JOURNAL OF CATALYSIS 7, 67–75 (1967)

Magnesium Oxide as a Catalyst

II. Acid-Base Properties of the Magnesium Oxide Surface

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Received February 22, 1966; revised June 30, 1966

The surface of magnesium oxide was investigated in terms of acid-base properties. Adsorption of carbon dioxide was studied at various temperatures and pressures and was found to obey the Langmuir isotherm. Potentiometric titration studies on magnesia in pyridine as solvent revealed the presence of centers of various acidity. Infrared spectra of steamed and deuterated magnesia specimens showed the presence of free and combined hydroxyl groups at the surface of specimens ignited up to 600°C. As the ignition temperature was raised (up to 1300°C), the free—but not combined—hydroxyl groups disappeared.

The previous paper (*1*) has reported the results of investigations on the magnesium oxide surface, carried out by the Walling indicator adsorption technique and by adsorption of water vapor and ammonia.

The present paper sets out to describe further investigations on magnesium oxide, involving adsorption of carbon dioxide, potentiometric titration in a nonsqueous solvent, and IR absorption spectra of various pretreated and deuterated specimens.

ADSORPTION OF CARBON DIOXIDE

The carbon dioxide used for adsorption investigations was obtained by treating C.P. calcium carbonate with C.P. hydrochloric acid (1:1); the evolving dioxide was passed through an absorption vessel filled with saturated sodium bicarbonate for removal of hydrogen chloride and then through silica gel and phosphorus pentoxide U-tubes. The dioxide was dried by being stored for 24 hr over phosphorus pentoxide.

Two series, A and B, of magnesium oxide specimens, each obtained by thermal decomposition of the hydroxide and subsequent ignition at 500°, 600°, 800°, 1000°, and 1300°C, were used for investigations.

Series A specimens, MgO-A, were not pretreated before adsorption measurements and were carefully precluded from the access of atmospheric water vapor. Series B specimens, MgO-B, were presteamed at 70°C. Preparative details and certain data concerning the specimens of either series have been reported in Part I (*1*).

Adsorption was measured in a conventional BET apparatus at 20° and 300°C. Carbon dioxide pressure was varied within 1–100 mm Hg. Before the measurement at 20°C, the specimen was degassed for 3–5 hr until the pressure fell to 5×10^{-4} mm Hg at 100°C. Before the adsorption at 300°C, the specimen was degassed at the experimental temperature also up to 5×10^{-4} mm Hg.

At either temperature, the Langmuir adsorption isotherm was found to be a good fit

$$a = a_m[\lambda p/(1 + \lambda p)] \qquad (1)$$

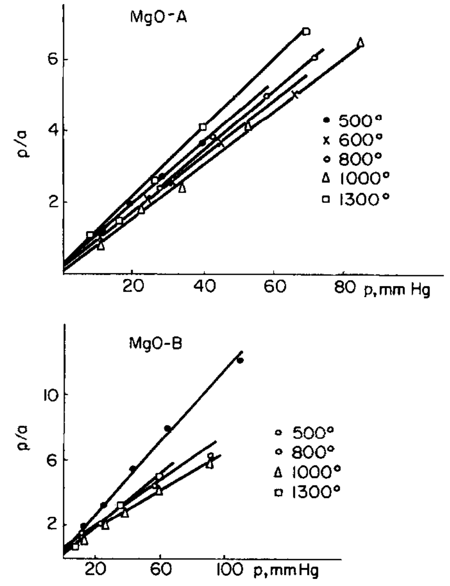

FIG. 1. CO_2 adsorption at 20°C, p/a vs. pressure for specimens MgO-A and MgO-B ignited at various temperatures.

