Adsorption of Hexane on Attrition-Milled Silica

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This note describes the initial study conducted by the U. S. Bureau of Mines on the effectiveness of attrition milling in producing high-specific-surface materials that would be effective adsorbents. Silica was selected as the test material, and adsorption of *n*-hexane on the attrition-ground material was compared with adsorption on two commercial silica adsorbents.

The attrition mill, developed and patented (Feld and Clemmons, 1963) by the U. S. Bureau of Mines, is designed to grind a powder slurry containing a grinding medium by intense agitation. The mill is a baffled vessel containing a radial flow, concentrically mounted impeller. It may be operated batchwise or continuously and is presently being used commercially in the paper-coating and paint pigment industries. The effectiveness of attrition-ground materials as adsorbents has not been previously investigated.

The surface area of a solid strongly influences the quantity of gas that can be adsorbed, and thus conventional adsorbents normally are prepared in a form having a large surface area.

Attrition milling offers a new approach to the manufacture of high-surface-area solids for use as adsorbents and has the potential of providing high-surface-area materials that have not been available previously. For example, certain substances that cannot be chemically precipitated to form high-specific-area materials can be milled to a size that achieves the desired surface.

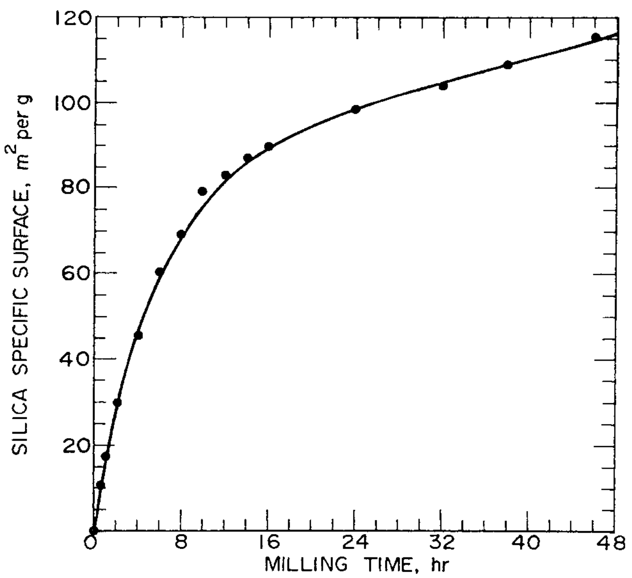

Fig. 1. Relationship of attrition milling time to specific surface area of silica powder.

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EXPERIMENT

High-purity (99+%) minus 400-mesh commercially available silica flour (α-quartz) produced from Ottawa sand was employed for attrition milling. A minus 14- plus 28-mesh Ottawa sand was used as milling medium. The product was compared with commercial (1) silica catalyst carrier (in the form of 1/8-in. extrusions) and (2) silica gel. Using the Brunauer-Emmett-Teller nitrogen adsorption technique, the carrier and gel surface areas were found to be 75.5 m^2/g and 725 m^2/g, respectively. X-ray analysis indicated that the carrier was amorphous silica, while microscopic examination revealed numerous fragmentary diatoms and sponge spicules. Linde dry grade nitrogen was employed as carrier gas for the Fisher 99+% normal hexane.

The volume of the attrition mill, described in detail elsewhere (Stanley et al., 1973), was 2250 cm^3 and it operated at a velocity of 1600 rev./min. A controlled-atmosphere thermogravimetric analyzer (TGA) with an electrobalance was used for adsorption measurements. Hexane was introduced into the gas stream by bubbling the nitrogen carrier gas through a fritted glass sparger submerged in liquid hexane maintained at 0°C.

