route. The objection does not, therefore, support the latter but rather argues for an alternative mechanism.

Recently, Rooney and co-workers have found strong evidence for roll-over rather than π-allylic intermediates from deuterium exchange and epimerization studies on bicyclic hydrocarbons of specially designed structure (*8*).

ACKNOWLEDGMENT

We wish to thank Dr. J. J. Rooney for his interest and for informing us of the results of recent work prior to publication.

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Received March 17, 1971

Adsorption of Carbon Monoxide, Nitrogen, and Krypton on Ultrastable Y Zeolite

When amorphous silica–alumina cracking catalyst (13% alumina) was evacuated at 800°C overnight, it was found to adsorb nitrogen and carbon monoxide specifically (*1*). The CO adsorption at room temperature had an initial uptake of about 0.8 cc(STP)/g below 20 Torr pressure. The heats of adsorption at 0.1% surface coverage were determined to be 9 and 15 kcal/mole, respectively, for nitrogen and carbon monoxide. They decreased to about 3 kcal/mole above 2% coverage. On the other hand, adsorption isotherms of argon and krypton were all linear at room temperature and the heat values were only 2.5 and 3.3 kcal/mole, respectively. They were independent of surface coverage. These results indicate that, after extensive heat treatment of the amorphous material, a very small fraction of highly energetic sites were formed, which were selective in adsorbing gas molecules with large quadrupole moment.

It is of interest to examine the crystalline material to see if similar type of energetic sites are present. Ultrastable Y zeolite was thus selected for the comparison.

EXPERIMENTAL METHODS

Research grade krypton and C. P. grade carbon monoxide, both supplied from Matheson Gas Products, were further purified by condensing, respectively, in a liquid nitrogen cold trap, pumping off the top portion, and distilling the middle portion into storage bulbs. H. P. grade nitrogen, also from Matheson Gas Products, was slowly passed through a liquid nitrogen cold trap before storage.

The ultrastable Y zeolite sample was provided by W. R. Grace Company. It had originally been ion exchanged from Linde NaY zeolite by ammonium sulfate solution. After the first exchange process, the sample, which yielded 3% Na_2O from chemical analysis, was calcined at 760°C and then exchanged again with ammonium sulfate solution. It was finally calcined at 820°C for 5 hr. Chemical analysis showed a SiO_2/Al_2O_3 ratio of 5.4 and a Na_2O content of 0.2–0.3%.

Adsorption was measured by an ordinary volumetric adsorption system. A sample of about 1 g, which was contained in a Vycor vessel, was evacuated first at 10^{-6} Torr and at 350°C overnight. It was then cooled down to desired temperatures for adsorption measurement between a temperature range of 0 to 145°C and a pressure range of 5 to 300 Torr. Temperatures above 50°C were controlled by a furnace, while at 0 and 25°C they were maintained by an ice bath and a water bath, respectively. Pressures were measured by a mercury manometer. At the end of a series of adsorption measurements for Kr, N_2, and CO, the sample was then evacuated overnight at 800°C before another series of measurements. In all cases, reversible adsorption was observed and reproducibility of data was checked. The surface area of the sample was measured by nitrogen adsorption at —195°C.

RESULTS AND DISCUSSION

Adsorption isotherms were all linear on the sample evacuated at 350°C except in the case of carbon monoxide, in which slight concavity toward the pressure axis was observed below 25°C. Henry's law constants for all isotherms are listed in Table 1. When the sample was evacuated at 800°C, the adsorption was practically unchanged for krypton, slightly increased for nitrogen, but increased at least 50% for carbon monoxide. The adsorption isotherms of carbon monoxide were concave at pressures lower than 50 Torr, as shown in Fig. 1.

TABLE 1

HENRY'S LAW CONSTANTS OF ADSORPTION ON ULTRASTABLE Y ZEOLITE EVACUATED AT 350°C

Henry's law constant, $K_H \times 10^3$ (cc/g-Torr).

T (°K)	Kr	N_2	CO
273	6.1	3.1	6.2
298	3.9	1.8	3.4
340	—	0.9	1.5
374	1.2	0.5	0.9

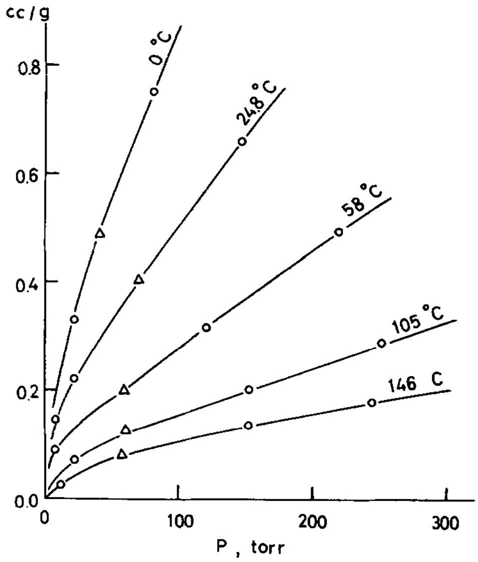

FIG. 1. Adsorption isotherms of carbon monoxide on ultrastable Y zeolite evacuated at 800°C: (○) adsorption; (△) desorption.

