SEMI-ANNUAL REPORT

Interaction of Hydrogen Chloride with Alumina

by

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A. INTRODUCTION

Research prior to December, 1975 has primarily concentrated on an investigation of the adsorption behavior of two aluminas, Alon-C (gamma form) and A16SG (alpha form). The influence of outgas conditions and temperature on the adsorptive properties of these two aluminas have been studied using adsorption isotherm measurements. Alon-C and A16SG have been characterized using X-ray powder diffraction, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and BET nitrogen surface areas. Some of these techniques were applied to two other aluminas but no isotherm data has been obtained. Studies using transmission infrared spectroscopy are now beginning. Table I summarizes the isotherm data and techniques applied to each alumina.

B. CHARACTERIZATION TECHNIQUES

1. Alon-C

Alon-C, a high surface area alumina was obtained from Cabot Co., Boston, Mass. It is a fumed alumina made by the hydrolysis of aluminum chloride in a flame process, similar to that described by Fricke and Jockers[1]. An X-ray powder diffraction exhibited diffraction lines at 1.98 and 1.39 kX characteristic of γ-Al_2O_3. The BET surface of 93.5 $\pm$ 0.5 m^2/g for Alon-C was determined by low temperature nitrogen adsorption. Thermogravimetric analysis (TGA) of Alon-C, because of a lack of sensitivity, did not show water loss from the Alon.

Scanning electron micrographs were obtained of Alon-C before and after exposure to 20 torr of hydrogen chloride. Micrographs at 5000 X magnification show the effect hydrogen chloride has on the texture of the alumina. The degree of roughness of the alumina decreases after HCl exposure.

2. <u>Al6SG</u>

An X-ray powder pattern of Al6SG showed lines characteristic of an alpha alumina. The BET surface area of Al6SG is 8.16 $\pm$ 0.2 m^2/g. SEM experiments on Al6SG, showed the particle size to be larger than that of Alon-C, however, the two aluminas have similar texture. Again a significant change is seen in the surface roughness of the alumina after exposure to 20 torr of hydrogen chloride. Thermogravimetric analysis of Al6SG, like that of Alon-C showed no weight loss due to water desorption.

3. <u>Other Aluminas</u>

Two gamma aluminas were prepared by heating two different aluminum trihydroxides obtained from Alcoa. The γ-alumina prepared by heating Alcoa's C-31 coarse at 600°C for 6 hrs. show the same two X-ray diffraction lines as Alon-C. A BET N_2 surface area of this preparation was taken. No other characterization techniques have been performed on the alumina.

No X-ray powder pattern was obtained on a sample of Hydral 710, an aluminum trihydroxide, after the heat treatment to transform it to a γ-alumina. Because of its small particle size less than 2 microns, it does not easily undergo transition to the γ-form. BET surface areas obtained before and after the heat treatment were markedly different. Hydral 710 had a surface area of 3.75 m^2/g and Hydral 710 after heating at 600°C for 6 hours showed an increase to 170.2 m^2/g.

C. ISOTHERM MEASUREMENTS

1. Experimental

Adsorption measurements were made manometrically in a constant volume apparatus with a base pressure of 10^{-5} - 10^{-6} torr. Prior to adsorption, the alumina sample was dried in situ under vacuum for a few hours at varying temperatures. The HCl gas was of reagent grade, and the pressure of the test gas (HCl or H_2O vapor) was varied to develop an isotherm.

2. H_2O/Alon-C

Adsorption of H_2O on Alon-C was used as a criteria to study the reproducibility of the alumina surface as a function of outgas temperature and the time of outgassing. No time dependence was found, but the temperature of the pretreatment was critical in defining the adsorption capacity of Alon-C for H_2O.

Isotherms of H_2O on Alon-C were taken after outgassing at 80^0 and 400^0, the 400^0 outgassed sample adsorbing significantly more water. Desorption experiments show the isotherm to be reversible. Comparison of the H_2O surface area obtained at these outgas temperatures and the N_2 BET surface areas gives an indication of the degree of hydrophilicity of the Alon-C surface. 100% reversibility was found for the H_2O adsorption at 40^0 and 50^0.

3. H_2O/A16SG

Adsorption of water vapor on the α-alumina (A16SG) was found to be sensitive to the outgas temperature. 40^0 isotherms taken at a series of outgas temperatures from 80^0 - 750^0C showed successive increases in BET water surface area indicating a change in degree of hydrophilicity of A16SG. After outgassing at 400^0C and H_2O area was the same as that for the BET N_2 area, a possible indication of the removal of all molecular water (hydrophobic site) from the Al6SG. A comparison of H_2O adsorption on Alon-C and Al6SG is shown in Figure 1. Al6SG is more adsorptive than Alon-C after outgassing at 400°C.