Attrition-milled silica was prepared by charging the mill with 360 g silica flour, 1100 g Ottawa sand, and 1700 cm^3 water and milling for 46 hours. Small samples of the material were removed periodically, and after drying, surface areas were measured. The milled powder on which hexane measure-

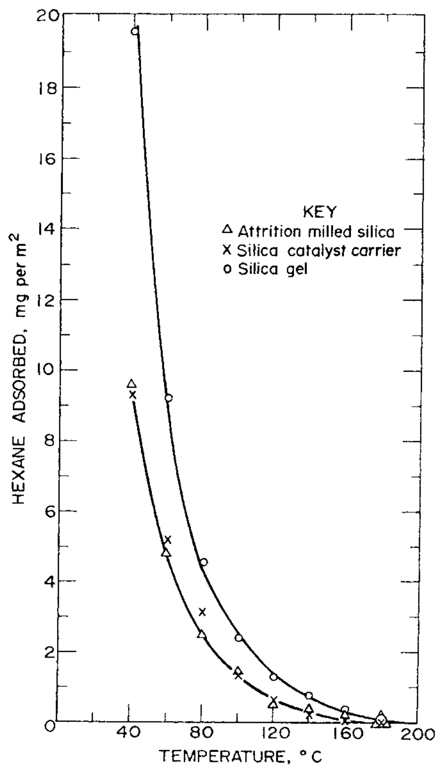

Fig. 2. Comparison of hexane adsorption on three silica materials.

ments were made was leached in concentrated HCl to remove small amounts of iron contamination, washed, and dried. Wet chemical analysis indicated 600 ppm of residual iron. The commercial silica catalyst carrier was tested after being crushed by mortar and pestle to minus 100-mesh powder, while the silica gel was tested as-received.

Nitrogen gas, flowing at 150 cm^3/min, was bypassed around the hexane sparger and connected directly to the atmosphere tube. Fifty-mg silica samples were heated in the TGA at 10°C/min to 500°C, held for 3 hours, cooled to 250°C, and weighed. Nitrogen gas was then passed through the sparger, and the resulting gas mixture (5.9% hexane) was passed over the silica. Gravimetric measurements indicated that the carrier gas was saturated with *n*-hexane at 0°C, at hexane partial pressure of 6.07 kN/m^2. Samples were cooled at a rate of 2°C/min and continuously weighed.

RESULTS

Specific surface measurements for milling times up to 46 hours are presented in Figure 1. In 5 hours of milling, 50 m^2/g specific surface was obtained. The end product (after 46 hours of grinding) had a specific surface of 115.6 m^2/g and was used for hexane adsorption tests.

Figure 2 presents the *n*-hexane adsorption measurements for the three materials investigated. Adsorbent capacities of each are compared on a unit surface basis. The effect of carrier gas flow and cooling rates on the amount of hexane adsorbed was determined by varying these rates as much as 100%. No change in the amount of hexane adsorbed was measured, indicating that equilibrium values were obtained. Attrition-ground and catalyst carrier silica exhibited similar hexane adsorption capacities per unit surface. The silica gel, however, exhibited a significantly higher adsorption capacity than the other two materials, which was attributed to a different concentration of hydroxyl groups on its surface.

CONCLUSION

It has thus been demonstrated that, in addition to chemically precipitated and naturally occurring solid materials, attrition-milled solids have sufficiently large active specific surface to make them suitable for use as adsorbents. It is also quite possible that high surface solids produced by attrition milling would be useful as catalyst and catalyst carrier materials.

LITERATURE CITED

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Effect of Reaction Rate on the Openloop Stability of Chemical Reactors

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The dynamic stability of chemical reactors has been extensively studied in the literature. An entire book has been devoted to the subject (Perlmutter, 1972). The effects of various design parameters, reaction kinetics, and reactor types have been explored.

Some of the most interesting dynamics and control problems have been shown to occur when exothermic, irreversible reactions produce the potential for openloop instability. For continuous stirred-tank reactors (CSTR), instability at a given operating level can be detected by observing the location of the roots of the characteristic equation of linearized system.

Most stability studies of CSTR's have used specific numerical examples where kinetic parameters (specific reaction rate k and activation energy E) are specified. The effects of design parameters such as heat transfer area A and coefficient U, operating temperature T, holdup volume V, throughput F, etc. have then been explored.

In some industrial reactors, the effective specific reaction rate k can be varied by operating parameters other than temperature. For example, the effective k can be changed by catalyst addition rate or by the levels of impurities in feed and recycle streams. Thus a given reactor, with fixed heat transfer area A, coefficient U, running at a constant temperature T, throughput F, and reactor volume V, can be operated with difference specific reaction rates k.

In a recent study of such a situation in an industrial reactor, some interesting results were observed. These observations are in hindsight perhaps obvious, but initially they were unexpected and surprising.

The reactor was observed to become unstable as the specific reaction rate k was reduced. With further reduc-