

## Adsorption of Hydrocarbons on Acidic Oxides as Measured Chromatographically

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Gas-solid chromatography has been used to measure the relative strengths of adsorption of hydrocarbons on acidic oxide catalysts at temperatures up to 475°C. Some of the results can be interpreted in terms of physical adsorption, but surface acidity of the adsorbent also influences the adsorption of aromatics. The binding between aromatics and acidic surfaces seems to be even more diffuse than in the  $\pi$ -bonds known in solution, in spite of the strong acids shown to be present on some of these surfaces by amine titration at room temperature. The heats of adsorption of hydrocarbons approximate the heats of liquifaction.

Since much higher temperatures are necessary for desorption of pyridine and the effect of water vapor on adsorption is larger, chemisorption seems to be indicated for nitrogen bases.

Following the use of gas-liquid chromatography (GLC) for determining solution behavior (1), several groups (2) have applied a similar pulse technique to the study of gas-solid interactions by substituting a column of adsorbent only for the solvent-laden adsorbent used in GLC. By virtue of the short contact times which may be used, this gas-solid chromatography (GSC) is especially suited to the study of adsorption on catalytically active surfaces at temperatures close to those of catalytic interest. Decomposition of the adsorbate is thereby avoided along with the attendant problems in interpretation. GSC is not without its own difficulties, however, chief among them being detailed quantitative interpretation of peak shapes obtained by this pulse technique (2). This study is not directed at such interpretation, but rather at elucidation of the nature of the adsorbed species present on oxide catalysts. It is found that the GSC technique provides useful information in this regard even without detailed interpretation.

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### METHODS

**Equipment.** The equipment used was a conventional gas chromatograph built in these laboratories. The only modification was the incorporation of a special furnace designed to hold 30-cm U-tubes of 1/4-inch metal tubing. The furnace was constructed of two aluminum plates milled out to accept the tubing. Electrical heating was supplied by nichrome ribbon wound on mica cards outside the aluminum plates. Temperature was controlled by a thermocouple and a Celectray, and precision thermometers graduated in 0.2°C intervals were used to measure temperatures of the plates. Adsorbates were introduced via a silicone rubber seal with a microsyringe. A thermal conductivity cell was used as a detector. The adsorbent bed was approximately 15 cm long and the amount of adsorbent was varied by changing the wall thickness of the tubing. Before adsorption experiments were started, the adsorbents were heated in a stream of helium at the highest temperature to be used (generally 450°C).

**Reagents.** Helium was used as carrier

gas. For most experiments tank helium was satisfactory, but for selected experiments the helium was saturated with water at room temperature and then chilled to 0°C or -78°C to maintain a known partial pressure of water. The silica-alumina used was 200-325 mesh American Cyanamid Co. low alumina cracking catalyst. Its specific surface was 609 m<sup>2</sup>/g (BET) and its pore volume 0.58 cc/g. The commercial silica-magnesia used was obtained from Davison Chemical Co. and had a specific surface of 664 m<sup>2</sup>/g and a pore volume of 0.38 cc/g. Phillips Pure Grade hydrocarbons and Baker and Adamson Analytical pyridine were used.

**Measurements.** Four types of measurements were made: retention times or volumes, and "initial" retention times or volumes. The retention time is the time between the maximum in the air peak and the maximum in the sample peak of the GSC trace. The retention volume is the volume of He carrier gas (at column conditions) which passed through the column in the time between these two maxima. Because of the characteristic shape of GSC peaks, i.e., a very sharp leading edge and a long tail, the "initial" retention time could sometimes be determined more precisely. This is the time between the initial emergence of air and the initial emergence of the sample. The initial retention volume is the volume of the carrier gas (at column conditions) passed through the column in the initial retention time. Helium flow rates were measured with a soap bubble meter and corrected for temperature, pressure, and water vapor content. Perfect gas laws and the conventional pressure correction factor of  $3/2\{[(P_i/P_o)^2-1]/[(P_i/P_o)^3-1]\}$ , where  $P_i$  = inlet pressure and  $P_o$  = outlet pressure, were used for the corrections.