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

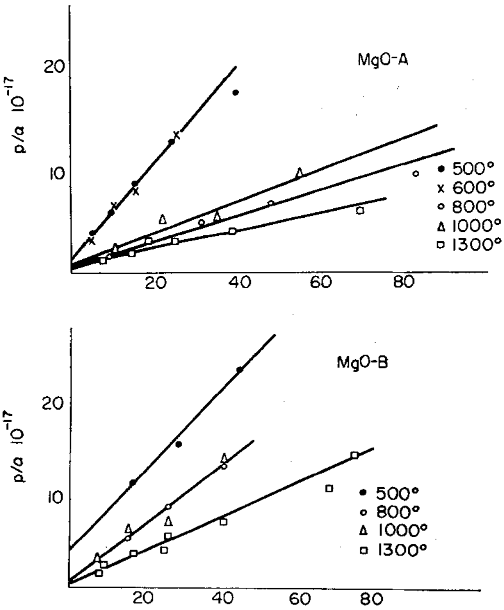

FIG. 2. CO_2 adsorption at 300°C, p/a vs. pressure for specimens MgO-A and MgO-B ignited at various temperatures.

By Eq. (1), the ratio (p/a) should be a linear function of pressure p. The relevant (p/a) vs. p plots for adsorptions at 20° and 300°C are given in Figs. 1 and 2. The plots were used for evaluation of the constants a_m and λ in the Langmuir equation by the least-squares method (Tables 1 and 2). Also, the statistical errors of the values were estimated.

TABLE 1
MgO-A

Ignition temp. (°C)	$a_m \times 10^{-17}$ (molecules CO_2/m^2)	
	20°C	300°C
500	12.6 ± 0.2	2.6 ± 0.2
600	14.1 ± 0.4	2.0 ± 0.2
800	12.3 ± 0.2	9.6 ± 0.6
1000	13.6 ± 0.5	9.0 ± 1.7
1300	10.6 ± 0.3	13.2 ± 1.2
Weighted mean	12.4 ± 0.4	—

As evident from Tables 1 and 2, the error in a_m evaluated for 20° and 300°C amounts to a few and to more than 10%, respectively. On the other hand, the error of the adsorption coefficient λ was much larger and often exceeded 100%. For this reason, no λ values are listed in the Tables.

TABLE 2
MgO-B

Ignition temp. (°C)	$a_m \times 10^{-17}$ (molecules CO_2/m^2)	
	20°C	300°C
500	9.1 ± 0.3	4.3 ± 1.1
600	—	—
800	16.0 ± 0.7	5.3 ± 1.4
1000	16.7 ± 0.5	4.6 ± 0.9
1300	12.4 ± 0.2	6.5 ± 1.0
Weighted mean	12.2 ± 1.3	5.2 ± 0.5

PROTON ACIDITY OF THE MAGNESIA SURFACE AS DETERMINED BY POTENTIOMETRIC TITRATION

For determination of proton, or Bronsted, acidity, magnesium oxide suspended in anhydrous pyridine was titrated potentiometrically with potassium methoxide dissolved in anhydrous benzene in the presence of a platinum/silver chloride electrode system. In this determination it was assumed that the protophilic medium, pyridine, would abstract a proton from the magnesia surface to yield a relatively strong acid, $C_5H_6N^+$, titratable with a base stronger than pyridine.

Before titration, the MgO-A specimen was dried 4 hr over silica gel in a vacuum desiccator at 80°C and 18 mm Hg. Five MgO-A specimens preignited at 500°, 600°, 800°, 1000°, and 1300°C were examined.

The magnesia titration curves and, for comparison, the curve for titration of 0.1 *N* benzoic acid in pyridine are given in Fig. 3.

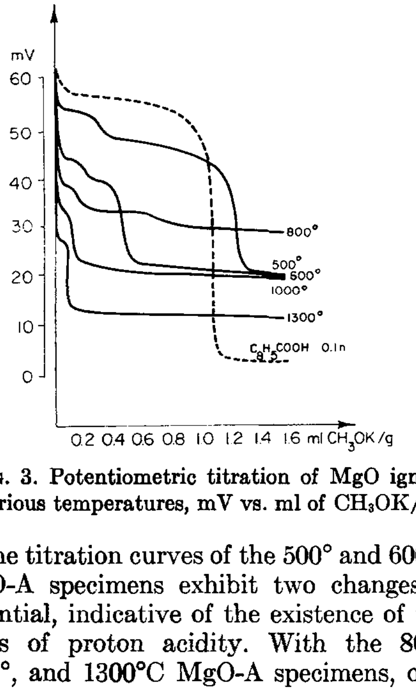

FIG. 3. Potentiometric titration of MgO ignited at various temperatures, mV vs. ml of CH_3OK/g.

