

Surface Properties of Silver Iodide

It is a rather curious fact that both low-energy and high-energy surfaces abound, but intermediate energy surfaces of high area are infrequently found and have been little studied. In a search of such intermediates, we recently examined the surface chemistry of silver iodide. One method is to compare the apparent water specific surface area to the nitrogen area. Another result which reflects the surface energy is the measurement of the heat of immersion in water and other liquids of particles of the solid sufficiently high in surface area to give meaningful results.

Interest in the surface chemistry of silver iodide increases when one comes to recognize that silver iodide is regarded as hydrophobic¹ in classical colloid chemistry but as hydrophilic in cloud physics^{2,3}. When the double layer on silver iodide sols is repressed or destroyed, the colloid chemist finds that the particles flocculate quickly and settle out. Yet this result may be due only to gravity and might have nothing to do with any hydrophobic character. Previous results on the water vapour adsorption on silver iodide are quite contrary. Birstein³ claims some 130 layers of water are adsorbed before P_0 is reached. It can be categorically stated that such a reported result is novel. Solids adsorb at most 5–10 nominal layers before condensation is reached, as Harkins⁴ showed years ago. In a recent paper, Dubinin *et al.*⁵ also concluded that the silver iodide surface is hydrophilic and that it accepts about 3 layers before the condensation pressure.

The cloud physicists regard silver iodide as the best 'cloud seeder' yet found presumably because its crystal parameters closely correspond to those of ice. Observations of the nucleation and growth of ice crystals on single silver iodide crystals (colour motion pictures taken by Prof. B. J. Mason, Imperial College, London) cast doubt on the concept of epitaxy. For one thing, the ice crystals preferentially form at steps in the silver iodide crystal face where epitaxy cannot exist in all directions. For another, the hexagonal pattern does not appear until the growing ice crystal has gained some size. Finally, many ice crystals are formed on a single silver iodide crystal so that the epitaxy does not extend over the entire face as in the usual case.

Some doubt was cast on the other direct measurements of the hydrophilic character of silver iodide by Halsey⁷ in a brief note on the matter. He concluded that ice and silver iodide surfaces are energetically incompatible although he was not considering cloud seeding at the time. He was freezing xenon on to various crystals to attempt to produce energetically uniform adsorbent surfaces.

Recent work in this Laboratory supports the contention that the silver iodide surface is rather hydrophobic. For one preparation, the value of the ratio of the Brunauer–Emmett–Teller areas for water to nitrogen surface area measurements were: $\Sigma H_2O / \Sigma N_2 = 7/100$, for another, $\Sigma H_2O / \Sigma Ar = 37/100$. For still another, $\Sigma H_2O / \Sigma N_2 = 27/100$. These results compare with the $\Sigma H_2O / \Sigma N_2 = 1/1,500$ obtained⁸ for the almost completely hydrophobic graphitized carbon black, 'Graphon'.

Further work is in progress to try to establish the surface characteristics of silver iodide. For this purpose, high surface area samples in sizeable quantity are desired. These are difficult to prepare, and then to outgas without severe sintering⁷.

Our present hypothesis is that the steps in the silver iodide surface possess hydrophilic, possibly oxide, sites. On these the water molecules first adsorb in clusters much as on 'Graphon' or graphites. Eventually, when the nucleation process is carried out at low temperatures, the ice crystal structure develops.

It seems reasonable to suspect higher sticking coefficient for the water on to earlier adsorbed molecules if they are not highly organized and 'busy' interacting strongly with the substrate. This situation would probably prevail if water molecules could be adsorbed all over the surface as on an oxide. This possible explanation of the efficacy of silver iodide is strengthened by the recent work of Eyring⁹ on the sticking coefficient of many atoms and molecules on a number of surfaces. He finds that the more ordered the molecules are in the surface, the lower is the sticking coefficient. The molecules do not want to pay the 'entropy price' and thus more of them rebound.

Possibly clays are good seeders because of the ion exchange sites which also build up water clusters; and proteins, reported by Vincent Schaefer to have excellent cloud seeding properties, are effective because of the separated polar sites at which water clusters can develop.

We wish to thank the National Science Foundation for a grant in support of this work.

A. C. ZETTEMAYER
NOUBAR TCHEUREKDJIAN
J. J. CHESSICK

Surface Chemistry Laboratory,
Lehigh University,
Bethlehem, Pennsylvania.