4. HCl/Alon-C

Hydrogen chloride adsorption at 0, 40, 50° on Alon-C shows no significant temperature dependence. Readsorption measurement, where HCl is pumped away from the alumina show the hydrogen chloride adsorption on Alon-C is 75% irreversible.

Sample pretreatment, as shown in Figure 2, greatly affects the adsorption capacity of Alon-C for HCl.

5. HCl/Al6SG:

Isotherms for HCl/Al6SG has been obtained at 40° for Al6SG after outgassing at 80° and 400°C. Again the temperature of outgassing affects the adsorptive properties of the alumina. Irreversibility of HCl adsorption is seen on Al6SG using readsorption experiments. Fig. 3 shows a comparison between HCl adsorption on Alon-C and Al6SG after outgassing at 400°C. A difference in the adsorptive behavior of these two alumina phases is evident at 400°C, outgassing at 80°C shows similar behavior but the effect is not as pronounced, Fig. 4.

D. I. R. STUDY

An infrared study of the aluminas, to determine the nature of the adsorbed species after HCl adsorption and the nature of the different alumina surfaces has just commenced. An infrared cell has been constructed which is capable of heating the alumina sample in vacuum to outgas temperature up to 800°C.

Some difficulty has been encountered in pressing the alumina into transparent disk for transmission infrared measurements. Alon-C can be pressed into disks and infrared measurements are now underway.

Spectra of Alon-C and Al6SG without a pretreatment have been obtained in nujol mulls.

REFERENCES

1. R. Fricke and K. Jockers, Z. Anorg. Chem. 263 3 (1950).

2. K. Werfers and G. M. Bell, Technical Paper No. 19, Aluminum Company of America, 1972.

Table I

Alumina	Characterization Technique				Isotherm			
					H_2O		HCl	
	X-ray diffraction	SEM	BET Area	TGA	Outgas	Isotherm Temp.	Outgas	Isotherm Temp.
Alon-C	X	X	X	X	80^0 400^0	RT. 40^0 50^0 40^0	80^0 400^0	0^0 40^0 50^0 40^0
Al6SG	X	X	X	X	80^0 400^0	50^0 40^0	80^0 400^0	50^0 40^0
γ-C-31	X		X					
Hydral 710			X					