The titration curves of the 500° and 600°C MgO-A specimens exhibit two changes of potential, indicative of the existence of two kinds of proton acidity. With the 800°, 1000°, and 1300°C MgO-A specimens, only one potential change was obtained; the higher was the specimen ignition temperature, the greater was the potential change and, so therefore, the greater was the strength of the resulting acid. The acidity, converted into the number of H^+ ions per square meter magnesia surface area, is given in Table 3.

The increase in the potential change with the magnesia ignition temperature indicates a simultaneous rise of the surface acid strength. This is consistent with our earlier finding (*1*) that, as the magnesia ignition temperature was increased, the quantity of the ammonia molecules adsorbed per unit area rose, and the strength of the resulting surface acid did likewise, as found by the indicator adsorption technique in nonpolar solutions.

The increase of the surface acid strength may be a result of interactions between various types of acidity centers, beneficial to an increased hydrogen mobility in the pyridine medium.

The second change of potential, obtained only with the 500° and 600°C specimens, attests to the presence of another kind of acidity centers. In comparison with the above-described acidity, the new centers are endowed with much more mobile hydrogens, as deduced from the potential's change being relatively large and well-defined, and their concentration appears to be highly dependent on the magnesia ignition temperature. As the ignition temperature is increased, the centers disappear and, in the 800°C specimen, are no longer detectable.

On the assumption that the centers are derived from the surface OH groups, the percentage of the remaining OH groups was calculated with reference to the maximum possible number of such OH groups at the surface. For the 500°C specimen, the value is 5.05% and for the 600°C specimen only 1.95%.

The data in Table 3 show that the numbers of acid centers per unit area, evaluated from the first potential change, differ only slightly between the individual specimens. It is solely between the 500° and 600°C specimens, for which the values are almost

TABLE 3

POTENTIOMETRIC TITRATION OF MgO

Ignition temperature	500°	600°	800°	1000°	1300°	
I change of potential	1.25	1.26	1.96	1.92	1.98	$H^+/m^2 \times 10^{17}$
II change of potential	5.43	2.11	—	—	—	$H^+/m^2 \times 10^{17}$

identical, and the remaining specimens, that the difference is larger.

This fact may be attributed to the greater specific surface (*1*), and thus to the higher fraction of micropores accessible to the small molecules of nitrogen used for specific surface determinations, but not to the relatively large pyridine molecules.

It follows therefore that the type (I) acidity is not related to the ignition temperature. The acidity may be due to water absorbed physically during handling of the specimen. This conclusion was confirmed by preliminary experiments with magnesia ignited at 500° and 600°C and not dried directly before use but stored in a usual desiccator over silica gel for prolonged periods of time. On titration of these specimens the first potential change shifted to the right, and the second potential change remained unshifted for the 600° specimen and slightly shifted to the left for the 500°C specimen. The shifts of the first potential change are small (0.05 and 0.03 ml) and thus inconclusive.

INFRARED SPECTRA

Spectra were taken on a Zeiss UR-10 spectrophotometer. The specimens were mulled with hexachlorobutadiene and applied as a film ~0.3 mm thick. The results are given as absorption vs. wavenumber plots.

The spectra were recorded for (a) original, (b) preignited at various temperatures and nonsteamed (MgO-A), (c) preignited and steamed (MgO-B), (d) MgO-A degassed in high vacuum, and (e) MgO-A deuterated magnesia specimens.

The spectrum of the original magnesia hydroxide specimen, from which the other series of specimens were prepared, is given in Fig. 4.

At short wavelengths, about 3700 cm^{-1}, an intense band occurs. This is consistent with the spectroscopic data of Benesi (*2*), who established the presence of a single intense band in the spectrum of a synthetic magnesium oxide. The 3700-cm^{-1} band is attributed to valence-stretching vibrations of free hydroxyl groups.

