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Magnesium Oxide as a Catalyst

I. Acid-Base Properties of Magnesium Oxide Surface

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The surface of magnesium oxide was investigated from the viewpoint of acid-base properties. Five specimens ignited at 500°, 600°, 800°, 1000°, and 1300° were examined. Specific surface, residual water content, and *pK* of the surface were determined for each specimen. Adsorption and desorption isotherms for water vapor and ammonia were determined at various pressures and temperatures. The adsorption of water vapor and ammonia were found to be irreversible and reversible processes, respectively. The ammonia adsorption isotherms were found to be consistent with the Langmuir-type isotherm. The heat of adsorption of ammonia was calculated; the value indicates that there are very weak interactions between the adsorption centers and adsorbate molecules.

Magnesium oxide has been used as catalyst for numerous technological processes.

Of various metal oxides, pure magnesium oxide has been found to be the most active in the reactions of hydrogen exchange between alcohols and aldehydes (*1–6*), esters (*7*), or olefins (*8*).

The mechanism of catalytic action of magnesium oxide is, however, still insufficiently elucidated. In particular, there are no data concerning the catalytic behavior of magnesium oxide in acid-base reactions.

It is the purpose of the present work, forming the first part of the series devoted to catalytic properties of magnesium oxide, to investigate the acid-base properties of the surface of magnesium oxide which was prepared by decomposition of magnesium hydroxide under varying conditions. The acid strength of the magnesium oxide surface is strongly dependent on the presence of interfacial hydroxyl groups forming on chemisorption of water vapor. For this reason, the present investigations are concerned with both hydrated and nonhydrated magnesium oxide surfaces. The acid strength of the magnesium oxide surface was measured by the Walling indicator-adsorption technique (*9*) and by adsorption of gaseous ammonia.

EXPERIMENTAL

Materials

Magnesium hydroxide was precipitated from aqueous magnesium nitrate with carbon-dioxide–free ammonia and dried at 120° and 0.2 atm. Ignition loss or water content was found to be 30.24% (Calcd. for $Mg(OH)_2:H_2O$, 30.85%).

For preparation of magnesium oxide, 50 g of hydroxide was heated 1 hr at 450° and then ignited for 3 hr at 500°, 600°, 800°, 1000°, or 1300°. The ignited specimen was allowed to cool in air to about 200° and was immediately placed in a bottle with ground-in stopper; the bottle was stored in a phosphorus pentoxide desiccator.

Specific Surface

For the specimens ignited at 500°, 600°, 800°, 1000° and 1300°, the specific surface, evaluated from the BET nitrogen adsorption isotherms (five experimental points; nitrogen molecule cross section taken as 16.1 Å^2), was 128.6, 122.6, 52.0, 32.7, and 23.2 m^2/g, respectively.

Surface Acid Strength

The Walling technique (*9*) involving adsorption of acid-type indicators from anhydrous benzene was used (Table 1).

TABLE 1
INDICATORS

Indicator	pK_a	pH transition interval
Bromphenol blue	3.8	3.0 ÷ 4.6
Methyl red	5.2	4.4 ÷ 6.2
Bromcresol purple	6.0	5.2 ÷ 6.8
Bromthymol blue	7.1	6.2 ÷ 7.6
Phenolphthalein	9.3	8.5 ÷ 10.5

The surface acid strength is plotted against the ignition temperature in Fig. 1.

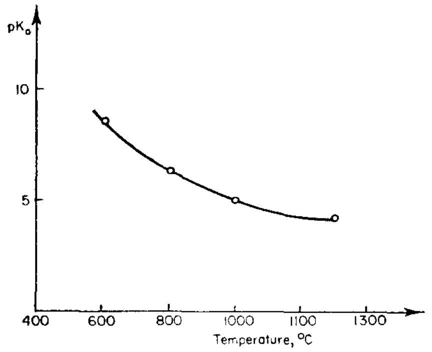

FIG. 1. *pK* of MgO surface vs. ignition temperature.

Residual Water

The magnesium hydroxide prepared was ignited for 3 hr at 500°, 600°, 800°, 1000°, or 1300°. The 1300° specimen, ignition loss 31.56%, was assumed to contain no residual water; other specimens had lower ignition losses. The respective differences were used for calculation of the residual water contents in the specimens (Fig. 2).

