

higher concentration than some acetate, radicals might be lost by such a reaction.<sup>15</sup> This should affect the calculation of the  $k_2/k_1$  based on the amount of  $\text{CH}_4$  formed, making it apparently larger, but it would leave approximately unchanged the  $k_2/k_1$  based on the  $\text{CH}_4/\text{CO}_2$  ratio. The results presented in Table IV may be accounted for in this way.

We are indebted to the referee for drawing our  
(15) H. J. Shine and J. R. Slagle, *THIS JOURNAL*, **81**, 6309 (1959).

attention to the paper presented in Cleveland by J. C. Martin at the recent (April, 1960) meeting of A.C.S. This worker claims that cyclohexene reacts *directly* with acetyl peroxide giving the corresponding cyclohexyl acetate radical. The finding of Shine and Slagle<sup>15</sup> therefore could be accounted for in an alternative way. We feel, however, that the problem of acetate radicals addition needs further studies and we intend to look closer into this reaction.

[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, BALTIMORE, MARYLAND]

## Adsorption Studies on Raney Nickel

BY R. J. KOKES AND P. H. EMMETT

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Chemisorption measurements at  $-195^\circ$  for carbon monoxide on a W-6 Raney nickel catalyst degassed at  $400^\circ$  indicate that the catalyst surface consists of 20% metal and 80% non-metal. The adsorption of hydrogen on such a sample in the range  $-78$  to  $0^\circ$  is in agreement with this interpretation. The average pore diameter of the Raney nickel catalyst was found to be 84 Å.

Raney nickel catalysts are used extensively for the hydrogenation of organic compounds. The high surface areas of these catalysts (50 to 120  $\text{m}^2/\text{g}.$ )<sup>1-3</sup> and their relatively high resistance to sintering suggests that alumina and possibly alkali retained in the activation process may be stabilizing the structure by acting as promoters. To obtain some idea as to the fraction of the surface that might be covered with these promoters,<sup>4</sup> we have now measured the chemisorption of carbon monoxide at  $-195^\circ$  and the chemisorption of carbon dioxide at  $-78^\circ$ . We also obtained an approximate value for the adsorption of hydrogen on a sample degassed at  $400^\circ$ . These results together with pore size measurements are being reported in the present note.

### Experimental

The two samples used in the present studies were obtained from a batch of W-6 catalysts<sup>5</sup> prepared by the modification used by Smith and co-workers<sup>6</sup> and stored under distilled water for about 10 months prior to use.

The adsorption studies were carried out on a standard BET apparatus.<sup>7</sup> All gas was purified in a manner consistent with common practice. Samples were cooled to  $-195^\circ$  in the presence of helium and corrections for departure from ideality were made. The extrapolated liquid vapor pressure was used for  $P_0$  in the isotherms with carbon dioxide.

### Results

Adsorption isotherms with carbon monoxide and nitrogen were obtained at  $-195^\circ$ ; those with carbon dioxide were obtained at  $-78^\circ$ . Amounts of chemisorption were estimated in the traditional fashion<sup>4</sup> by determining the physical plus chemical adsorption at the standard temperatures indi-

cated above, warming the sample to a higher temperature ( $-78^\circ$  for nitrogen and carbon monoxide,  $25^\circ$  for carbon dioxide), evacuating for 1 hr. and then redetermining the amount of adsorption, presumably all physical, at the standard temperature.

To identify the various isotherms the following nomenclature has been adopted: CO(T) refers to carbon monoxide adsorption (at  $-195^\circ$ ) on the clean catalyst; CO(P) refers to adsorption at  $-195^\circ$  (presumably physical) on a catalyst which had been exposed to carbon monoxide at  $-195^\circ$  and evacuated for 1 hr. at  $-78^\circ$ ; N(OT) refers to nitrogen adsorption on top of a layer of chemisorbed carbon monoxide, *i.e.*, on a catalyst exposed to carbon monoxide at  $-195^\circ$  and evacuated 1 hr. at  $-78^\circ$ . The symbols  $\text{CO}_2(\text{T})$  and  $\text{CO}_2(\text{P})$  have the same significance, *mutatis mutandis*.