## RESULTS AND DISCUSSION

### *Adsorption of Xylenes on Silica-Alumina*

Consider the interactions to be expected between a monocyclic aromatic and a strongly acidic surface such as silica-alumina cracking catalyst. At least two

types of acid-aromatic interactions are known in liquid protonic acids. The stronger results in a  $\sigma$ -bond with the proton attached to a particular carbon atom (3). It is postulated to occur in the HF-BF<sub>3</sub> system. The weaker interaction, denoted  $\pi$ -bonding, occurs in solutions of HCl in hydrocarbons and results in a looser attachment of the proton to the  $\pi$ -electrons of the aromatic ring. The relative basicities of the three xylene isomers are not the same for these two reactions with protons. As is well known, the  $\sigma$ -basicity varies much more with structure than  $\pi$ -basicity. This fact allows us to use the relative adsorption of xylenes as an indicator of the type of binding present in the adsorbed phase.

The retention volume of an adsorbate is a convenient measure of the strength of adsorption (4). The retention volumes of the xylenes on silica-alumina are compared

TABLE I  
BASICITIES AND RETENTION VOLUMES OF  
XYLENES ON SILICA-ALUMINA

Compound	Basicity constants relative to <i>p</i> -xylene		Retention volume $\times P^0$ relative to <i>p</i> -xylene	
	HCl <sup>a</sup> c	HF-BF <sub>3</sub> <sup>b</sup> c	280°C	350°C
<i>o</i> -Xylene	1.13	2	0.97	0.95
<i>m</i> -Xylene	1.26	20	0.93	0.95
<i>p</i> -Xylene	1.00	1	1.00	1.00

<sup>a</sup>  $\pi$ -Complexes postulated.

<sup>b</sup>  $\sigma$ -Complexes postulated.

<sup>c</sup> The data of ref. (3a) were used. Those of ref. (3b) indicate larger differences between the xylenes and further support our conclusion that adsorption does not involve  $\sigma$ -complexes.

in Table 1 with the  $\sigma$ - and  $\pi$ -basicities. Since the vapor pressures of the xylenes differ slightly, the retention volumes have been corrected for the differences in volatility. It is apparent that the strength of adsorption does not correlate with  $\sigma$ -basicity. The effect of structure on strength of adsorption is far too small and the differences are in the wrong direction. Neither is adsorption to be correlated with the less well defined  $\pi$ -basicity. Here, also, both the

magnitude and direction of the effects fail to correlate. In fact, it may almost be said that structure has no effect on strength of adsorption. This is strong evidence for physical adsorption and against chemisorption, i.e., the binding is even more diffuse than in  $\pi$ -bases.

*Heats of Adsorption*

Heats of adsorption are often used to distinguish between physical and chemical adsorption. Eberly has shown (4) that the change in retention volume with temperature may be used to estimate the heat of

adsorption. The effect of temperature on the adsorption of toluene on silica-magnesia is illustrated in Fig. 1. From the slope of the line a heat of adsorption of 13 kcal/mole may be calculated. This is to be compared with a heat of condensation of 8.0 kcal at 110°C. The 5 kcal difference suggests rather strong binding to the surface when compared with the heat of protonation of aromatics in hydrogen fluoride (3b). This interaction is presumably the result of the acidic nature of the surface. Lack of information on solvation energies as well as the above data on xylene adsorption