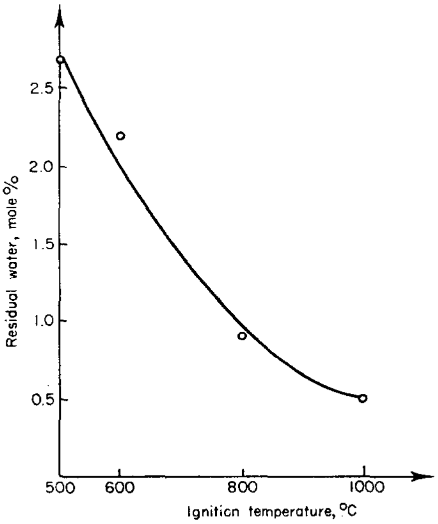

FIG. 2. Residual water content vs. ignition temperature.

Sorption of Water Vapor

The apparatus described earlier (*10*) was used for studying the adsorption of water vapor on magnesium oxide (adsorbate weighing accuracy: ±0.0004 g). The specimen was heated *in vacuo* at 70° to constant weight; water vapor was introduced at 17.5 mm Hg and, after establishment of equilibrium, the adsorbate was weighed. The adsorption proceeded too rapidly to follow the kinetics of the process. The temperature was then decreased to 60° and, at equilibrium, the adsorbate was weighed; the determinations were continued up to 20° and then the temperature was increased and desorption was measured at the same temperatures. The whole measurement was carried out at a constant water vapor pressure of 17.5 mm Hg. After the equilibrium had been reestablished at 70°, water vapor was removed and the specimen was degassed to constant weight. The adsorbate (in terms of H_2O molecules/m^2) is plotted against adsorption temperature in Figs. 3–7.

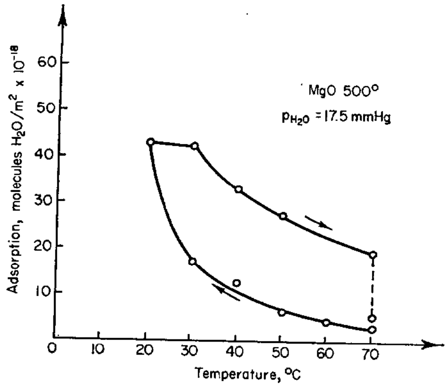

Fig. 3. Molecules of H_2O adsorbed on, and desorbed from MgO ignited at 500° vs. adsorption temperature.

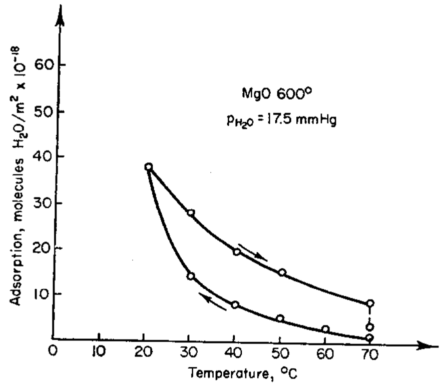

Fig. 4. Molecules of H_2O adsorbed on, and desorbed from MgO ignited at 600° vs. adsorption temperature.

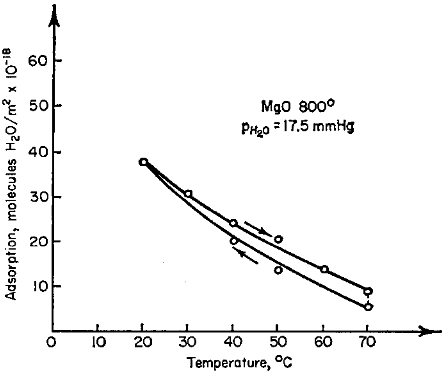

Fig. 5. Molecules of H_2O adsorbed on, and desorbed from MgO ignited at 800° vs. adsorption temperature.

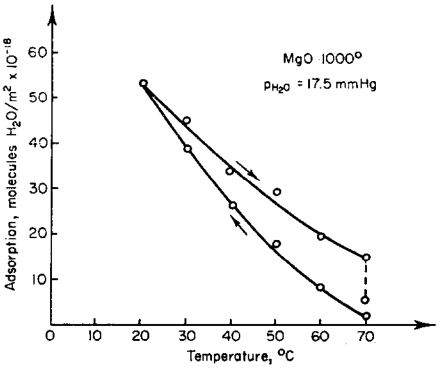

Fig. 6. Molecules of H_2O adsorbed on, and desorbed from MgO ignited at 1000° vs. adsorption temperature.