The spectra of the MgO-A specimens, ignited at 500°–1300°C, are given in Fig. 5. The 500° and 600°C specimens produced a narrow band at 3730 cm^{-1}, overlapped by a broad band with maximum at 3400 cm^{-1}. In the spectra of the specimens ignited at higher temperatures, the 3730-cm^{-1} band disappears and the 3400-cm^{-1} band diminishes in intensity.

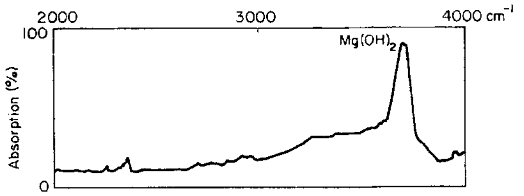

FIG. 4. IR absorption spectra of $Mg(OH)_2$.

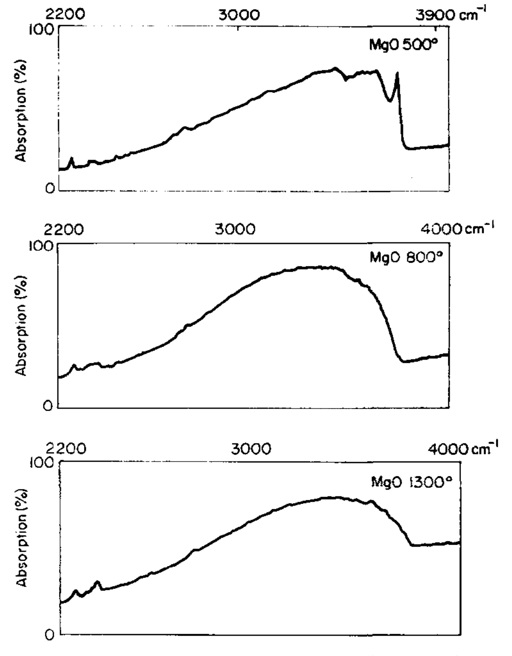

FIG. 5. IR absorption spectra of MgO specimens (A) ignited at various temperatures.

The spectra of the ignited and steamed MgO-B specimens are shown in Fig. 6. They are strictly similar to the spectra produced by the MgO-A specimens, slight intensity differences being attributable to possible variations in film thickness.

The 3730-cm^{-1} band in the 500° and 600°C specimen spectra undoubtedly indicates the presence of hydroxyl groups in these preparations. The 3400-cm^{-1} band may well be

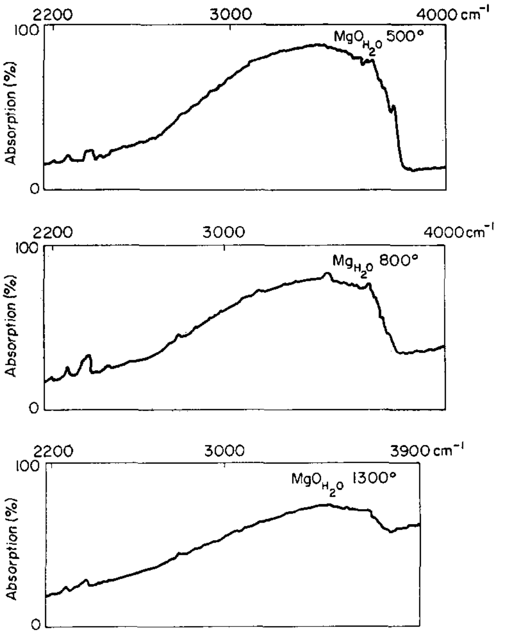

FIG. 6. IR absorption spectra of MgO specimens (B) ignited at various temperatures and hydrated.

attributed to hydrogen-bonded hydroxyl groups. Such bands have been found in the spectra of silica gels (*3*, *4*) and alumina (*5*, *6*).

