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# The Effect of Exchanged Cations and Heat Treatment on the Adsorption of Carbon Monoxide, Nitrogen, Argon, and Krypton on Amorphous Silica–Alumina Cracking Catalysts

YUN-YANG HUANG* AND PAUL H. EMMETT†

*Department of Chemistry, The Johns Hopkins University,*
*Baltimore, Maryland 21218*

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Adsorption isotherms for CO, $N_2$, Ar, and Kr were measured over the temperature range −50–250°C over a pressure range of 2–350 Torr on exchanged and unexchanged silica–alumina cracking catalysts that had been evacuated at 250, 450, and 800°C, respectively. Isosteric heats of adsorption were calculated at surface coverages ranging from 0.1 to 1%.

When the samples were evacuated at 250°C, the adsorption of CO was increased by a factor of about 3.5 when the exchanged cations were Ca and Ba and about 50% for K cations and also for ions of La and Mg. The influence of cations became even greater when the samples were evacuated at 450°C, the adsorption for the samples exchanged with cations being three times as great on specimens evacuated at 450°C as for samples evacuated at 250°C. Evacuation of samples at 800°C caused the adsorption of CO on the H form of the sample to be substantially the same as for the ones exchanged with calcium ions. The isotherm for the Ca exchanged specimen was substantially the same as for the sample evacuated at 450°C.

Isosteric heats of adsorption in general were highest for La and Ca exchanged samples, somewhat lower for those exchanged with K and least for those containing protons on the exchange sites. However the heats of adsorption on samples evacuated at 800°C approached 15 kcal/mole of CO both for samples exchanged with Ca ions and for the protonic samples. Corresponding heats of adsorption of nitrogen were in the range of 7–9 kcal/mole of $N_2$. Heats of adsorption of argon and krypton remained down in the range of 2.5–3.5 kcal/mole for all samples, and were not much influenced by the temperature of evacuation or the exchange of ions on the catalyst surface. The molecules for which the big changes in adsorption with temperature of evacuation and ion exchange of samples were noted were carbon monoxide and nitrogen, both of which have rather high quadrupole moments.

## INTRODUCTION

The study of the interaction between simple gas molecules and the surface of a solid can often lead to knowledge of the nature and of the distribution of cations on the surface. These cation sites frequently show interesting adsorption properties and catalytic activities. In this connection cation-exchanged zeolites have been studied extensively. In particular, the presence of multivalent cations on the surface of Y-type zeolite usually enhances catalytic activity, for reactions such as cracking, isomerization, or polymerization (*1*). Specific interaction due to electrostatic forces between adsorbed molecules and the exchanged cations has also been noted (*2–4*).

It was observed by Egerton and Stone

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[*] Present address: Division of Tribophysics, CSIRO, University of Melbourne, Parkville, Vic., 3052, Australia.

[†] Present address: Department of Chemistry, Portland State University, Portland, Oregon 97207.

that Y-zeolites exchanged with calcium or other bivalent cations are capable of adsorbing carbon monoxide specifically (*5*). About one CO was adsorbed on each cation in the supercage at 0°C and about 10 Torr. Infrared spectra of adsorbed CO on X- and Y-type zeolites containing various kinds of cations have been investigated by Angell and Schaffer (*6*). An infrared absorption band was observed on all bivalent cation samples, with frequencies higher than the stretching band for CO. Its origin was explained on the basis of the polarization interaction between carbon monoxide and the cations.

On the surface of amorphous silica–alumina, there are protons which can be exchanged by cations (7). Since amorphous silica–alumina catalysts have the same local tetrahedral arrangement of $SiO_4$ and $AlO_4$ as in the zeolites but lack the regularity of the crystalline material, it seemed of interest to study the adsorption of carbon monoxide on exchanged and unexchanged and heat-treated amorphous catalysts. For comparison the adsorption of nitrogen, argon and krypton have also been studied.

## EXPERIMENTAL

### *Materials*

Argon, carbon monoxide and krypton were purified respectively by condensing in and fractionating from a liquid nitrogen cold trap. Nitrogen was passed through a liquid nitrogen cold trap slowly before storage in a bulb. All gases were supplied by Matheson Gas Products, with purities at least better than C.P. grade (99.5%).

The unexchanged silica–alumina was obtained from W. R. Grace Company as Davison 980 cracking catalyst; it contained 13.2% alumina. Cations were incorporated by exchanging the original sample in 1.5 *M* acetate solutions of various cations except lanthanum ions, for which 0.8 *M* $LaCl_3$ solution was used. The cation-exchanged silica–aluminas were then thoroughly washed with distilled water and dried in an oven at 120°C overnight. The amounts of exchanged cations on all samples are shown in Table 1. The surface area of samples following each heat treatment was determined by nitrogen adsorption at 77K. and are shown in Table 2. Throughout this paper, silica-alumina will be designated as SA. A prefix will indicate the exchanged cation.