¹ Overbeek, J. Th. G., in *Colloid Science*, edit. by Kruyt, H. R., 1 (Elsevier Pub. Co., Amsterdam, 1952).

² Mason, B. J., *The Physics of Clouds* (Oxford Univ. Press, London, 1957).

³ Birstein, S. J., *J. Meteorol.*, **12**, 324 (1955).

⁴ Harkins, W. D., *The Physical Chemistry of Surface Films*, Chap. 3 (Rheinhold Pub. Corp., 1952).

⁵ Moskvitin, N. N., Dubinin, M. M., and Sarakhov, A. I., *Izvest. Akad. Nauk. S.S.R., Otdel. Khim. Nauk*, **12**, 2080 (1959).

⁶ Vonnegut, B., *J. App. Phys.*, **18**, 593 (1947).

⁷ Karasz, F. H., Champion, W. M., and Halsey, jun., A. D., *J. Phys. Chem.*, **60**, 376 (1956).

⁸ Young, G. J., Chessick, J. J., Healy, F. H., and Zettlemoyer, A. C. *J. Phys. Chem.*, **58**, 313 (1954).

⁹ Eyring, H., and Wanlass, F. M., *Abstr. Papers, Div. Colloid and Surface Chem. Amer. Chem. Soc.* (St. Louis, Missouri, March 1961).

Production of 'Active' Magnesium Oxide by heating in Vacuum

WHEN samples of precipitated magnesium hydroxide were heated in air for a fixed period of 2 hr. at a succession of temperatures (T° C.) Gregg and Packer¹ found that the specific surface area S (determined by the Brunauer–Emmett–Teller method with nitrogen at -183° C.) when plotted against T gave the curve I reproduced in Fig. 1.

Conducting a similar experiment with starting material similarly prepared and having a similar specific surface ($60 \text{ m}^2 \text{ gm}^{-1}$ as compared with $56 \text{ m}^2 \text{ gm}^{-1}$), but heating *in vacuo*, we obtained curve II of Fig. 1: the temperature at which the maximal area was obtained has been lowered from c. 390° C. to c. 300° C. and the maximal area has been raised from $190 \text{ m}^2 \text{ gm}^{-1}$ to $340 \text{ m}^2 \text{ gm}^{-1}$, which is unusually high for 'active' magnesium oxide.

This effect of heating in air as compared with vacuum is qualitatively similar to that reported by Razouk and Mikhail² working with the mineral brucite, but their areas were considerably lower, and the

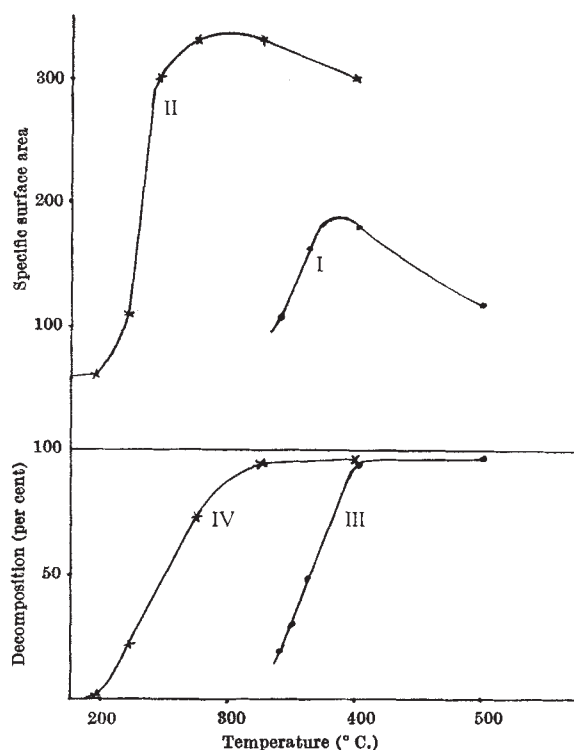


Fig. 1. Calcination of magnesium hydroxide in air (curves I and III, see ref. 1) and *in vacuo* (curves II and IV, present work)

maximum was situated at a higher temperature (air, maximal area, 37 m.² gm.⁻¹, at 500° C.; vacuum, maximal area, 124 m.² gm.⁻¹, at 350° C.). This is possibly due to the larger crystallite size of the mineral brucite as compared with precipitated magnesium hydroxide.