TABLE I  
ADSORPTION ON DEGASSED W-6<sup>a</sup> CATALYST

	Sample A (cc./g.)	Sample B (cc./g.)
$V_m \text{ N(T)}$	19.7	21
$V_m \text{ N(P)}$	19.7	..
$V_m \text{ N(OT)}$	19.5	19.1
$V_m \text{ CO}_2(\text{T})$	..	18.4
$V_m \text{ CO}_2(\text{P})$	..	18.4
$V_m (\text{CO})\text{T}^c$	24.2	25.4
$V_m (\text{CO})\text{P}$	20.8	21
Carbon monoxide chemisorp- tion CO(T) - N(OT)	4.7 (19%) <sup>b</sup>	6.3 (24%) <sup>b</sup>

<sup>a</sup> See text for definitions. <sup>b</sup> These figures are the calculated % coverage of the catalyst with chemisorbed carbon monoxide provided the value to the left is a valid measure of chemisorbed carbon monoxide and this has a cross sectional area of 13 Å.<sup>2</sup> per molecule. This method for estimation has been used since part of the chemically adsorbed carbon monoxide may be removed by evacuation at  $-78^\circ$ .<sup>8</sup>  
<sup>c</sup> This is the amount of carbon monoxide adsorbed at the  $P/P_0$  value corresponding to  $V_m \text{ N(OT)}$ .

- (1) G. W. Watt, *THIS JOURNAL*, **73**, 5791 (1951).
- (2) H. A. Smith, W. C. Bedoit and J. F. Fuzek, *ibid.*, **71**, 3769 (1949).
- (3) R. J. Kokes and P. H. Emmett, *ibid.*, **81**, 5032 (1959).
- (4) P. H. Emmett and S. Brunauer, *ibid.*, **59**, 310, 1553 (1937).
- (5) H. Adkins and H. Billica, *ibid.*, **70**, 695 (1948).
- (6) H. A. Smith, A. J. Chadwell and S. S. Kirdis, *J. Phys. Chem.*, **59**, 820 (1955).
- (7) P. H. Emmett, "Catalysis," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, Chapter 2.

- (8) R. J. Kokes and P. H. Emmett, *THIS JOURNAL*, **82**, 1037 (1960).

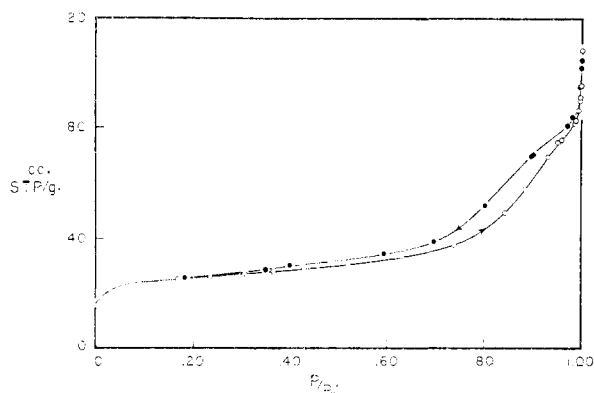


Fig. 1.—Nitrogen isotherm on a degassed W-6 catalyst (0.174 g.): O, adsorption; ●, desorption.