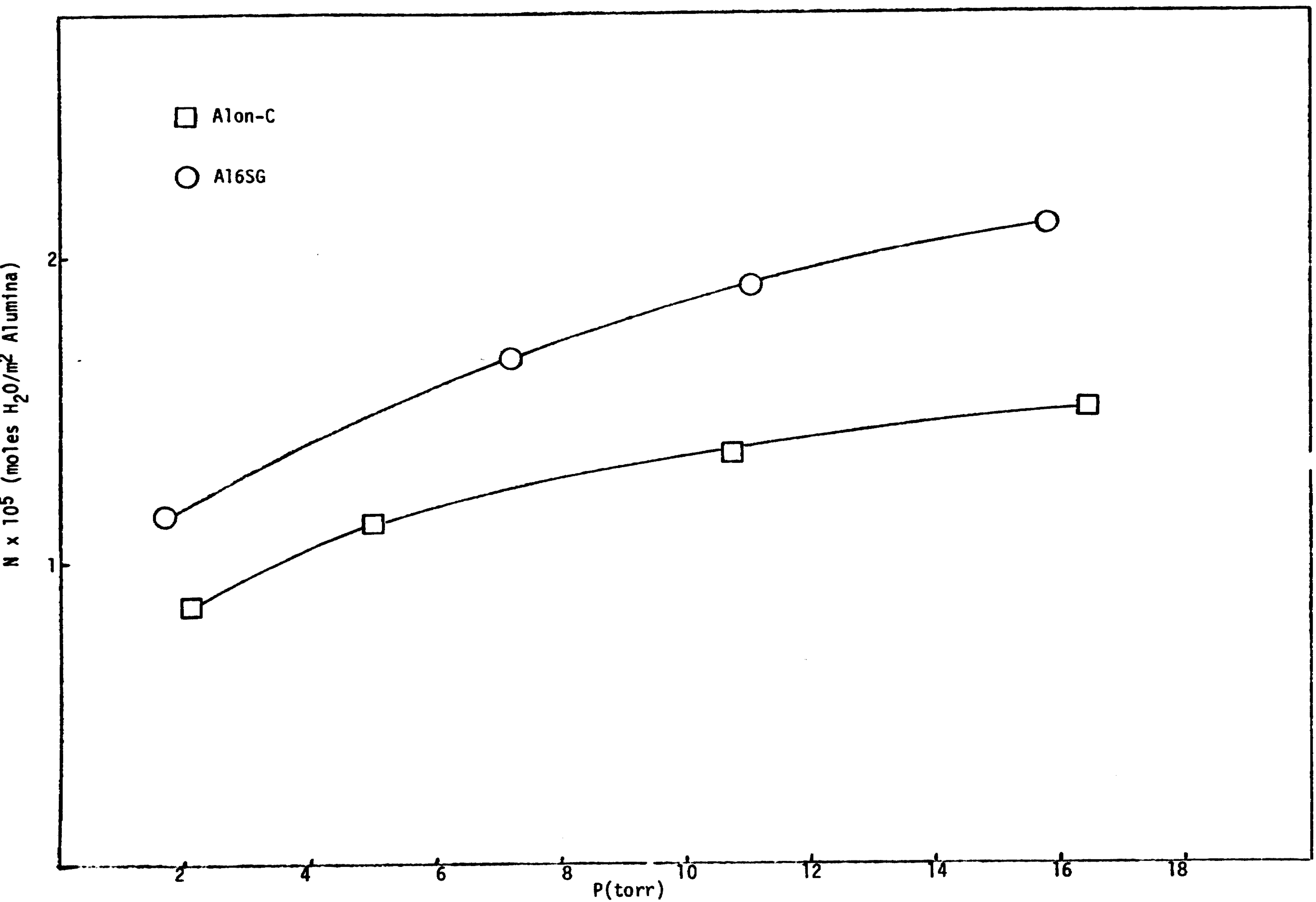

Figure 1. Comparison of H_2O/Alon-C and H_2O/A16SG After 400°C Outgas.