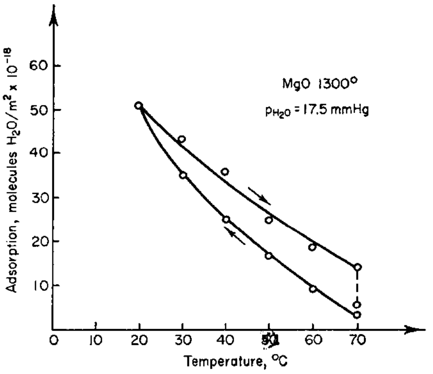

Fig. 7. Molecules of H_2O adsorbed on, and desorbed from MgO ignited at 1300° vs. adsorption temperature.

Adsorption of Ammonia

1. Preparation of ammonia for adsorption. Aqueous ammonia was refluxed with calcium oxide (for removal of carbon dioxide) and the evolving gaseous ammonia was passed through calcium oxide vessels and stored over anhydrous calcium oxide for 48 hr. Residual water was gettered with metallic sodium dispersed in a vessel.

2. Pretreatment of magnesium oxide. The magnesium oxide specimens prepared as described above and used for adsorption of ammonia were pretreated in two ways:

(A) Magnesium oxide was degassed for 2 hr at 300° and at a final pressure of 10^{-4} mm Hg.

(B) Magnesium oxide was degassed at 70°, water vapor was introduced at 17.5 mm Hg, the temperature was decreased to 20°, and the specimen was degassed for 2 hr at 100° and at a final pressure of 10^{-4} mm Hg.

3. Adsorption of ammonia. The adsorption was studied in a conventional BET

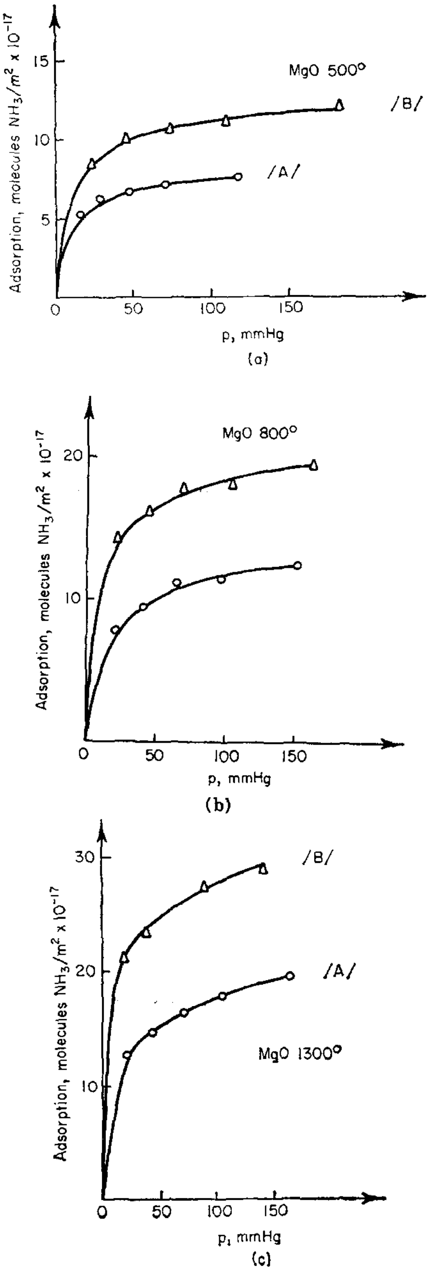

FIG. 8. Molecules of NH_3 adsorbed at 20° on MgO; ignited at (a) 500°; (b) 800°; (c) 1300° vs. pressure of NH_3. A, nonhydrated MgO; B, prehydrated MgO.