### *Apparatus and Procedures*

Adsorption was measured by a volumetric adsorption system evacuated by a mercury diffusion pump and connected to a mercury manometer for pressure measurements. A sample of about 6 g was contained in a quartz vessel having a deadspace of about 5 cc. At each temperature indicated, the sample was evacuated at $10^{-6}$ Torr overnight. It was then cooled down to the desired temperature for adsorption measurements. Temperatures at and below 45°C were maintained by a liquid bath; those at and above 50°C, by a furnace. Adsorption isotherms were measured at each temperature in a successive order of argon,

TABLE 1
EXTENT OF CATION EXCHANGE

| Sample | Exchanged cation<br>% by weight | Cation density (m moles/g) | Method of analysis |
|---|---|---|---|
| K-SA | 2.38 (K) | 0.60 | Flame photometry |
| Mg-SA | 0.48 (Mg) | 0.20 | Flame photometry |
| | 0.49 (Mg) | 0.20 | Atomic absorption |
| Ca-SA | 0.78 (Ca) | 0.20 | Flame photometry |
| Ba-SA | 3.96 (BaO) | 0.26 | Gravimetric analysis of $BaSO_4$ |
| La-SA | 1.30 ($La_2O_3$) | 0.08 | Gravimetric analysis of $La_2O_3$ |

TABLE 2
SURFACE AREA OF SILICA–ALUMINAS AS A FUNCTION OF CATIONIC EXCHANGE AND TEMPERATURE OF EVACUATION

| | BET surface area (m$^2$/g dry) | | |
|---|---|---|---|
| Sample | (250°C) | (450°C) | (800°C) |
| SA | 383.6 | 383.6 | 349.0 |
| K-SA | 324.5 | 322.4 | 271.6 |
| Ca-SA | — | 339.1 | 296.1 |

TABLE 3
PERCENTAGE WEIGHT LOSS AFTER HEAT TREATMENT

| | Percent weight loss after heat treatment, % | | |
|---|---|---|---|
| | | (800°C) | |
| Sample | (450°C) | Total | Additional |
| SA | 6.7 | 7.5 | 0.8 |
| K-SA | 11.4 | 12.1 | 0.7 |
| Mg-SA | 10.0 | — | — |
| Ca-SA | 16.5 | 17.3 | 0.8 |
| Ba-SA | 8.2 | — | — |
| La-SA | 10.7 | 11.9 | 1.2 |

krypton, nitrogen and then carbon monoxide. Between each run, the sample was always evacuated at $10^{-6}$ Torr for several hours at 25°C. Adsorption and desorption were determined at pressures ranging from 2 to 350 Torr and temperatures from −50 to 250°C, depending on the uptake of the gases. The coverages were between 0.1 and 1.5%. Reversibility of the adsorption process is best indicated in the results in Figs. 4–6 where circular points represent adsorption and triangular points desorption. The amounts of adsorption are all expressed in CC at STP per gram of dehydrated sample. At the end of a series of adsorption runs after each high temperature evacuation, the sample vessel was removed from the adsorption system and weighed. The percentage weight losses after evacuation at 450°C and at 800°C are shown in Table 3.

To study the effect of the pretreatment of unexchanged silica–alumina with various gases, on the adsorption of CO, $N_2$, or argon the gas was admitted to the sample vessel at 800°C for at least 1 hr before being evacuated at 800 or 400°C as shown in Fig. 9. Water vapor was admitted at 600°C and then evacuated at 400°C overnight. The sample was then cooled down to room temperature for adsorption measurements.

The rate of oxidation of carbon monoxide was studied by a gas circulating system with a total volume of about 290 cc. About 180 Torr of a stoichiometric mixture of CO and $O_2$ (2:1) was diluted with helium to a total pressure of 650 Torr and then circulated over 0.5 g of sample (smaller than 35 mesh), supported by a fritted Vycor disk and maintained at a reaction temperature of 450°C. A liquid nitrogen cold trap was installed to trap carbon dioxide formed during the reaction. The gas mixture was circulated at 500 cc/min. The reaction was followed by measuring the decrease in pressure with a mercury manometer. A blank test was run without the catalyst but otherwise at the same conditions. The conversion in the blank was only 2.5% after 120 min., whereas at this time the reaction had almost completed itself over all catalysts.

## RESULTS

When the samples were evacuated at 250°C, the adsorption isotherms for all gases were linear for the unexchanged sample and correspond at room temperature to a coverage of about 1% at one atmosphere pressure. However, the samples containing exchanged $La^{3+}$, $Ca^{2+}$, $Ba^{2+}$, $Mg^{2+}$, or $K^+$ ions all exhibited enhanced adsorption for carbon monoxide. The adsorption isotherms were not linear but were concave to the pressure axis (Fig. 1). The enhancement in CO adsorption was only small for $K^+$, $Mg^{2+}$, or La3$^+$, but much greater for $Ca^{2+}$ or $Ba^{2+}$.