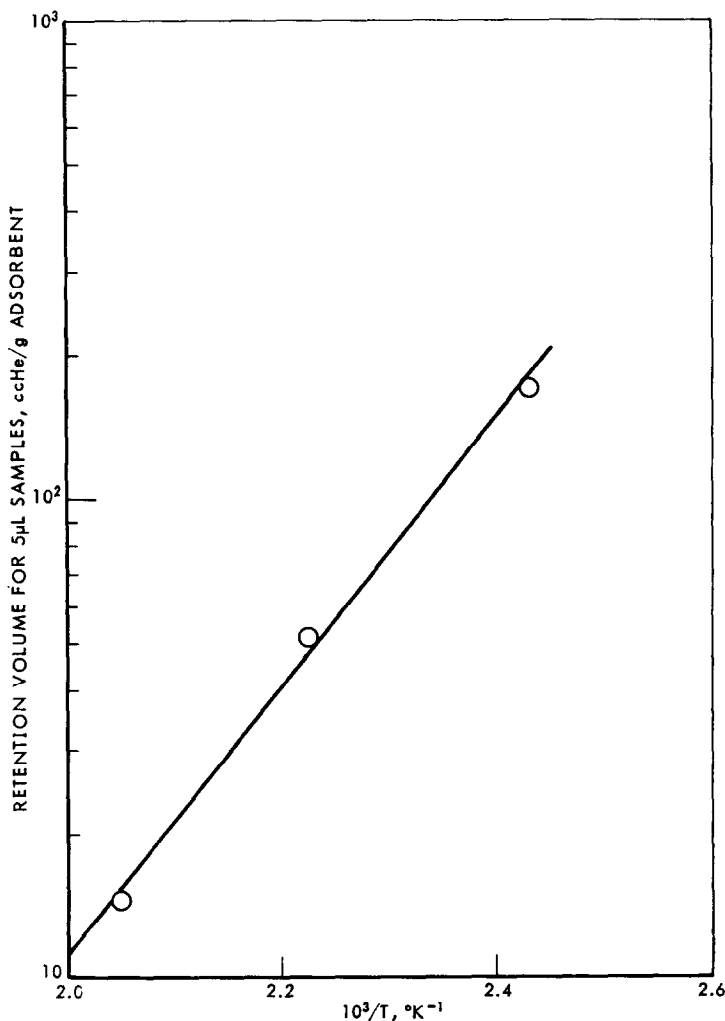


Fig. 1. Adsorption of toluene on silica-magnesia.

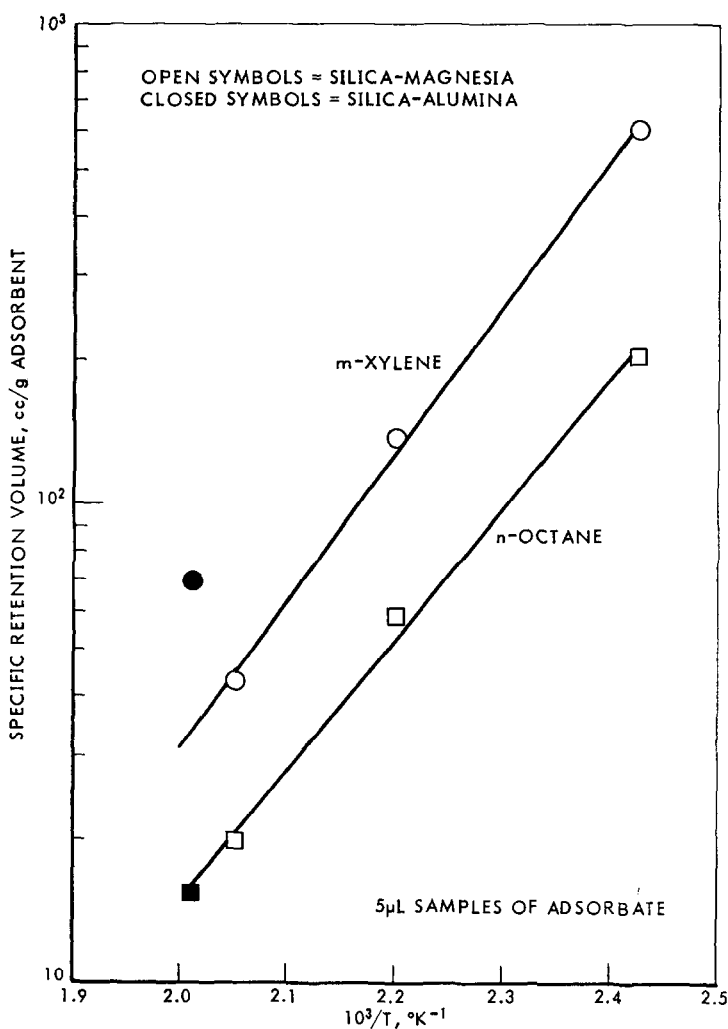


FIG. 2. Adsorption of *m*-xylene and *n*-octane on silica-magnesia and silica-alumina.