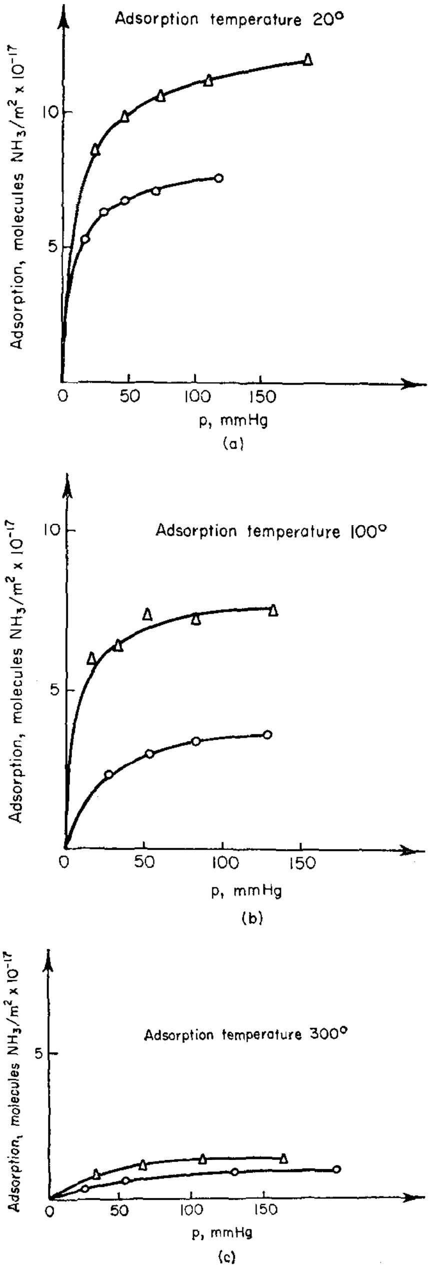

FIG. 9. Molecules of NH_3 adsorbed at (a) 20°, (b) 100°, (c) 300° on MgO, ignited at 500° vs. pressure of NH_3. A, nonhydrated MgO; B, prehydrated MgO.

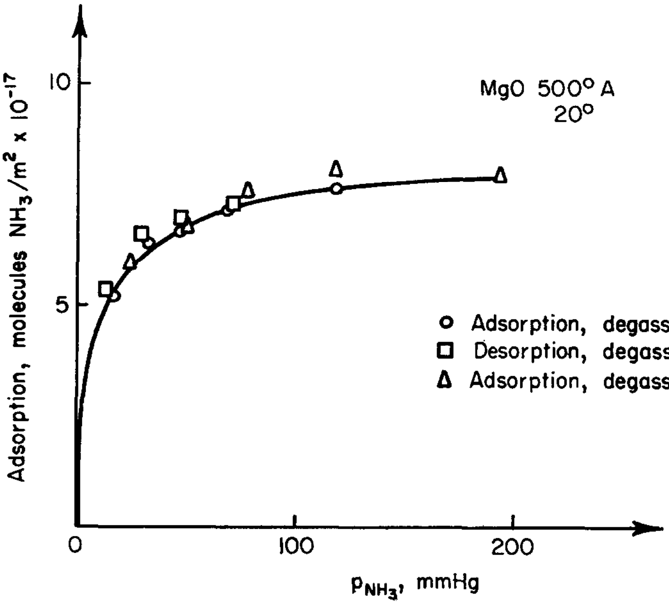

FIG. 10. Adsorption and desorption of NH_3 on MgO ignited at 500°, Specimens A. Dependence between adsorption and degassing temperature.

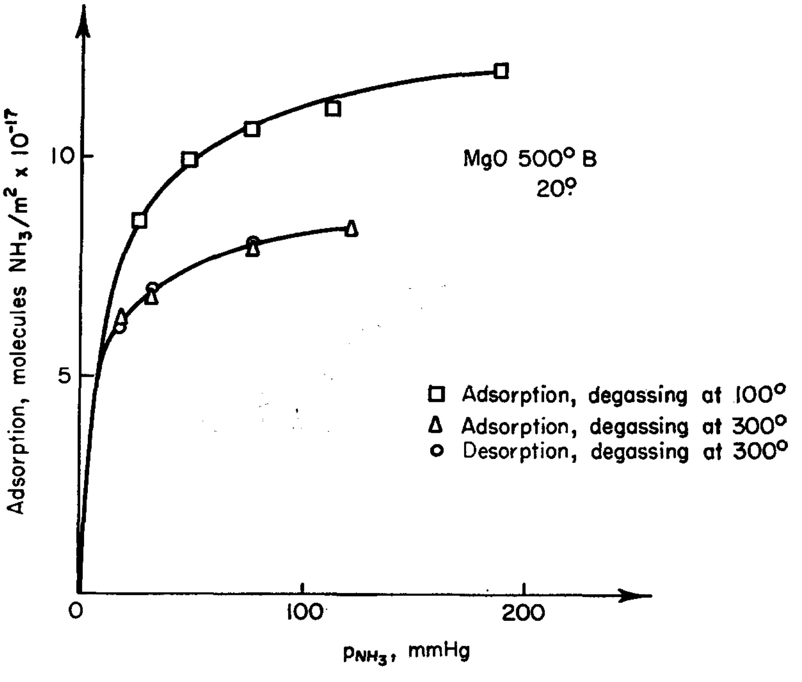

FIG. 11. Adsorption and desorption of NH_3 on MgO ignited at 500°, Specimens B. Dependence between adsorption and degassing temperature