When the samples were evacuated overnight at 450°C the influence of cations was magnified. Much more carbon monoxide was adsorbed on $Ca^{2+}$ and $Ba^{2+}$ samples than on $K^+$ and unexchanged samples (Fig. 2). However, all samples showed a considerable amount of initial uptakes at pressures below 20 Torr. Comparing to the samples evacuated at 250°C, the increments of CO adsorption at 20 Torr and at 25°C

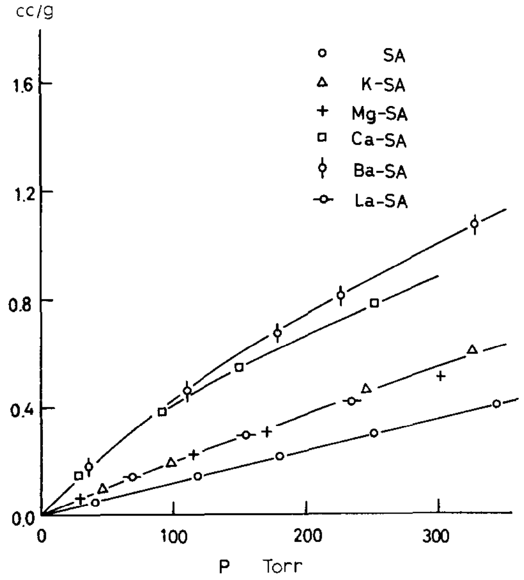

FIG. 1. Adsorption of carbon monoxide on silica-alumina samples evacuated at 250°C.

for all samples evacuated at 450°C are listed in Table 4.

TABLE 4
INCREMENTS OF CO ADSORPTION

| | Adsorption at 20 Torr and 25°C | | Increment, ΔCO (cc/g) | ΔCO/cation (moles CO/cation) |
|---|---|---|---|---|
| | (250°C)[a] | (450°C)[a] | | |
| SA | 0.03 | 0.23 | 0.20 | — |
| K-SA | 0.05 | 0.16 | 0.11 | 0.01 |
| Mg-SA | 0.05 | 0.46 | 0.41 | 0.09 |
| Ca-SA | 0.13 | 0.77 | 0.64 | 0.14 |
| Ba-SA | 0.10 | 0.51 | 0.41 | 0.07 |
| La-SA | 0.04 | 0.45 | 0.41 | 0.23 |

[a] Temperature of evacuation.

Enhancement of CO adsorption was even greater for all samples except $Ca^{2+}$ following evacuation overnight at 800°C. In fact, adsorption isotherms were almost the same for $La^{3+}$, $Ca^{2+}$ and unexchanged samples (Fig. 3). In the case of $Ca^{2+}$ sample, the uptake below 10 Torr was greater than that following evacuation at 450°C. But at higher pressures, the slope became smaller and, as a result, the adsorption was smaller.

Nitrogen behaved very much like carbon monoxide, except that it was adsorbed in smaller amounts. Irrespective of the temperature of evacuation, adsorption isotherms at 25°C were all linear for argon and krypton on all samples, except for krypton on Ca-SA evacuated at 450°C which was concave slightly to the pressure

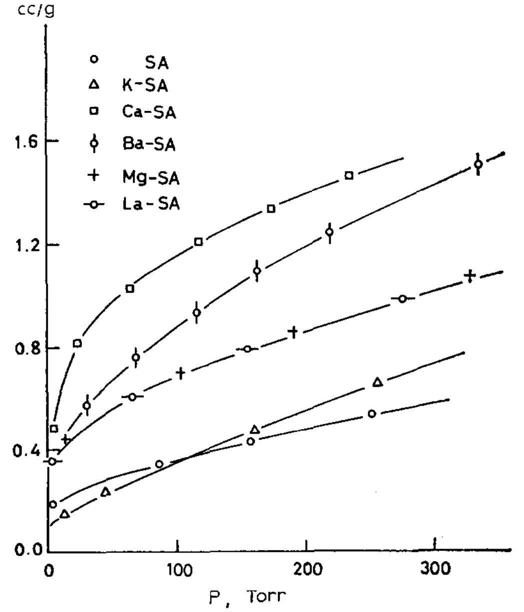

FIG. 2. Adsorption of carbon monoxide on silica-alumina samples evacuated at 450°C.

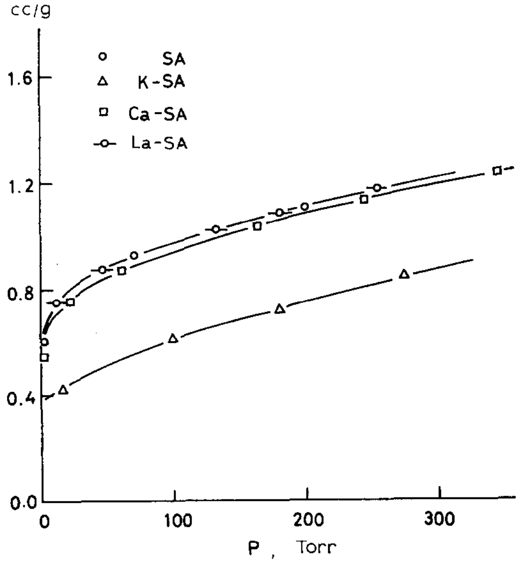

FIG. 3. Adsorption of carbon monoxide on silica-alumina samples evacuated at 800°C.

