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Basic Sites and Reducing Sites of Calcium Oxide and Their Catalytic Activities

TOKIO IIZUKA, HIDESHI HATTORI, YASUHIRO OHNO,
JUNKICHI SOHMA, AND KOZO TANABE*

Department of Chemistry, Faculty of Science; and Department of Synthetic Chemistry, Faculty of Technology, Hokkaido University, Sapporo, Japan

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The amounts of basic and reducing sites of calcium oxides prepared by heat-treating the hydroxide at various temperatures were measured, respectively, by titration with benzoic acid, using bromothymol blue, etc., as indicators and by observing ESR spectra or visible reflectance spectra of adsorbed nitrobenzene or *m*-dinitrobenzene. The maximum amount of basic sites was found to be 0.57 mmole/g when the hydroxide was calcined at 500° in air, while that of reducing sites to be 5×10^{14} and 10^{16} sites/g, respectively, when calcined at 700° in air and at 500° in a vacuum. It has been found that the catalytic activity of various calcium oxides for the esterification of benzaldehyde correlates well with the basicities, whereas that for the polymerization of styrene does with the amounts of reducing sites. On the basis of the above results together with infrared spectra of adsorbed benzaldehyde, isopropyl alcohol, and chloroform, the nature of basic and reducing sites was discussed, the reducing sites being shown to be entirely different from the basic sites.

INTRODUCTION

Calcium oxides are known to catalyze the double-bond isomerization of olefins, hydrogen disproportionation, dehydrogenation, and isomerization of cyclohexadienes, dehydrogenation of alcohols, etc. (*1*). Schächter and Pines have showed that calcium oxide catalyst prepared from its hydroxide and calcined at 500°C is most active towards the isomerization of olefins, but much less activity is found when the catalyst was calcined at higher or lower temperature (*1*). Recently, we have also observed a similar catalytic activity of calcium oxides for the synthesis of benzyl benzoate from benzaldehyde (*2*). In order to elucidate the nature of active centers on calcium oxide surface, the changes in surface area, surface hydroxyl group, adsorption state of various acidic compounds, and basic and reducing properties with change of calcination temperature have been studied. In the light of the observed surface properties, the catalytic action of calcium oxide for the reaction of benzaldehyde and the polymerization of styrene is discussed.

EXPERIMENTAL METHODS

1. *Catalysts*

Calcium oxide or partially dehydrated calcium oxide was prepared from calcium hydroxide (guaranteed reagent, Kanto Chemical Co.) which was calcined in an electric furnace at temperature ranging from 100 to 900° for 3 hr. The samples for IR and ESR measurements were calcined in air or in a vacuum for 3 hr.

2. *Measurements of Surface Properties*

Surface areas and pore sizes of calcium oxides calcined at various temperatures were measured respectively by BET method using nitrogen gas and by Cranston and Inkley's method (*3*) using the nitrogen adsorption data.

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* (Department of Chemistry) to whom inquiries should be addressed.

Infrared spectra of calcium oxides calcined at various temperatures in air were observed in the region of their OH-stretching by Nujol mull method using a Hitachi EPI-2 infrared spectrophotometer. The spectra of benzaldehyde, isopropyl alcohol, chloroform, and toluene adsorbed on calcium oxides pressed into discs which were calcined in a vacuum *in situ* cell were observed similarly in the OH-stretching region, in order to see the reactivity of the surface with acidic compounds.

The anion radicals of nitrobenzene or *m*-dinitrobenzene which had been formed by adsorption on calcium oxides were observed by a *X*-band ESR spectra. The amount of the spin was obtained from the measurement using double cavity, using ultramarine blue and DPPH as standards. Nitrobenzene vapor was adsorbed on the samples through a breakable seal. The amount of the adsorbates was controlled by heating the sample in a tube attached with a liquid nitrogen trap.

Electronic spectra of *m*-dinitrobenzene and phenolphthalein adsorbed on calcium oxide were measured by means of diffuse reflectance spectroscopy. The adsorbates were adsorbed from the benzene solution on calcium oxide suspended in benzene. An electronic spectrum of adsorbed styrene was observed by ordinary transmittance measurement. Styrene vapor was adsorbed on the catalyst pressed into a disc in *in situ* cell.

The basicity was measured by titrating the sample suspended in benzene with benzene solution of 0.1 N benzoic acid, using bromothymol blue ($pK_a = 7.1$) as an indicator. To determine the distribution of basic strength, phenolphthalein ($pK_a = 9.3$) and a series of nitroaniline indicators (*4*) such as 2,4,6-trinitroaniline (12.2), 2,4-dinitroaniline (15.0), 4-chloro-2-nitroaniline (17.2), and 4-nitroaniline (18.4) were also used as indicators in the above titration.

Nitrobenzene and *m*-dinitrobenzene were purified by repeating a procedure of a freezing–thawing cycle. Other reagents used for measuring surface properties were all guaranteed reagents of Wako Pure Chemical Co. Tokyo.