indicate that these conclusions should be accepted with caution.\*

#### *Acid Strength of Adsorbent*

The importance of acidity is supported by comparison of adsorption on silica-alumina and on silica-magnesia. The former

\* The above value of 13 kcal/mole may also be compared with isosteric heats of adsorption of ammonia on silica-aluminas of 10 to 40 kcal/mole observed by Clark, Holm, and Blackburn (5). Such a comparison also suggests that moderately strong interaction occurs between monocyclic aromatics and silica-alumina.

is generally believed to have some very strong acid sites while the latter has almost exclusively weak acid sites (6). Thus, one might expect more easily polarizable molecules such as aromatics to be more strongly adsorbed (relative to the less polarizable paraffins) on the more strongly acidic silica-alumina. Figure 2 shows that this is the case. *n*-Octane is no more strongly adsorbed on silica-alumina than on silica-magnesia; *m*-xylene, on the other hand, is adsorbed two to three times as strongly on silica-alumina. It is concluded that the adsorption here measured does depend to

some extent on the acidity of the adsorbent in spite of the evidence cited above for physical adsorption.

#### *Effect of Water on Adsorption*

Several investigators have noted sizable effects of the water content of silica-alumina on its catalytic activity (7). A cursory survey of the effect of water content on the strength of adsorption was therefore made, primarily to ascertain whether close control of the water content of the carrier gas was required. Two water concentrations in He carrier gas were examined,  $4 \times 10^{-4}$  mm and 3 mm. No difference in retention time of *m*-xylene was observed (Fig. 3). Pyridine, by contrast,

has been neutralized (with water or with pyridine). Then, with a dry catalyst, as the sample size increases to the point where only a negligible fraction of pyridine is required to neutralize most of the strongly acidic sites, the retention time should decrease to a value near that observed for a "wet" catalyst. With a "wet" catalyst, however, the most strongly acidic sites have already been neutralized. The effect of increasing sample size should thus be smaller. Figure 4 shows that the retention time of pyridine from dry silica-alumina is indeed much more strongly affected by sample size than the retention time from more moist silica-alumina and that the retention times approach each other at large

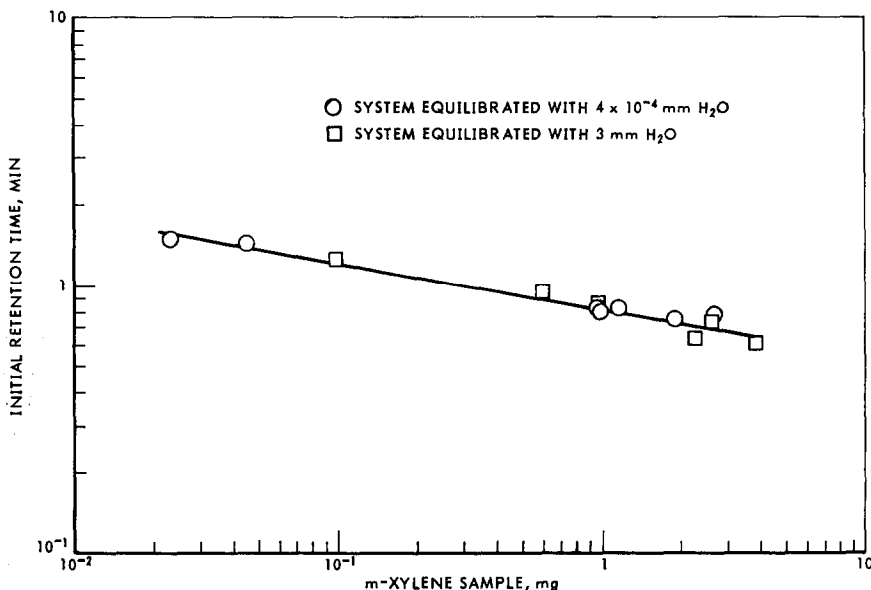


Fig. 3. Adsorption of *m*-xylene on silica-alumina at 250°C.