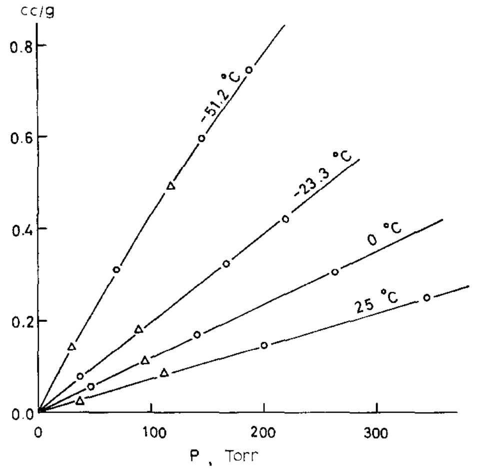

FIG. 4. Adsorption of argon on Ca-SA sample evacuated at 450°C.

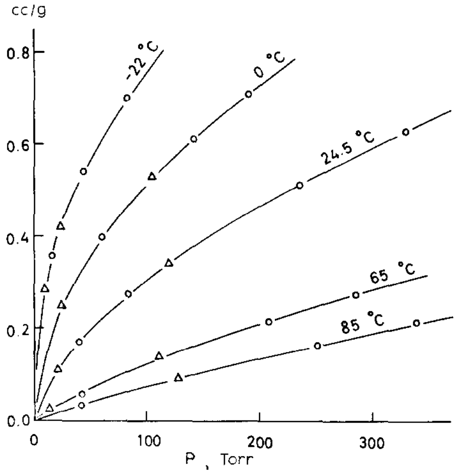

FIG. 6. Adsorption of nitrogen on Ca-SA sample evacuated at 450°C.

axis. In contrast to carbon monoxide and nitrogen, the adsorption of argon and krypton decreased for all samples evacuated at 800°C, the decrease being approximately proportional to the decrease in surface area.

To examine the energetics of surface sites, sets of adsorption isotherms were measured. Typical sets for various gases adsorbed on Ca-SA evacuated at 450°C are shown in Figs. 4–6. It is seen that all the adsorptions were reversible within the experimental region. From the slopes of Clausius–Clapeyron plots, isosteric heats of adsorption, $q_{st}$, were determined; a typical example of CO on Ca-SA is indicated in Fig. 7. The plots were always linear within experimental error, except for $N_2$ adsorbed on an unexchanged sample evacuated at 800°C. In this case detectable dependence of isosteric heat (Fig. 8) on the temperature was observed between 0 and 150°C. More details concerning this unusual behavior will be discussed later.

Dependence of isosteric heats on the coverages of various gases for $Ca^{2+}$, $K^+$, and

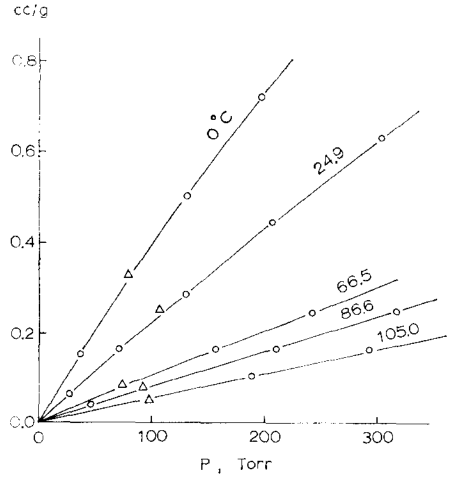

FIG. 5. Adsorption of krypton on Ca-SA sample evacuated at 450°C.

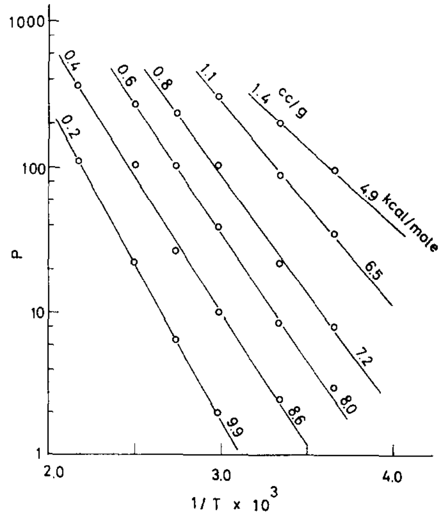

FIG. 7. Clausius–Clapeyron plot (carbon monoxide on Ca-SA evacuated at 450°C); $P$ in Torr; $T$ in K.