The hydroxyl groups in the magnesia preparations may occur both in the body and at the surface of the crystallites, either as the residual groups which failed to undergo condensation with elimination of water during decomposition of the hydroxide or as the groups of water vapor readsorbed at the surface. For establishment of the percentages of the surface and interior hydroxyl groups, experiments were carried out with MgO-A specimens preignited at 600°, 1000°, and 1300°C and degassed in vacuum. The procedure was as follows: The specimen, about 1 g, was heated for 2 hr in a glass tube at 300°C and 10^{-4} mm Hg and then the tube was sealed off under vacuum. The specimen was examined spectroscopically with due precautions to minimize the time of contact with atmospheric air. The spectra thus prepared (Fig. 7) do not differ from those of nondegassed specimens, but the intensity of the broad band characteristic of combined OH groups is markedly reduced upon degassing.

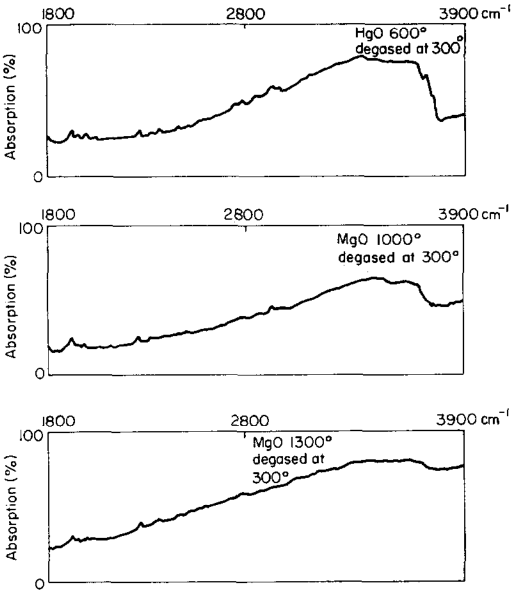

FIG. 7. IR absorption spectra of MgO specimens (A) ignited at various temperatures and degassed at 300°C.

The 600°, 1000°, and 1300°C MgO-A specimens were deuterated and examined spectroscopically. The procedure was as follows: The specimen, about 1 gm, was

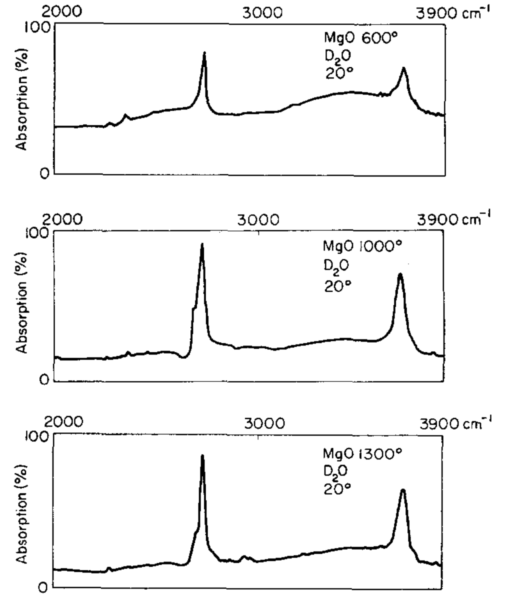

FIG. 8. IR absorption spectra of MgO specimens (A) ignited at various temperatures and deuterated at 20°C.

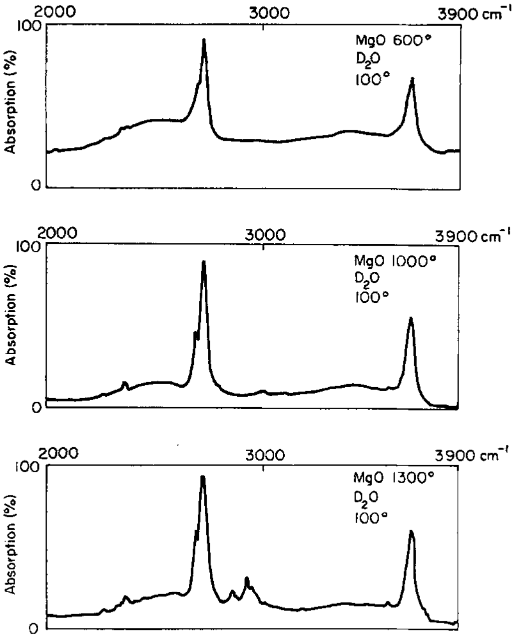

Fig. 9. IR absorption spectra of MgO specimens (A) ignited at various temperatures and deuterated at 100°C.