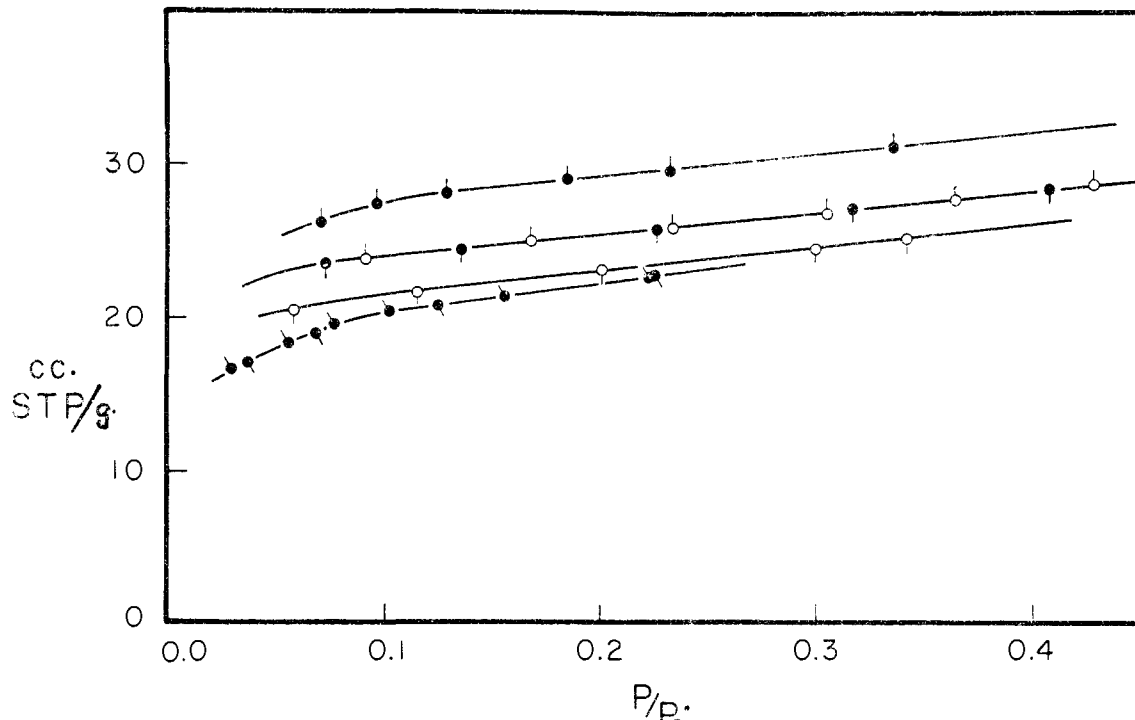


Fig. 2.—Adsorption isotherms on a degassed W-6 catalyst (0.174 g.): ●, CO<sub>2</sub>(T); ●, CO(T); ○, N(T); ●, CO<sub>2</sub>(P); ○, CO(P); ⊙, N(OT). See text for definitions.

Sample A (3.8 g.) of the Raney nickel catalysts was evacuated at 400° for an hour following a few adsorption experiments on hydrogen. The adsorptions of nitrogen and carbon monoxide were measured at -195° as outlined above. The results expressed in terms of the values of  $V_m$  as calculated from B.E.T. plots are shown in Table I.

Sample B (0.174 g.) was a small sample of the Raney catalyst used for the nitrogen isotherms needed for pore size calculations (Fig. 1) and for a redetermination of adsorption data for nitrogen and carbon monoxide at -195°. It also was employed for the measurements of carbon dioxide chemisorption at -78°. The results on a per gram basis are shown in Table I and Fig. 2.

No detailed study of the adsorption of hydrogen on the samples was made though an isobar was run at 1 atmosphere pressure between -78 and

400°. Sample A, evacuated at 400°, showed an adsorption maximum of about 4.5 cc. per gram at a temperature of about 100°.