Isosteric heats of adsorption were determined from the slope of Clausius-Clapeyron plots. The variation of heats with respect to coverages from 0.07 to 0.5% is shown in Fig. 2. As shown, for the sample evacuated at 350°C, the isosteric heats of adsorption are virtually independent of the coverage and are 3.4, 3.8, and 4.3 kcal/mole

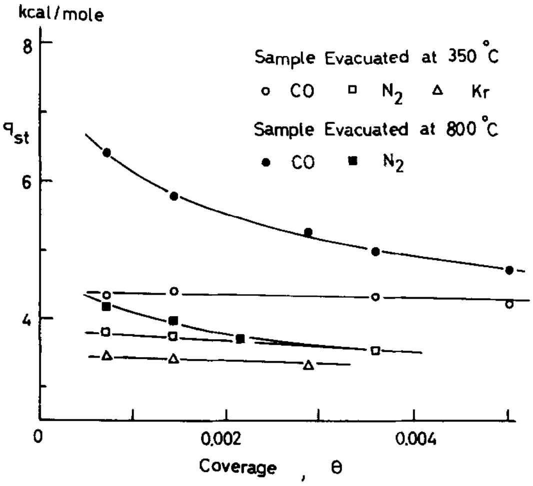

FIG. 2. Isosteric heats of adsorption as a function of surface coverage on ultrastable Y zeolite.

for krypton, nitrogen, and carbon monoxide, respectively. After evacuation at 800°C, the heat of CO adsorption on the ultrastable Y zeolite increased to 6.4 kcal/mole at 0.1 cc(STP)/g, which corresponds to 0.07% of the surface coverage. However, no heat value comparable to that found on amorphous silica–alumina was obtained. The heat was increased only slightly for nitrogen at lower coverages but remained almost unchanged for krypton. The nitrogen adsorption isotherms at —195°C were identical for the sample after two heat treatments, having a plateau value of 140 cc(STP)/g or 610 m^2/g, if 16.2 $Å^2$ was used for the area of a nitrogen molecule. After evacuation at 800°C, the weight loss was only 5.3% of the original sample.

Obviously, the specific adsorption sites similar to those observed on amorphous silica–alumina were not present on the crystalline material, at least within the same surface coverages. However, this does not rule out the possibility that they could be inside the sodalite cages and were not accessible to carbon monoxide, or that they were exposed to supercages but in a much smaller fraction. It must be noted that by the study of ammonia adsorption on decationized Y zeolite, Benson, Ushiba, and Boudart (*2*) indicated the absence on the zeolites of surface sites capable of binding ammonia more strongly than silica–alumina gels. The main difference between the two is that the crystalline material has a wide range of intermediate energetic sites where on the amorphous material, the isosteric heat of ammonia adsorption drops steeply from an initial value of 40 kcal/mole to values less than 10 for a surface coverage of 1×10^{14} $molecules/cm^2$.

The heats of adsorption of krypton and nitrogen on the ultrastable Y zeolite are very similar to those of the amorphous material. An increase of about 2 kcal/mole for CO adsorption following evacuation at 800°C suggests a minor contribution of electrostatic interaction, most likely by a quadrupole force. In fact, structural defects due to the removal of oxygen and aluminum atoms from the framework were observed (*3*). These could be responsible for the slight increase in heat of CO adsorption and might be occupied by hydroxyl groups which were not removed by evacuation at 350°C.

Egerton and Stone (*4*) investigated the adsorption of carbon monoxide on CaY as well as on HY zeolites. It was concluded that the specific adsorption was a property of the bivalent cation and was not due to the hydroxyl groups or protons present in HY. However, when NH_4Y was decomposed at temperatures above 500°C, strong CO adsorption was observed. It was presumably due to the interaction of the weak base CO with the Lewis sites of the sample, although, no detailed information concerning the heat of adsorption and the amount of adsorption was given.

ACKNOWLEDGMENTS

The ultrastable Y zeolite sample was kindly provided by Dr. P. K. Maher of W. R. Grace Company. Special thanks are due to Professor P. H. Emmett for his interest and encouragement of this work and to Dr. J. Scherzer for his helpful discussion. This work was supported by Atomic Energy Commission through Grant No. AT (30-1) - 2008.

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