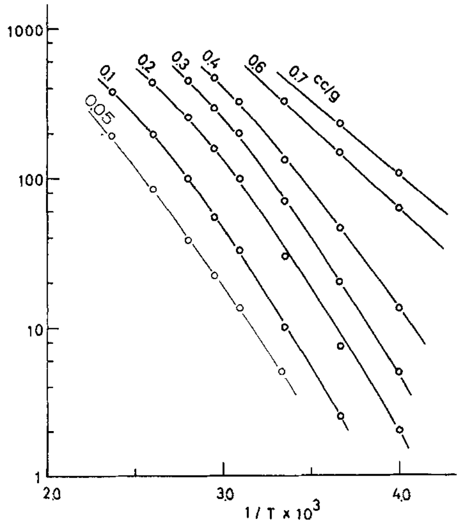

FIG. 8. Clausius-Clapeyron plot (nitrogen on SA evacuated at 800°C); $P$ in Torr; $T$ in K.

unexchanged silica-alumina samples are shown in Table 5.

To investigate the nature of energetic sites on unexchanged silica-alumina evacuated at 800°C, the adsorptions of carbon monoxide, nitrogen and argon at room temperature were measured following various treatments of the sample by several gases. The effect of pretreatment by various gases is shown in Fig. 9, on which the adsorptions at 25°C and 200 Torr are compared. It is obvious that while the adsorption of argon remained practically unchanged, various treatments had similar effects on the adsorptions of carbon monoxide and nitrogen.

The influence of exchanged cations on the oxidation of carbon monoxide was also studied. In general, a constant rate of reaction was observed on all samples for conversions up to at least 60%. Both $Ca^{2+}$ and $K^+$ ions apparently served as promoters, the rates being 50–100% higher on the exchanged catalysts than on the unexchanged. However, the potassium exchanged catalyst was invariably more active than the calcium exchanged.

## DISCUSSION

The adsorption of carbon monoxide at room temperature obviously indicates the influence of exchanged cations when the samples were evacuated at moderate temperatures. Multivalent cations enhance the adsorption much more than univalent cations. While magnesium and lanthanum ions showed little effect on the adsorption

TABLE 5
ISOSTERIC HEATS OF ADSORPTION ON SILICA–ALUMINAS

| Sample | Samples evacuated at 450°C | | | Samples evacuated at 800°C | | |
|---|---|---|---|---|---|---|
| | $\theta$ = 0.001 | 0.005 | 0.010 | $\theta$ = 0.001 | 0.005 | 0.010 |
| (Argon) | | | | | | |
| SA | 2.6 | 2.6 | 2.6 | — | — | — |
| K-SA | 2.9 | 2.8 | 2.6 | 2.6 | 2.5 | — |
| Ca-SA | 3.4 | 3.1 | — | 2.7 | 2.5 | — |
| (Krypton) | | | | | | |
| SA | 3.4 | 3.4 | 3.4 | 3.3 | 3.3 | 3.3 |
| K-SA | 3.8 | 3.6 | 3.6 | 3.4 | 3.3 | 3.3 |
| Ca-SA | 4.1 | 3.8 | 3.6 | 3.6 | 3.3 | 3.3 |
| (Nitrogen) | | | | | | |
| SA | 4.7 | 3.2 | 3.0 | 9.0 | 6.8 | 3.8 |
| K-SA | 4.5 | 3.9 | 3.7 | 6.7 | 4.2 | 3.3 |
| Ca-SA | 7.5 | 6.0 | 4.7 | 8.5 | 6.5 | 4.0 |
| (Carbon monoxide) | | | | | | |
| SA | 10.4 | 3.8 | 3.6 | 15 | 12.3 | 8.0 |
| K-SA | 9.0 | 4.7 | 4.5 | 15 | 9.0 | 5.0 |
| Ca-SA | 12 | 8.8 | 7.3 | 15 | 12.0 | 9.8 |
| Ba-SA | 11 | 7.8 | 6.2 | — | — | — |
| La-SA | 12.5 | 7.8 | 4.1 | 14.5 | 12.0 | 9.4 |