An explanation of the superior 'activating' effect of heating in vacuum must await the results of experiments now in progress in this laboratory, but it is probably connected with the higher rate of decomposition *in vacuo*, and the reduction in sintering because of the lower temperature required for nearly complete decomposition (see curves III and IV).

R. VALVERDE
J. P. SÁENZ

Facultad de Química,
General Flores 2124,
Montevideo, Uruguay.

¹ Gregg, S. J., and Packer, R. K., *J. Chem. Soc.*, 51 (1955).

² Razouk, E. I., and Mikhail, R. Sh., *J. Phys. Chem.*, 61, 888 (1957).

Catalytic Decomposition of Ethylene on Nickel

THE mechanism of the hydrogenation of ethylene on nickel has been studied intensively for at least thirty years; but there is still little agreement as to the exact nature of the intermediates present on the metal surface during the reaction. On the other hand, examination of the chemisorption and dissociation of ethylene on nickel in the absence of gaseous hydrogen has been slight and mostly confined to ambient temperatures^{1,2}. This is surprising as the products and mechanism of ethylene dissociation can play an important part in hydrogenation, exchange and other reactions.

The decomposition of ethylene on nickel has been studied as a function of temperature in the range -30° C. to 200° C. 14.8 gm. of high-purity carbonyl nickel were loosely pressed into pellets $\frac{1}{4}$ in. in diameter, reduced in a stream of hydrogen at 400° C. for 6 hr. and then evacuated at 400° C. for 12 hr. to a residual pressure of 1×10^{-6} mm. Experiment showed that no hydrogen remained on the metal after this treatment. 6 mm. of purified ethylene were then allowed to stand over the catalyst for a period of 4 hr. at each of the temperatures studied, the volume of the system being about 130 c.c. At the end of this period, the contents of the gas phase were condensed in a trap cooled in liquid nitrogen. The non-condensable pressure was found to be due to methane. The contents of the trap were analysed with a gas-chromatograph, using helium as carrier gas and a silica gel column. The results are shown in Fig. 1, in which the composition of the gas phase is plotted against the temperature of the catalyst.

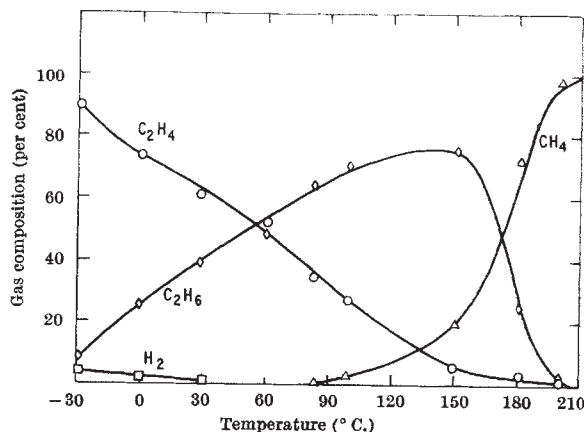
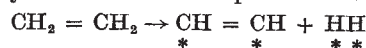


Fig. 1. Temperature-dependence of the products of reaction of ethylene (6 mm. pressure) with nickel after 4 hr. Gas concentrations: O, C₂H₄; ◇, C₂H₆; △, CH₄; □, H₂

At temperatures below 60° C., the products are ethane and hydrogen, obtained by self-hydrogenation of the ethylene. This effect has been studied at 20° C. by Rideal and Jenkins¹, who suggest that ethylene in the gas phase reacts with chemisorbed hydrogen, obtained by dissociative adsorption of ethylene:



The self-hydrogenation of ethylene was further studied by Beeck³, who states that at -39° C. no ethane was produced. In the present work, however, appreciable quantities of ethane were found after reaction at -30° C. and the rate of self-hydrogenation was found to be measurable down to -78° C. The quantity of hydrogen evolved on self-hydrogenation was always small and less than 5 per cent of the ethane produced. No C₃, higher hydrocarbons or polymerization products were detected at low temperatures; this result is at variance with that of Morikawa *et al.*⁴, who found 29 per cent butane among the products at 0° C. Above 60° C., methane began to appear in the gas phase due to the cracking of ethylene and ethane present; the concentration of the latter decreased rapidly above 150° C. and, at 200° C., the gas phase consisted entirely of methane.

The overall composition of the adsorbed residues on the surface can be calculated in the form (CH_n)_x, as shown in Fig. 2. At 0° C., these residues have an