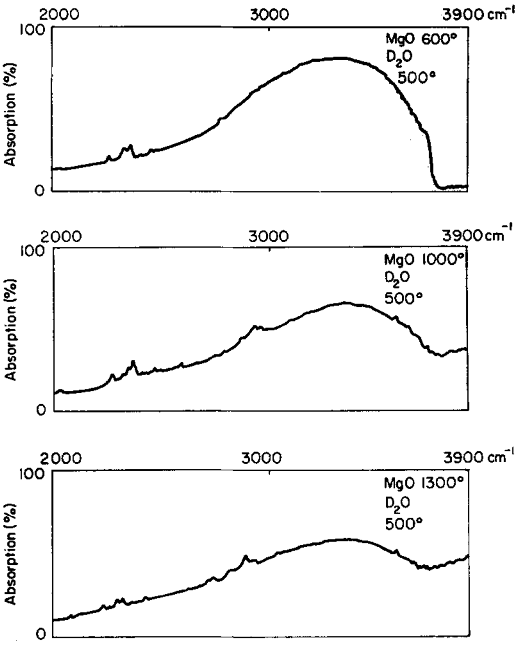

Fig. 10. IR absorption spectra of MgO specimens (A) ignited at various temperatures and deuterated at 500°C.

degassed in a glass tube at room temperature until a pressure of 10^{-8} mm Hg was obtained; then deuterium oxide vapors (the heavy water used was at least 95%) were introduced at pressures of 0.02, 1, 5, and 0.05 atm, the tube was sealed off and the contents were heated 2 hr at 20°, 100°, 150°, and 500°C, respectively. The spectra of the deuterated specimens are presented in Fig. 8.

In the spectra of the specimens deuterated at 20°, 100°, and 150°C the broad 3400-cm^{-1} band has practically completely disappeared, the narrow 3730-cm^{-1} band characteristic of free hydroxyl groups has markedly diminished in intensity, and a new narrow band, 2720 cm^{-1}, characteristic of free OD groups has appeared. The spectra of the specimens deuterated at 500°C are strictly similar to those of nondeuterated specimens. They exhibit no OD, but only free and combined OH bands.

Discussion

In the preceding paper (*1*) attention was turned to the presence of residual water in magnesia preparations obtained by thermal decomposition of magnesium hydroxide and subsequent ignition of the oxide. The residual water was determined gravimetrically. The present spectral investigations allow some conclusions to be drawn concerning the nature of the residual water.

The 3730-cm^{-1} band in the spectra of the 500° and 600°C specimens and the second (II) change of potential during potentiometric titration indicate the presence of free hydroxyl groups. The broad 3400-cm^{-1} band and the first change of potential are most likely associated with the presence of water adsorbed on the specimen surface. This is in agreement with Anderson's (*8*) suggestion.

Comparison of the spectra in Figs. 5 and 6 allows the conclusion that treatment of the magnesia specimens with water vapor at not too high temperatures (up to 70°C) has led neither to formation of surface hydroxyl groups nor to any marked increase in the concentration of adsorbed water. The constancy of adsorbed water concentration appears to be explicable in terms of the residual water present in the specimens studied in amounts large enough to produce nearly complete monomolecular coverage. On such a surface only physical adsorption may occur. Absorption of radiation by physically adsorbed water, expected to occur in the long-wavelength region (1640 cm^{-1}), was beyond the scope of the present investigations.

The degassing of the specimens at elevated temperatures contributes undoubtedly to a partial removal of adsorbed water from their surface. This in turn results in a reduced intensity of the absorption band, as evident from the comparison of Figs. 5 and 7.