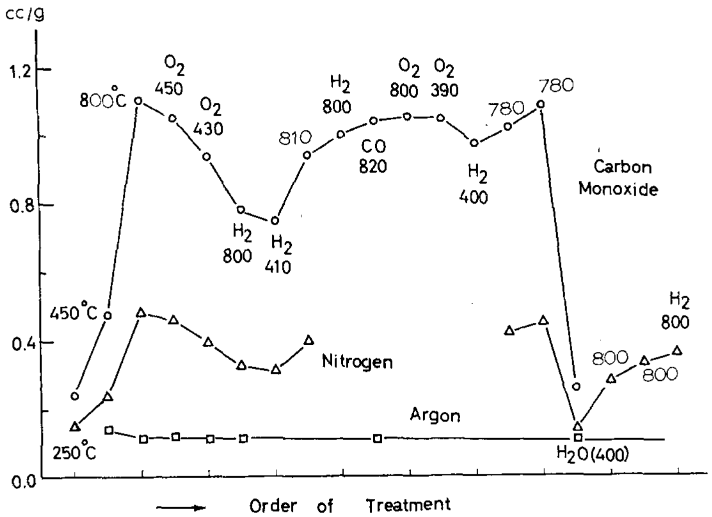

FIG. 9. Effect of pretreatment on the adsorption on SA at 25°C and 200 Torr. Pretreating gases or vapor and final temperatures of evacuation are indicated. When the pretreating gas is not shown, it means the sample was heated *in vacuo*. The evacuation was carried out for several hours.

after evacuation at 250°C, calcium and barium ions had increased the adsorption about three folds as compared to the unexchanged sample. Nevertheless, the adsorptions on all samples increased steadily with pressure and were small at very low pressures. If the samples were evacuated at 450°C, however, all showed an initial uptake at pressures below 20 Torr. Above this pressure, all isotherms have about the same slopes as those due to the previous heat treatment. This shows that the pronounced cationic effect could be reflected from the initial uptakes. In fact, the study of adsorption of carbon monoxide on cation-exchanged Y-zeolites by Egerton and Stone (*5*) indicates that the ratio of the number of CO molecules adsorbed at 0°C and at pressures between 1 and 10 Torr to the number of bivalent cations exposed to the supercage is approximately one. This is not so in the case of Na-Y zeolite. In other words, carbon monoxide is specifically adsorbed on bivalent cation sites.

Similarly, the number of exchanged multivalent cations exposed on the surface of amorphous silica–alumina could be estimated, even though their exact locations and coordination are not available. The increments of CO adsorption at room temperature and at 20 Torr are listed in Table 4. From the CO to cation ratios calculated, one might conclude that about 10% of the exchanged bivalent cations are exposed on the surface. The lack of specific interaction of carbon monoxide with potassium ions is also obvious. It is interesting that lanthanum ions also adsorb carbon monoxide specifically, with about 20% of the ions apparently being on the surface of the amorphous material. This is further proved from the heat of CO adsorption on La-SA evacuated at 450°C. On the contrary, no interaction between carbon monoxide and lanthanum ions was observed on La-Y zeolite (9), indicating that lanthanum ions were not exposed to the supercages.

When the samples were evacuated at 800°C, the adsorption and heats of adsorption of carbon monoxide on the cation-exchanged were practically the same as on the unexchanged, and only slightly less on K-SA. Apparently, the role of multivalent cations has been subdued. They could possibly have moved away from the surface layer by diffusing into smaller pores that are not accessible to probing gases, or have been completely screened by the oxide ions. However, the effect of surface potassium ions is still present.

The normal influence of exchanged cations is better reflected from the isosteric heats of adsorption of various gases on samples evacuated at 450°C. Within the range of coverages where cations are exposed to the surface, heats are invariably higher on multivalent cations than on univalent cations, which in turn are higher than those of the unexchanged samples. The electrostatic interactions between the adsorbed molecules and the cations are definitely involved. Depending on the nature of the probing molecules, the electrostatic interactions include polarization and quadrupole forces. The polarization energy for a molecule with polarizability $\alpha$ and in the presence of an electrostatic field $E$, is given by

$$\phi_P = -\tfrac{1}{2}\alpha E^2. \tag{1}$$

The quadrupole energy for a linear molecule with a quadrupole moment $Q$, and in the presence of an electrostatic field gradient $E'$, is given by

$$\phi_Q = -\tfrac{1}{2}QE'. \tag{2}$$

Thus, the interaction energy due to electrostatic forces is $\phi_P$ for argon and krypton, but $\phi_P + \phi_Q$ for nitrogen and carbon monoxide. In addition to the electrostatic forces, both dispersion and repulsive forces must also be considered to account for the interaction energy in the case of physical adsorption.

A calculation of the energy of adsorption would be impossible without knowing the exact positions of atoms or ions in the vicinity of the adsorption sites. It is likewise impossible to estimate the electrostatic field and field gradient at the adsorption sites. Nevertheless, the reverse can be done easily, that is, one can set a possible limit for the field and the field gradient from heats of adsorption determined experimentally. Polarization energy with varying field and quadrupole energy with varying field gradient for the four probing molecules, together with their molecular constants, are listed in Table 6. It can be seen that, even if electrostatic interaction is entirely responsible for the energy of adsorption, the reasonable values of the field on cation-exchanged samples would be about 1–1.5 V/Å and the field gradient would be about −1 to −2.0 V/Å². The electrostatic field and field gradient at a distance $r$ from an isolated charge $+ne$ are given by

$$E = ne/r^2, \quad E' = -2ne/r^3, \tag{3}$$

respectively. These values as a function of distance are also listed in Table 7. Screening of the cation charges by the negative ions surrounding them is expected on the surface of a solid. Assuming that the adsorption sites are on the exchanged cations, the contact distances between them and the four probing molecules are about 2.5–3.5 Å. Clearly, similar to the conclusion from the work on cation-exchanged Y-zeolites (*4*), the electrostatic charges in the vicinity of multivalent cations on amorphous silica–alumina, $Ca^{2+}$ or $La^{3+}$, are closer to one. It is also likely that these cations are coordinated with hydroxyl groups or oxygen ions after evacuation at 450°C.