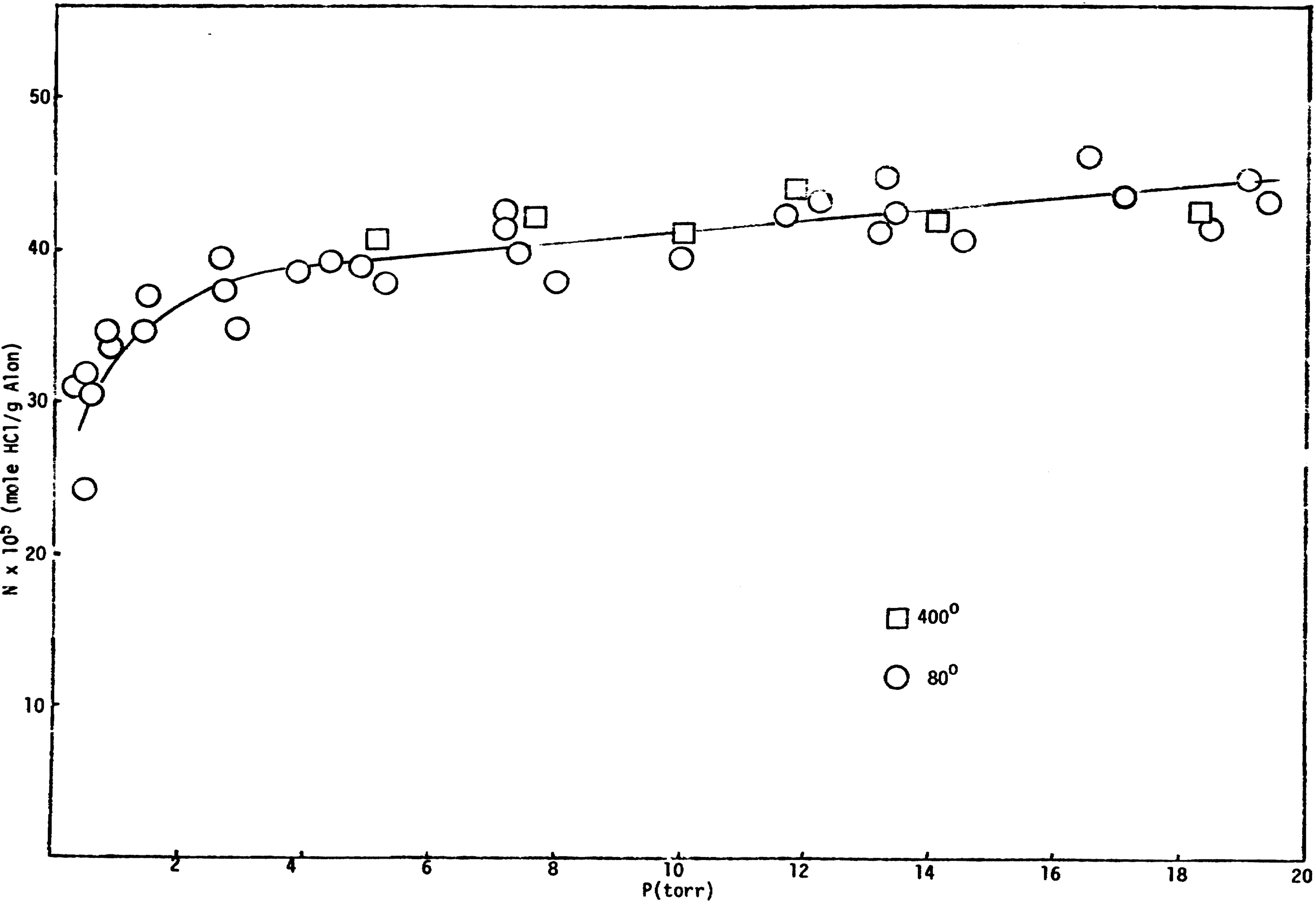

Figure 2. HCl/Alon-C at different outgas temperatures.

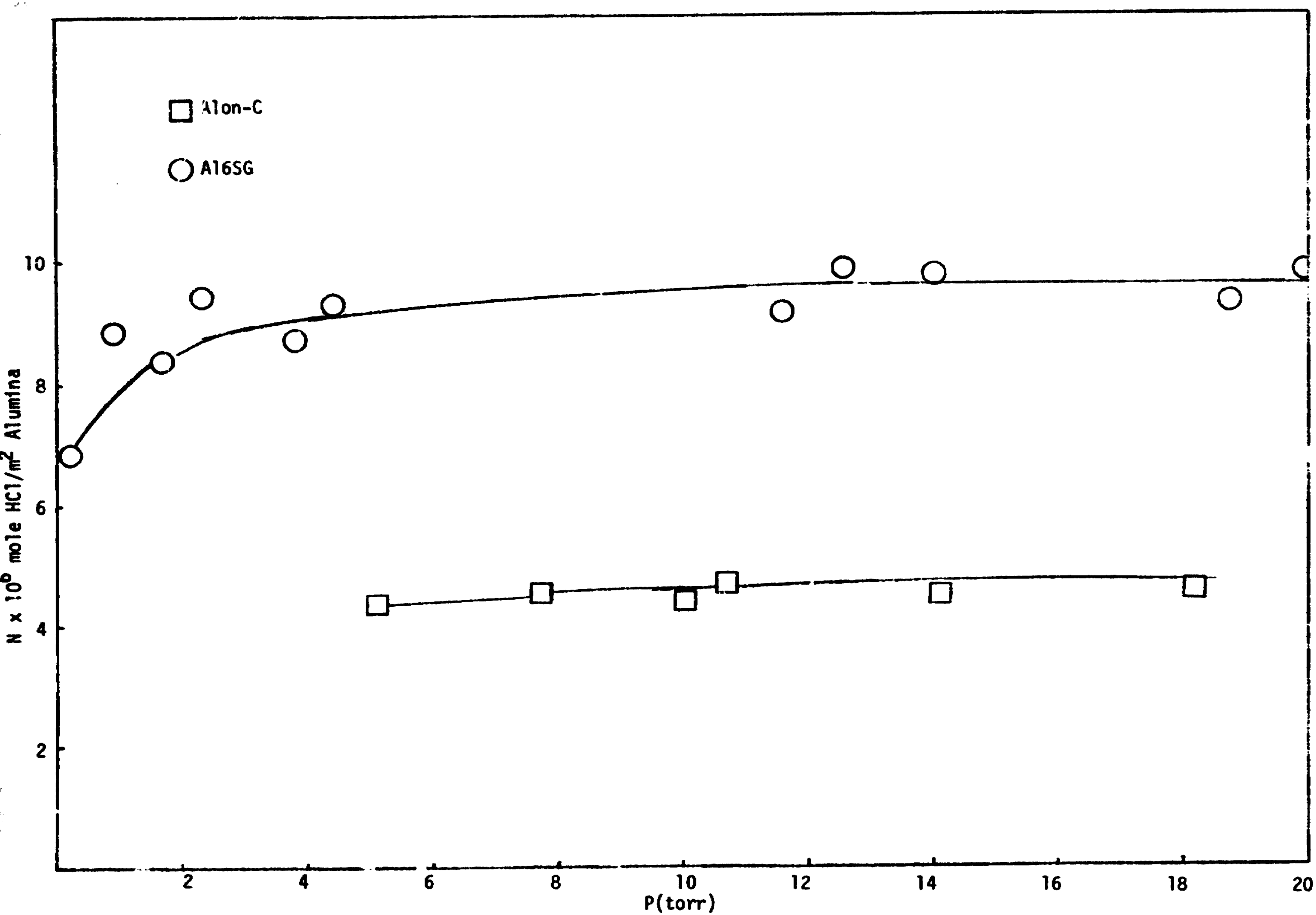

Figure 3. Comparison of HCl Adsorption on Alon-C and A16SG after 400°C Outgassing.