was much more strongly adsorbed on the catalyst which had been equilibrated with the drier helium, especially when small samples of pyridine were used (Fig. 4). This suggests that water and pyridine compete for acidic sites on the surface and that some sites are more acidic than others. Assume a large difference between the free energy of adsorption of pyridine on a strongly acid site and on such a site which

sample size. It is concluded that, although hydrocarbons are adsorbed via long-range, nonspecific forces, small amounts of nitrogen bases are adsorbed on acid sites. This conclusion is consistent with the observation that much higher temperatures are required to desorb pyridine than to desorb monoaromatic hydrocarbons.

It will be noted that the point of intersection of the two lines in Fig. 4 corresponds

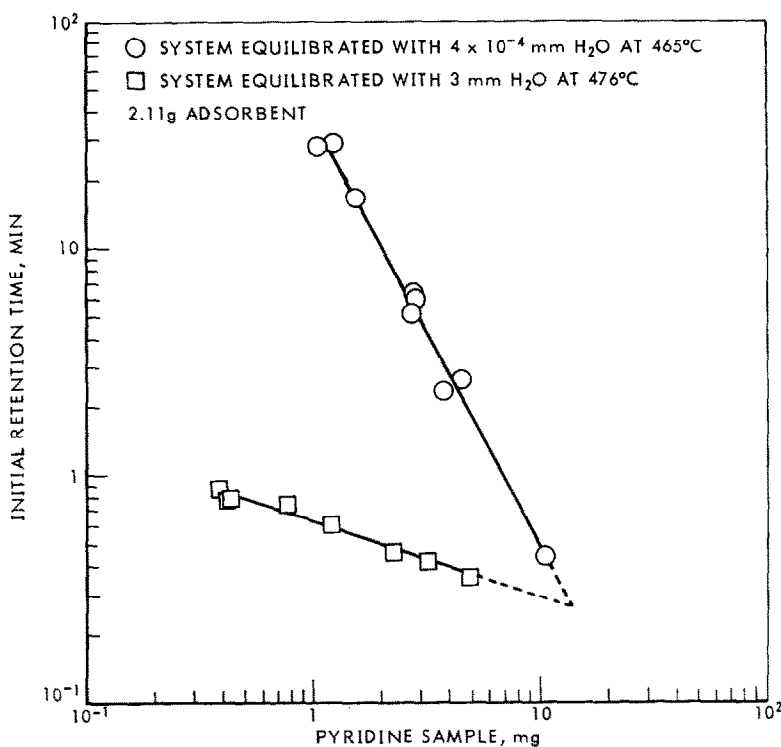


FIG. 4. Adsorption of pyridine on silica-alumina.

to a 14-mg sample of pyridine. This is equivalent to 0.08 meq pyridine/g catalyst, which may be considered a measure of the acid sites strong enough to be "poisoned" by water under the conditions noted. This value is substantially lower than that obtained by amine titration at 25°C for total acidity (6), as it should be, and is in agreement with currently accepted theories that a distribution of acid strengths exists (6).

A complementary interpretation of these experiments is that those acid sites which could strongly adsorb *m*-xylene (via  $\sigma$ -complexes) are covered by water even at the lower water concentration. This view also implies a distribution of acid strengths and a greater acid strength necessary to adsorb the weaker base, *m*-xylene, than the stronger base, pyridine.

#### CONCLUSIONS

Gas-solid chromatography has been used to elucidate the nature of binding of adsorbed species on acidic oxide catalysts. In

agreement with other work, nitrogen bases are chemisorbed on acid sites. Acidity also influences the adsorption of monocyclic aromatics, but less specific forces are involved. *n*-Paraffins are only physically adsorbed.

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