apparatus at pressures of 20–100 mm Hg and temperatures of 20–300°. The adsorbate was recorded in terms of ammonia molecules per square meter. The ammonia adsorption isotherms (at 20°) are presented for specimens A and B ignited at various temperatures (Fig. 8) and at 500° (Fig. 9) for adsorption temperatures of

20°, 100°, and 300°. Figure 10 shows that for Specimen A ignited at 500° the ammonia adsorbate is unrelated to the temperature of degassing; the desorption curve is also presented. For Specimen B ignited at 500° (Fig. 11) the ammonia adsorbate is plotted against the degassing temperature; the desorption curve is also included.

In each case the data were found to be reproducible by the Langmuir isotherm equation

$$a = a_m[\lambda_p/(1 + \lambda_p)]$$

where a is the number of molecules adsorbed per square meter; a_m, the number of molecules adsorbed per square meter at saturation; λ, the coefficient of adsorption; and p, the gas pressure.

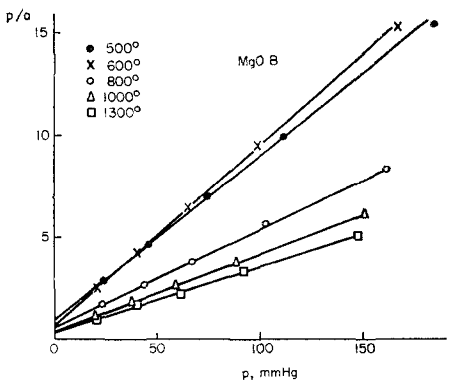

FIG. 13. p/a vs. gas pressure for Specimens B ignited at various temperatures.

According to this equation, the p/a ratio should be a linear function of pressure p. This is illustrated in Figs. 12 and 13 for Specimens A and B ignited at various temperatures. Constants a_m and λ were estimated by the least-squares method (Tables 2 and 3). Table 2 contains the data con-

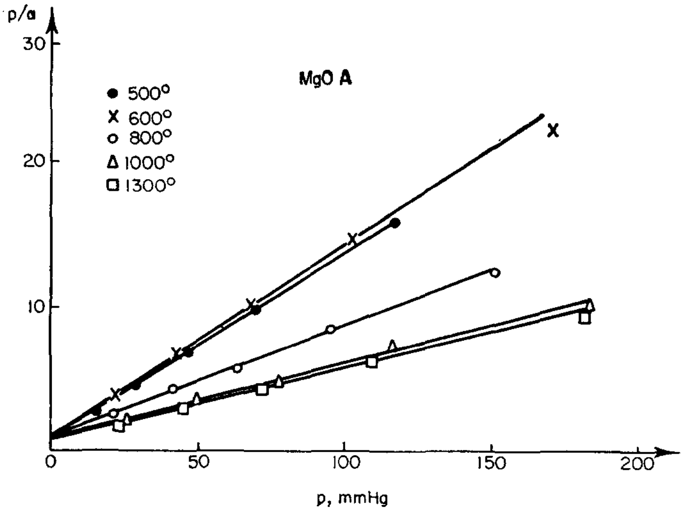

FIG. 12. p/a vs. gas pressure for Specimens A ignited at various temperatures.