### Discussion

The value for the chemisorption of carbon monoxide as shown in Table I suggests that about 20% of the surface of the Raney nickel catalyst consists of metallic nickel. As pointed out in the footnote in this table the estimate is based on the assumption that the difference between the value for the total carbon monoxide adsorption at -195° [CO(T)] and the physical adsorption of nitrogen on a surface saturated with chemisorbed carbon monoxide [N(OT)] is equal to the chemisorption of carbon monoxide and that each chemisorbed molecule of carbon monoxide occupies an area of

13 Å.<sup>2</sup> units. The reason for using N(OT) rather than N(T) or CO(P) in this calculation has already been discussed.<sup>8</sup>

The adsorption values for hydrogen are consistent with chemisorption values of 4.7 and 6.3 cc. per gram for carbon monoxide because the ratio of chemisorption of hydrogen to chemisorption of carbon monoxide is in the usual range of 0.5 to 1.0.<sup>9</sup>

Carbon dioxide chemisorption was used successfully to estimate the amount of alkali promoter on the surface of iron synthetic ammonia catalysts.<sup>4</sup> Its chemisorption on nickel catalysts has been found very extensive provided alkali was used in the preparation of the catalyst.<sup>8,10</sup> It was, therefore, surprising to find a complete ab-

(9) S. C. A. Schuit and L. L. van Reijen, "Advances in Catalysis," Vol. X, 242 (1958).

(10) P. H. Emmett and N. Skau, *THIS JOURNAL*, 65, 1029 (1943).

sence of chemisorption of carbon dioxide at  $-78^\circ$  on sample B of the Raney nickel since in preparing the catalyst a sodium hydroxide solution was used for leaching the aluminum from the nickel-aluminum alloy taken as starting material. No explanation for the absence of carbon dioxide chemisorption can be given until further work is done.

The adsorption isotherms for nitrogen in Fig. 1 enable one to estimate the average pore size to have a value of about 84 Å. in diameter. This is

based on the usual equation  $d = 4V/A$  where  $d$  is the diameter in centimeters,  $V$  is the pore volume and  $A$  is a surface area in square centimeters.

In summary, the data suggest that Raney nickel is a porous catalyst and that only about 20% of its surface is metallic. The remainder is non-metallic and probably consists largely of alumina formed during the leaching process by which the catalysts are prepared.

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## Radiation Chemistry of Polydimethylsiloxane.<sup>1</sup> II. Effects of Additives

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The electron-irradiation of polydimethylsiloxane oil  $[-\text{Si}(\text{CH}_3)_2\text{O}]_n$  in the presence of several additives was studied. Oxygen decreases the crosslinking yield from the normal value of  $G = 3$  to a limiting minimum value of  $G = 1$ , and it is concluded that these "residual" crosslinks are not peroxide ( $-\text{O}-\text{O}-$ ) bonds. Reactive hydrogen transfer agents, such as mercaptans, are more effective than aromatic free-radical inhibitors (e.g., di-*t*-butyl-*p*-cresol, quinone) in retarding the crosslinking. The use of 10% mercaptan allows a direct measurement of primary  $>\text{Si}-\text{CH}_3$  scissions and the yield for these is  $G = 4$ , only slightly dependent on temperature between  $-40$  and  $+100^\circ$ . The yield of  $>\text{SiOH}$  end-groups formed by irradiation in the presence of 10% mercaptan indicates that, compared to crosslinking, radiation-induced free-radical scission of the siloxane backbone is negligible. The effects of  $\text{H}_2$ , diethyl disulfide, benzene and tetralin on the radiation-crosslinking of polydimethylsiloxane also are described.

### Introduction

The preceding paper<sup>2</sup> has described the electron-irradiation of polydimethylsiloxane  $[-\text{Si}(\text{CH}_3)_2\text{O}]_n$  with emphasis on the gas and crosslinking yields as a function of temperature and radiation intensity. In the present paper, the effects of several additives:  $\text{O}_2$ ,  $\text{H}_2$ , aromatic free-radical inhibitors, mercaptans and a disulfide, and benzene and tetralin at solvent concentrations will be considered.