As mentioned above, when the samples were evacuated at 800°C, exchanged cations seem to have no effect on the adsorption of all gases, except for nitrogen and carbon monoxide on K-SA at slightly higher coverages (Table 5). The heats of adsorption of argon and krypton on all samples decreased to a value of 2.5 and 3.3 kcal/mole, respectively. However, it is rather striking that the heats of adsorption of nitrogen and carbon monoxide increased to 9 and 15 kcal/mole, respectively, on all samples at a coverage of 0.1%. These values are quite high in terms of physical adsorption, especially above room temperatures. Even under strong interaction of electrostatic forces due to bivalent cations of Y-type zeolites, the heat values are only about 7 and 12 kcal/mole, respectively, for $N_2$ and CO (*10*, *5*). A heat of 8.2 kcal/mole has been reported for nitrogen on chromic oxide (*11*), but it was measured at a much lower temperature of −183°C. In general, the heat of adsorption decreases slightly with increasing temperature.

The present results show that when samples are evacuated at 800°C, a small number of very highly energetic sites are

TABLE 6
ENERGY OF INTERACTION DUE TO ELECTROSTATIC FORCES

| Gas | Ar | Kr | $N_2$ | CO |
|---|---|---|---|---|
| Molecular diameter,[a] Å | 2.94 | 3.69 | 3.15 | 3.12 |
| Polarizability,[b] $Å^3$ | 1.63 | 2.48 | 1.76 | 1.95 |
| Quadrupole moment,[c] $Q \times 10^{10}$ esu. $Å^2$ | 0.0 | 0.0 | −1.52 | −2.5 |
| Heat of liquefaction[d] kcal/mole | 1.568 | 2.158 | 1.333 | 1.444 |
| Polarization energy, kcal/mole | | | | |
| E = 0.2 V/Å | 0.05 | 0.08 | 0.06 | 0.06 |
| 0.5 | 0.33 | 0.50 | 0.35 | 0.39 |
| 1.0 | 1.30 | 1.98 | 1.41 | 1.56 |
| 1.5 | 2.92 | 4.45 | 3.16 | 3.51 |
| 2.0 | 5.20 | 7.93 | 5.62 | 6.24 |
| 3.0 | 11.7 | 17.8 | 12.6 | 14.0 |
| Quadrupole energy, kcal/mole | | | | |
| E′ = −0.2 V/$Å^2$ | 0 | 0 | 0.73 | 1.20 |
| −0.5 | 0 | 0 | 1.82 | 3.00 |
| −1.0 | 0 | 0 | 3.65 | 6.00 |
| −1.5 | 0 | 0 | 5.47 | 9.00 |
| −2.0 | 0 | 0 | 7.30 | 12.0 |
| −3.0 | 0 | 0 | 10.95 | 18.0 |

[a] Van der Waals diameter, From "Handbook of Chemistry and Physics," 47th ed., 1966–1967, The Chemical Rubber Co., page F-123.

[b] Landolt-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik, Band I, Teil 3, Molekeln II," page 510, 1951.

[c] $Q = \frac{1}{2}\int\rho(r,\theta)(3\cos^2\theta - 1)r^2dV$. Recommended values from D. E. Stogryn and A. P. Stogryn, *Mol. Phys.* **11**, 371 (1966).

[d] K. K. Kelley and E. G. King, U. S. Bureau of Mines Bulletin 592, 1961.

formed, which are inherent on the amorphous silica–alumina rather than as a result of the dehydration of exchanged cations. An electrostatic interaction due to surface cations, should, according to that mentioned previously, have an effect on the adsorption of argon and krypton similar to that for nitrogen and carbon monoxide. A decrease in heats for argon and krypton but a considerable increase for nitrogen and carbon monoxide could only suggest that a large field gradient, but not the field itself, is present at these highly energetic sites. In other words, molecules possessing large quadrupole moments will be adsorbed specifically on these sites. This is, indeed, supported from the work of others. Huang for example has correlated the adsorption of carbon dioxide on silica–alumina with the quadrupole moment of carbon dioxide (*16*). By infrared spectroscopic study, Peri observed selective adsorption of carbon dioxide ($Q = -4.3 \times 10^{-10}$ esu $Å^2$) on silica–alumina and γ-alumina (*12*). The surface concentration of these sites, so-called α-sites, is about $7 \times 10^{12}/\text{cm}^2$. Similar result was obtained by Lunsford (*13*) using EPR spectroscopy to investigate adsorbed nitric oxide ($Q = -1.8 \times 10^{-10}$ esu $Å^2$) on silica–alumina. The spin concentration was found to be $4 \times 10^{12}/\text{cm}^2$. From the room temper-

