

tribution curves showing fraction of reduced nickel *versus* particle size. These curves show that nickel-kieselguhr catalyst as reduced at, say, 360° for ten hours, possesses few nickel particles in excess of 50 Å. on a side, but many particles ranging from 10 to 50 Å. The distribution of particle sizes is altered by time and temperature of reduction, nature of support, proportion of total nickel, and so forth.

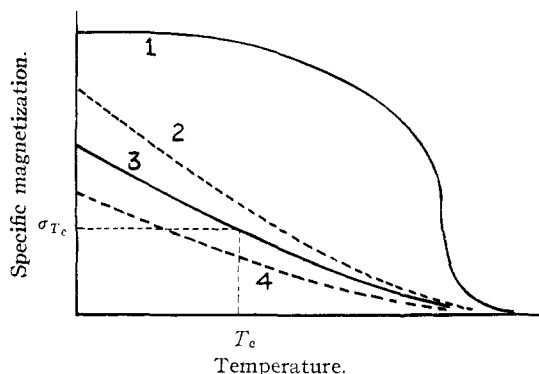


Fig. 1.—Thermomagnetic curves for (1) massive nickel, (2) reduced nickel-silica catalyst with chemisorbed nitrogen, (3) reduced nickel-silica catalyst in helium or vacuum, and (4) reduced nickel-silica catalyst with chemisorbed hydrogen.

The interesting feature of these results is that particle sizes in the 10–50 Å. range possess such a large ratio of surface to volume that chemisorbed gases are able to modify the magnetic moment of the nickel. If nickel possesses 0.6 electron hole per atom in the d-band, then a particle about 20 Å. on a side would lose all its ferromagnetism if covered with a monolayer of hydrogen molecules each of which donates one electron to the nickel particle.

We have found that adsorbed hydrogen on a nickel-silica catalyst reduces the specific magnetization of the nickel by about 20%. Ethylene has a similar effect. The temperatures at which adsorption and desorption take place are indicated with considerable precision. Nitrogen and oxygen which are chemisorbed, presumably, by abstraction of electrons from the catalyst particle, give an increase of magnetization.

Benzene, in the temperature range so far investigated, namely 100°, is almost without effect. A mixture of benzene and hydrogen at 100° gives only the decrease of magnetization due to hydrogen alone. This suggests that the hydrogenation of benzene does not necessarily involve chemisorption of the benzene and that, at least for this reaction, the Balandin geometric factor is without significance.

The method may readily be extended to other reacting systems, *in situ*, and may, in general, be expected to yield information concerning the electronic state of catalytically active systems involving ferromagnetic substances under a variety

of temperature and pressure conditions approximating those used in actual catalytic practice.

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#### FRIEDEL-CRAFTS ACYLATIONS OF PHENYLSILANES<sup>1</sup>

Sir:

We wish to report the first successful Friedel-Crafts acylation reaction carried out with a phenylsilane. In previous attempts to acylate phenylsilanes it was found that aryl-silicon bonds were easily cleaved when aluminum chloride catalyst was employed<sup>2</sup> and this cleavage has been generally attributed to the acidic nature of the catalyst. A careful consideration of the probable mechanism of the cleavage of aryl-silicon bonds has led us to the conclusion that the above-mentioned cleavage reaction depends not only on the acidity of the acylation catalyst but also on the nucleophilicity of the anion produced during the reaction, and after considerable experimentation with various acylation procedures we were able to acetylate and to benzoylate trimethylphenylsilane.

Thus, when trimethylphenylsilane, 40 g., was stirred for five hours with a mixture of 32 g. of acetyl fluoride in 150 cc. of chloroform saturated with boron trifluoride, there was obtained upon working up of the reaction mixture 12 g. of the starting material and approximately 10 g. (*ca.* 35%) of high boiling product, b.p. 80–100° (3 mm.), which gave the solid trimethylsilylacetophenone, m.p. 40–41° (*Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>OSi: C, 68.72; H, 8.39. Found: C, 69.12; H, 8.25). The 2,4-dinitrophenylhydrazone was prepared in the usual way, m.p. 194–195° (*Anal.* Calcd. for C<sub>17</sub>H<sub>20</sub>O<sub>4</sub>N<sub>4</sub>Si: C, 54.83; H, 5.41; N, 15.05. Found: C, 54.84; H, 4.95; N, 14.68). Similarly, the reaction of trimethylphenylsilane with benzoyl fluoride in the presence of boron trifluoride gave trimethylsilylbenzophenone, m.p. 64° (*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>OSi: C, 75.55; H, 7.13. Found: C, 75.86; H, 7.23) from which the corresponding 2,4-dinitrophenylhydrazone, m.p. 211–213° (*Anal.* Calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub>N<sub>4</sub>Si: C, 60.80; H, 5.11; N, 12.89. Found: C, 61.03, H, 5.23, N, 12.46) was prepared.

The experimental details of the above acylations, the proof of the positions of the substitution, and the experiments employing other acidic catalysts, will be described in a forthcoming publication.

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(2) W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2774 (1931), and references cited by R. A. Benkeser and H. R. Krysiak [*This Journal*, **76**, 599 (1954)].