### Experimental

The silicone oil (30,000 c.s. viscosity), irradiation procedures and gel measurements were described in the previous paper.<sup>2</sup> A gel yield *vs.* irradiation dose curve was determined for this oil at  $25^\circ$  and an irradiation intensity of 14 Mr./min. For these conditions the radiation crosslinking yield is  $G(\text{c.l.}) = 3/100$  e.v. In the present work, the effect of additives on the crosslinking was determined by measuring the gel yield for a given irradiation dose,  $D$ , and converting this gel yield to the relative crosslinking yield by means of the standard gel *vs.* dose curve (ref. 2, Fig. 1). For example, a 10 Mr. dose in the pure silicone oil gave a gel yield of 80%. If, in the presence of additive, the same dose gave a gel yield of only 53%, this corresponds to an "equivalent dose,"  $D'$ , of 5 Mr., and it can be concluded that with the additive the relative crosslinking yield is 0.5 and, therefore,  $G(\text{c.l.}) = 1.5/100$  e.v.

For irradiations under elevated pressures of gas ( $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ ) a special pressure cell was used. The cell window was of 2-mil stainless steel backed by a honeycomb grid of  $1/4$ " steel with  $1/4$ " diameter holes. The cell was sealed by flange and a neoprene O-ring gasket, which was shielded from the radiation. The gas pressures were measured by a Bourdon gage. Weighed samples of the silicone oil in an aluminum irradiation dish were equilibrated with the gas at the desired pressure for 30 minutes, although this was probably much longer than required for the attainment of gas solubility equilibrium in the 1 mm. thickness of oil. As usual, all irradiations were done in the same geometry with respect to the electron-beam. The dosimetry for the

cell was established from the gel yields for irradiations in the cell under 1 atmosphere of pure nitrogen.

The inhibitor-type additives (phenols and quinones) were purified by recrystallization from petroleum ether, followed by vacuum-drying. These were dissolved directly in the silicone oil, forming homogeneous solutions, before irradiation. The mercaptan additives were used without purification: *n*-butyl mercaptan and di-ethyl disulfide (Eastman) and dodecyl mercaptan (Delta Chemical Company).

In some cases irradiated products were analyzed by differential infrared absorption. The calibration for  $>\text{SiOH}$  absorption at  $2.72\mu$  was made using known amounts of trimethylsilanol,  $(\text{CH}_3)_3\text{SiOH}$ , in a 10% solution of the silicone oil in  $\text{CCl}_4$  solvent. A linear correspondence between the  $2.72\mu$  differential absorbance and amount of added silanol was obtained. The resulting absorption coefficient for  $>\text{SiOH}$  was  $1.1 \times 10^5$  cm.<sup>2</sup>/mole. The infrared analysis for  $>\text{SiH}$  groups was described in the experimental part of the preceding paper.

### Results and Discussion

**Effect of Oxygen.**—Figure 1 shows the relative crosslinking yields, from gel measurements, normalized to the yield under nitrogen at 1 atmosphere, as a function of oxygen and nitrogen pressures. The slight decrease in the crosslinking with  $\text{N}_2$  pressure may be attributed to an increasing absorption of the radiation by the 1-cm. thickness of gas above the polymer sample. Under oxygen pressure, the crosslinking yield decreases rapidly and attains a limiting minimum value at about 35% of the nitrogen control, corresponding to  $G(\text{crosslink}) \approx 1.0$ . This limiting value above 150 p.s.i. oxygen, together with the observation that in this region, irradiations at 0.1 and 0.05-fold lower dose rates gave no further reduction in gel yield, show that this is a true limiting value and is not determined by the  $\text{O}_2$  concentration or the diffusion rate of  $\text{O}_2$  into the sample. It was established, also, that this "residual" crosslinking was not a post-irradiation effect since the same residual gel yield was obtained by irradiation under 200 p.s.i.  $\text{O}_2$  whether the samples were extracted immediately, stored at room

(1) Presented, in part, at a Symposium on Chemical Effects of High Energy Radiation, A.A.A.S. Meeting, Washington, D. C., Dec. 26-31, 1958.

(2) A. A. Miller, *THIS JOURNAL*, **82**, 3519 (1960).