TABLE 7
ELECTROSTATIC FIELD AND FIELD GRADIENT OF AN ISOLATED CATION

| | Isolated +1 charge | | Isolated +2 charge | |
|---|---|---|---|---|
| Distance (Å) | Field (V/Å) | Field gradient (V/$Å^2$) | Field (V/Å) | Field gradient (V/$Å^2$) |
| 1.5 | 6.4 | −8.5 | 12.8 | −17.0 |
| 2.0 | 3.6 | −3.6 | 7.2 | −7.2 |
| 2.5 | 2.3 | −1.8 | 4.6 | −3.6 |
| 3.0 | 1.6 | −1.1 | 3.2 | −2.2 |
| 3.5 | 1.2 | −0.7 | 2.4 | −1.4 |
| 4.0 | 0.9 | −0.5 | 1.8 | −1.0 |
| 4.5 | 0.7 | −0.3 | 1.4 | −0.6 |

ature adsorption isotherm of CO on samples evacuated at 800°C, the initial uptake at 20 torr was about 0.8 cc/g or $6 \times 10^{12}$ molecules/$cm^2$, which is in close agreement with their estimates for the number of high energy sites. It may be noted also that the heat of adsorption of CO on $\gamma$-alumina has been determined by Menon *(14)*. However, it was only 8 kcal/mole at 0.1% coverage and dropped to 2.6 kcal/mole at higher coverages.

The adsorption isotherm at 25°C for CO on an unexchanged sample evacuated at 450°C indicate an initial uptake of about 0.2 cc/g, the heat of adsorption being 10.4 kcal/mole at 0.1% coverage. This means that the highly energetic sites were present in smaller number than on sample evacuated at 800°C. Increased number of sites would be formed by increasing temperature of evacuation, as also shown by Lunsford and by Peri.

The effect on the adsorption of pretreatment of an unexchanged sample with various gases gives additional information on the nature of these sites (Fig. 9). It confirms that only nitrogen and carbon monoxide, but not argon, are selectively adsorbed. Treatment with oxygen and carbon monoxide seems to have no definite effect. Treatment with hydrogen followed by evacuation at 400°C reduced the adsorption of $N_2$ and CO slightly. However, treatment with water vapor followed by evacuation at 400°C almost eliminated the specific adsorption. Prolonged evacuation at 800°C would recover most of these sites. All of these point to the fact that the energetic sites are formed by the removal of certain hydroxyl groups on the surface of the amorphous material, as indicated by Peri. It could be the site of an exposed aluminum ion, so screened by the oxygen ions that no significant electrostatic field but a field gradient would be exerted to the probing molecule.

The rate of oxidation of carbon monoxide was studied in an effort to ascertain whether the high heat of adsorption of carbon monoxide might indicate a chemisorption. However, even though the presence of $Ca^{2+}$ or $K^+$ ions and evacuation at higher temperatures all increased the rate by a factor of about two, K-SA was invariably more active than Ca-SA. So, presumably there is no direct correlation between the enhanced adsorption of CO and the activity toward carbon monoxide oxidation.

The temperature dependence of isosteric heat of nitrogen adsorption on unexchanged silica–alumina is rather unusual. Similar observation has been reported by Barrer on the nitrogen adsorption of $Li^+$, $Na^+$, and $K^+$ exchanged X-type zeolites *(2)*. In the case of K-X zeolite, the isosteric heat, $q_{st}$, is independent of coverage. But the temperature dependence, $q_{st}$ vs $T$, has a slope of $-7$ cal/mole degree. This was explained by Barrer in terms of the change in rotational state of the adsorbed nitrogen molecule. At higher temperatures, the rotation will be less restricted on the surface. The quadrupole moment, which generally decreases with onset of rotation, will cause a decrease in $q_{st}$. However, for Li-X and Na-X zeolites, $q_{st}$ decreases with coverage and $-\delta q_{st}/\delta T$ has a larger value of about 15 cal/mole degree. No explanation was given for this.

For as recently pointed out *(15)* amorphous silica–alumina, the value $-\delta q_{st}/\delta T$ is even higher, 30 cal/mole degree, which could not possibly be interpreted as due to the change of adsorbed state on the same site. Instead, a combined effect due to different kinds of energetic sites would be more plausible. This has been discussed in detail by Huang, Benson, and Boudart *(4)*. Also, a model of the adsorption equation considering two types of surface sites and describing both the adsorption isotherms and the temperature dependence of the isosteric heat of adsorption has recently been presented *(15)*.

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