As seen from Fig. 8, deuteration of the specimens at temperatures up to 150°C has led to disappearance of the adsorbed water band and to appearance of the band characteristic of OD stretching vibrations. It should be noted that the spectra of deuterated specimens exhibit no bands characteristic of adsorbed heavy water. In this region, the spectrum of the deuterated specimen is affected neither by the deuteration temperature nor by the pressure of D_2O vapors. The experimental data lead to the conclusion that the 3400-cm^{-1} band is due to the water adsorbed at the surface. This water easily enters into an exchange reaction affording, in the presence of D_2O vapors, free OD groups. It should be emphasized that the mechanism of this exchange is still obscure. Inexplicable is the absence of a band corresponding to D_2O adsorbed at the surface, a counterpart of the 3400-cm^{-1} band characteristic of H_2O adsorbed. It is, after all, still possible that the 3400-cm^{-1} band is not associated with adsorbed water, but is to be ascribed to other causes, such as, e.g., the occurrence of anionic vacancies at the surface. The spectrum of the specimen deuterated at 500°C indicates the lack of any exchange, which also requires individual explanation.

Proceeding to interpretation of the results of adsorption of carbon dioxide, it should be emphasized that, as deduced from the data in Tables 1 and 2, the a_m value, i.e., the number of carbon dioxide molecules adsorbed per square meter at saturation at 20°C, which may be considered a measure of the concentration of basic centers at the surface, ranges within relatively narrow limits. The mean values for the MgO-A and MgO-B specimens are identical, thereby indicating that steaming of the magnesia surface has not resulted in the formation of additional centers of carbon dioxide adsorption. This appears to be compatible with the spectral data indicating that the steaming has led neither to an increase of adsorbed water concentration nor to formation of surface OH groups.

The a_m values obtained from adsorption at 300°C are lower than those for 20°C, a fact indicative either of nonuniformity of the magnesia surface towards adsorption of carbon dioxide or of removal of some amount of carbon dioxide adsorption centers owing to the specimen's having been degassed at an elevated temperature before measurement.

Recently, Krylov *et al.* (*7*) have investigated adsorption and isotopic exchange of carbon dioxide at the magnesium oxide and at the partially dehydrated magnesium hydroxide surfaces. They established the presence of several types of basic centers at the surface of partially dehydrated magnesium hydroxide. These are (a) strongly basic O^{2-} centers which during adsorption are transformed to CO^{2-} ions in agreement with the mechanism postulated by Garner; (b) strongly basic centers derived from the O^{2-} ions adjacent to the surface OH groups; and (c) surface OH groups constituting weakly basic centers.

In the present specimens, the type C centers should be ruled out as a possibility, at least for the specimens ignited at temperatures higher than 600°C in which no free hydroxyl groups were detected. The fact, however, that the number of active centers in adsorption of carbon dioxide is constant, irrespective of the specimen ignition temperature, appears to indicate that in all specimens the same type of active centers is operative, which cannot be identified with surface OH groups.

REFERENCES

1. MALINOWSKI, S., SZCZEPAŃSKA, S., BIELAŃSKI, A., AND STOCZYŃSKI, J., *J. Catalysis* **4,** 324 (1965).

2. BENESI, H. A., *J. Chem. Phys.* **30,** 852 (1959).

3. Fraissard, J., and Imelik, B., *Bull. Soc. Chim. France*, p. 1710 (1963).
4. Davydov, V. Ya., and Kisielev, A. V., *Zh. Fiz. Khim.* **37**, 2593 (1963).
5. Naito, K., *Bull. Osaka Ind. Res. Inst.* **10**, 156 (1959).
6. Uvarov, A. V., *Zh. Fiz. Khim.* **36**, 1346 (1962).
7. Krylov, O. V., Markova, Z. A., Tretiakov, I. I., and Fokina, E. A., *Kinetika i Kataliz* **6**, 128 (1965).
8. Anderson, P. J., Horlock, R. F., and Oliver, J. F., *Trans. Faraday Soc.* **61**, 2754 (1965).