁽³⁾ Three purification cycles yielded ~ 50 mg of uranium oxide whose gamma-ray spectrum was identical to the published spectrum of U-237⁽⁴⁾ and whose specific radioactivity was $\sim 5 \times 10^6$ d min⁻¹ mg⁻¹.

Preparation of Exchange Solution

Solutions 0.001 M in $Na_2P_4O_7$ were saturated with the tagged uranium oxide ($U_3O_8^*$) by stirring or shaking a few milligrams of the oxide with ~ 30 ml portions of sodium pyrophosphate solution for 1-3 hours. The pyrophosphate was used to break up agglomerates of both the $U_3O_8^*$ particles and, more importantly, the uranium oxide particles whose surface area was subsequently to be determined. After the solution was saturated, undissolved $U_3O_8^*$ particles were removed by centrifugation for $\sim 1/2$ hour.

Rate of Exchange

The rate of the exchange reaction between the $U_3O_8^*$ saturated solution and a uranium oxide powder was studied in a few experiments. A typical

experiment is described below. Ten milliliters of the $U_3O_8^*$ saturated solution was stirred with 0.1267 g of the uranium oxide powder in a stirrer-sampler exchange apparatus (see Fig. 1) and, at timed intervals after mixing, samples of the solution were withdrawn and the radioactivity of the 60 kev gamma ray of U-237 determined by means of a scintillation spectrometer. After each sample was counted, it was returned to the exchange vessel before the next sample was taken. To provide a zero-time point as a basis for calculating the fraction exchanged, an aliquot of the original $U_3O_8^*$ saturated solution was counted under the same conditions as the samples from the exchange apparatus. The fraction of $U_3O_8^*$ originally present which had exchanged with the powder (or the fraction adsorbed) at each sampling was plotted versus time of sampling (see Fig. 2). As can be seen from the curve surface exchange was essentially complete in ~ 40 minutes. In other experiments the time required for complete surface exchange was 30-50 minutes.

Surface Area Measurement

In order to determine the precision attainable with the surface-exchange method, the following experiment was performed. Samples of uranium oxide powder were weighed into 50 ml plastic tubes, 10 ml aliquots of the $U_3O_8^*$ saturated solution added, and the tubes stoppered with corks. The tubes were shaken for 1 hour with a wrist-action shaker and then centrifuged for 20 minutes. Two milliliter portions of the clear supernates were taken and their radioactivity (R_A) compared to that of 2 ml aliquots of the original $U_3O_8^*$ (R_B). Data and results of the experiment are given in Table I.

Table I
Surface Area of Uranium Oxide Powder

<u>w</u>	<u>R_B</u>	<u>R_A</u>	<u>S</u>
0.3148	685 c/m	411 c/m	$1.5 \times 10^3 \text{ cm}^2 \text{ g}^{-1}$
0.0484	719	670	1.2×10^3
0.2039	870	691	1.3×10^3
			$(1.3 \pm 0.1) \times 10^3 \text{ Av.}$

Appreciable improvement in precision should be obtained by simple refinements in apparatus and techniques.

Summary

The rate of heterogeneous isotopic exchange between uranium atoms in UO_2 particles and U-237 atoms in a 0.001 M $\text{Na}_2\text{P}_4\text{O}_7$ solution saturated with uranium oxide was investigated. The fraction of U-237 removed from solution was observed initially to increase fairly rapidly and then to approach much more slowly an equilibrium value. The initial rapid adsorption of U-237 (complete in 30-50 minutes) was considered to be due to isotopic exchange between the U-237 atoms in solution and uranium atoms on the surface only of the UO_2 particles. The subsequent, slower adsorption of U-237 was considered to be due to incorporation of the U-237 atoms into the interior of the particles by diffusion and/or recrystallization processes.

Replicate determinations of the fractions exchanged after one hour for samples of UO_2 powder shaken with solutions of 0.001 M $\text{Na}_2\text{P}_4\text{O}_7$ saturated with U-237-tagged uranium oxide gave a precision of $\pm 10\%$. The specific surface area of the samples calculated from the measured fraction exchanged and the known amount of uranium in the saturated solution were 1.5×10^3 ,

1.2×10^3 , and $1.3 \times 10^3 \text{ cm}^2 \text{ g}^{-1}$. The determinations were completed in
~ 2 hours.

Principles of the method have been described and experimental
details given.

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Surface-exchange Method for Determination
of Surface Area of UO_2 Powder

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VACUUM APPLIED TO DRAW
SUPERNATE INTO SAMPLER.
AIR PRESSURE USED TO
RETURN TO EXCHANGE
VESSEL

Figure 1
EXCHANGE VESSEL-SAMPLER

Figure 2
RATE OF SURFACE EXCHANGE