TABLE 2

COEFFICIENTS OF ADSORPTION (λ) AND THE NUMBER (a_m) OF MOLECULES ADSORBED PER SQUARE METER AT SATURATION ON SPECIMENS A AND B IGNITED AT 500°C FOR VARYING ADSORPTION TEMPERATURES

Specimen A, 500°			Specimen B, 500°		
Adsorption temp (°C)	$\lambda \times 10^2$ (mm Hg)$^{-1}$	$a_m \times 10^{-17}$ NH_3 molecules	Adsorption temp (°C)	$\lambda \times 10^2$ (mm Hg)$^{-1}$	$a_m \times 10^{-17}$ NH_3 molecules
20	12.1	8.0	20	7.3	12.8
50	6.0	8.2	50	21.0	10.0
100	4.3	4.4	100	17.8	7.8
200	2.6	1.7	200	—	—
300	1.6	1.3	300	4.4	1.5

TABLE 3

COEFFICIENTS OF ADSORPTION (λ) AND THE NUMBER (a_m) OF MOLECULES ADSORBED PER SQUARE METER AT SATURATION ON SPECIMENS A AND B ADSORBED AT 20°C FOR VARYING IGNITION TEMPERATURES

Specimen A			Specimen B		
Ignition temp (°C)	$\lambda \times 10^2$ (mm Hg)$^{-1}$	$a_m \times 10^{-17}$ NH_3 molecules	Ignition temp (°C)	$\lambda \times 10^2$ (mm Hg)$^{-1}$	$a_m \times 10^{-17}$ NH_3 molecules
500	12.1	8.0	500	7.3	12.8
600	7.4	8.3	600	13.1	11.4
800	5.8	13.8	800	9.5	20.5
1000	4.6	20.5	1000	11.9	25.8
1300	5.1	21.3	1300	11.0	30.5

cerning Specimens A and B ignited at 500°, for varying adsorption temperatures. Table 3 lists the 20° adsorption data for Specimens A and B ignited at various temperatures.

DISCUSSION

The Walling-type acid strength ranges from $pK = 8.5$ for the 600° specimen to $pK = 5$ for the 1300° specimen.

The surface acidity as determined by the adsorption of indicators from nonpolar solutions, is the resultant of both the acid and the basic center contributions. The increase in the surface acidity of magnesium oxide as the ignition temperature is raised may be attributed to either an increase in the number of the acid or decrease in the number of the basic centers.

Adsorption of water vapor on magnesium oxide has already been investigated by Razouk and Mikhail (*11*). The present investigations were intended to examine the behavior of the oxide pretreated with water vapor before adsorption of ammonia. The curves in Figs. 3–7 exhibit that, as has already been reported (*12*), water vapor undergoes, at least in part, an irreversible adsorption. This appears to be associated with chemisorption, which gives rise to the formation of interfacial hydroxyl groups. Preliminary IR spectral studies also speak in favor of this suggestion.

Whether on Specimen A degassed at 300° and nonhydrated or Specimen B prehydrated, ammonia—in contract to water vapor—is sorbed reversibly over the entire pressure and temperature ranges investigated. Hydration is seen to result in increased adsorption of ammonia, which indicates that the interfacial OH groups become centers of adsorption.

The conformity of the ammonia adsorption isotherms to the Langmuir equation indicates that virtually the surface of magnesium oxide is homogeneous or quasi-homogeneous (in the Balandin sense) toward ammonia. It should be noted that the a_m value, i.e. the number of ammonia molecules adsorbed at saturation, is in each case lower than that required to coat the BET surface in a monolayer. The portion of the surface involved in adsorption of ammonia attains maximum 30%. The a_m value is therefore a measure of the number of adsorption centers per unit surface area.

The percentage content of the ammonia molecules in the adsorbate was calculated in relation to the magnesium oxide surface assumed to be coated completely in a monomolecular layer. The latter value was estimated by assuming the magnesium oxide to have the rock-salt–type lattice with the lattice constant $a = 4.20$ Å. Faces (100), (110), and (111) were assumed to occur equally frequently in the magnesium oxide crystals, and the number of the oxygen ions per square meter of surface area was calculated as 1.08×10^{19}. This number corresponds also to the maximum number of the adsorption centers for ammonia.

Table 3 shows that this number increases as the ignition temperature is increased. This increase parallels the rise in surface acid strength as determined after Walling.

The adsorption of ammonia on the specimens ignited at 500°, hydrated and nonhydrated, was studied within 20–300°. For the dehydrated specimens, the adsorption coefficient λ diminished with increasing adsorption temperature according to the equation

$$\lambda = \lambda_0 e^{Q/RT}$$

The heat of adsorption, $Q = 2.3$ kcal/mole, evaluated from this equation, indicates that there are weak interactions between the adsorption centers and adsorbate molecules, weaker even than the forces causing liquefaction of ammonia.

For rehydrated specimens, the data were too disperse to be conclusive.

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