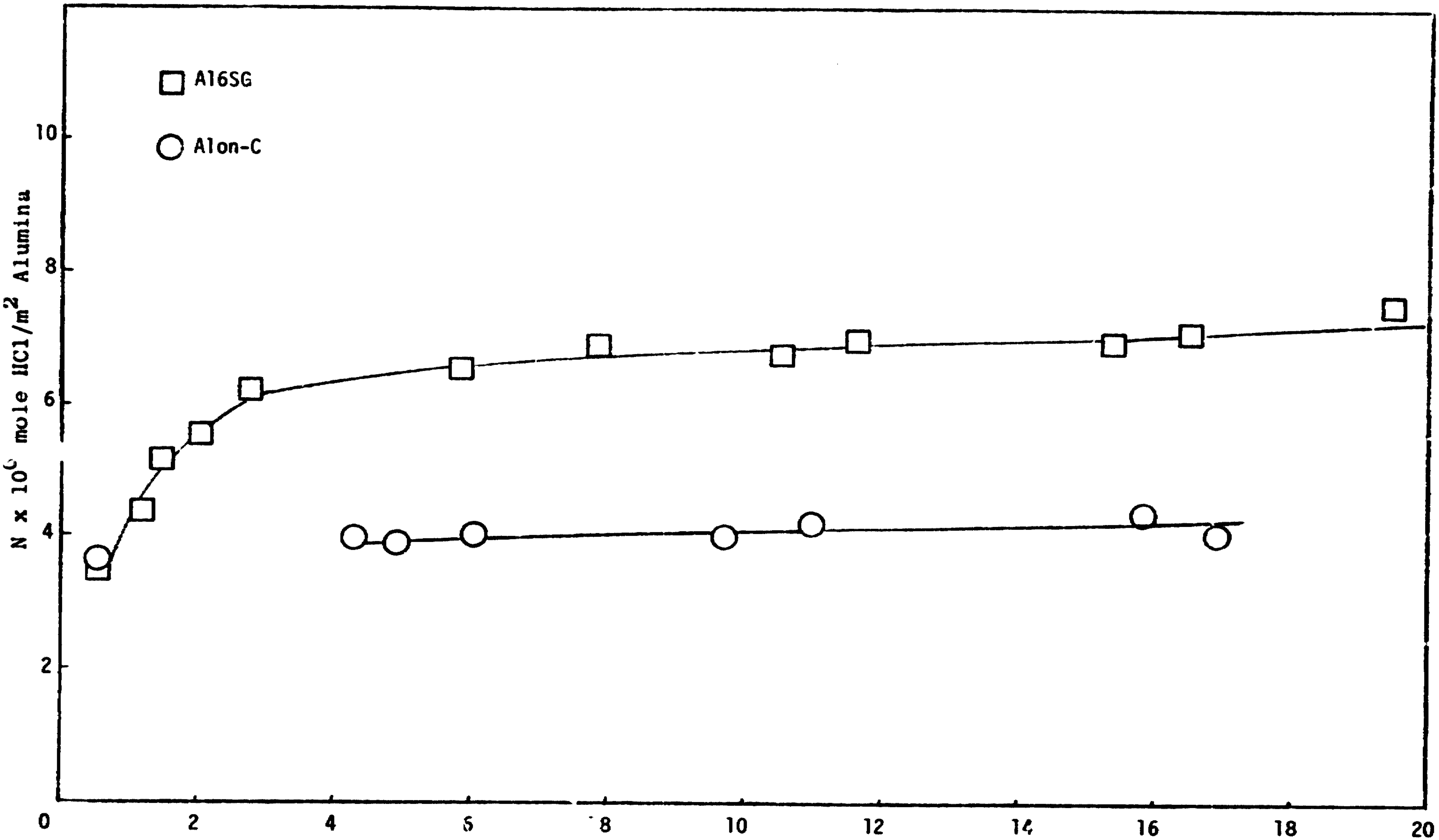

Figure 4. Adsorption of HCl at 50^0 on Alon-C and Al6SG after 80^0 Outgas.