3. Kinetic Measurements

The reaction of benzaldehyde over calcium oxide catalysts was carried out in the absence of any solvent at 180 ± 0.3°C. A 30-ml sample of benzaldehyde and 1 g of the catalyst were used; and the reaction mixture was stirred in a flask by a magnetic stirrer, the small amount of nitrogen gas being passed to prevent the benzaldehyde from its oxidation. The reaction products were analyzed by gas chromatography (Shimadzu Mfg. Co. GC-2C type), using a column of silicon DC 550 on Celite. Benzaldehyde used was purified by twice distillation under reduced pressure and stored under nitrogen gas before use. The main product was benzylbenzoate; and the reaction was first order with respect to the concentration of benzaldehyde. The first order rate constant was taken as a measure of catalytic activity.

The polymerization of styrene over calcium oxide catalysts was carried out at 30°C for 10 hr. Styrene was added to the catalyst in a stream of nitrogen gas. Styrene was purified by an ordinary method and dried over calcium chloride and molecular sieve (4A). The formed polymer of styrene was precipitated with methanol and the amount was weighed after drying in a vacuum. The amount of polymer per unit amount of catalyst was taken as catalytic activity.

RESULTS

Basic Property

The basicity of calcium oxide calcined at various temperatures, which was measured by using bromothymol blue as an indicator is shown in Fig. 1, where the change of specific surface area on heat treatment and the extent of dehydration of calcium hydroxide are also shown. As shown, calcium hydroxide begins to be rapidly dehydrated to form calcium oxide at around 350°. As the dehydration proceeds, the basicity in-

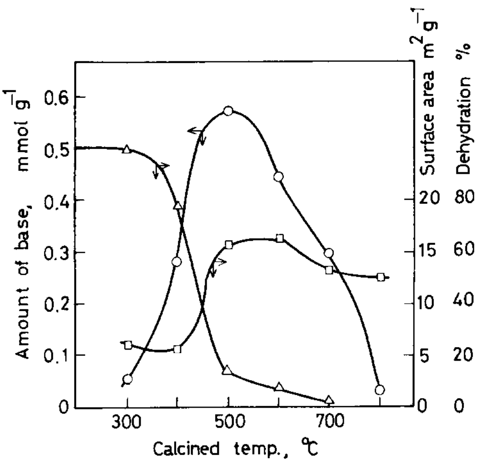

FIG. 1. Changes in basicity, surface area, and dehydration percentage of CaO on calcined temperature.

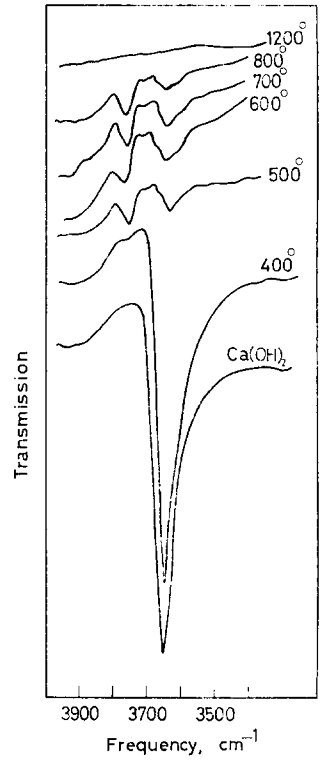

FIG. 2. Infrared spectra of $Ca(OH)_2$ calcined in air for 3 hr at various temperatures.

creases rapidly and attains a maximum value at 500° and then begins to decrease at higher temperature. Specific surface area begins to increase at around 450° and attains a maximum value at 500–600°, but the extent of the increase is far smaller than that of the basicity and it does not much decrease at higher temperature. This indicates that the basicity change is not due to the change of surface area. The basicities measured by using a series of nitroaniline indicators change similarly as the basicity in Fig. 1 does, the maximum values being obtained at around 500°. The basicity value measured by an indicator of larger pK_a was naturally smaller than that measured by an indicator of smaller pK_a. For example, the basicity at higher basic strength ($pK_a = 18.4$) was found to be less than half of that at lower basic strength ($pK_a = 7.1$).

To study what kinds of surface species exhibit the observed basic property in Fig. 1, the infrared spectra of surface OH group on calcium oxides were observed first, since about 10% of calcium hydroxide remains on the oxide as shown in Fig. 1. The infrared spectra of calcium hydroxide heat treated at various temperatures are shown in Fig. 2, where the absorption bands of OH group appear at 3650 and 3765–3770 cm^{-1}. The strong band at 3650 cm^{-1} is seen for calcium hydroxides calcined up to 400°, but decreases at temperatures above 500°. This band does not appear when the hydroxide was calcined in a vacuum above 500°C. The band at 3765–3770 cm^{-1} begins to appear when calcined in air above 400° or in a vacuum at 350°.

The infrared spectra of benzaldehyde, isopropyl alcohol, chloroform, and toluene adsorbed on calcium oxides calcined in *in situ* cell were also observed to elucidate the nature of basic sites. Figure 3 shows the spectra of adsorbed benzaldehyde. The band at 3765–3770 cm^{-1} appeared in calcium oxide shifted to around 3720 cm^{-1} and became broad by the adsorption of benzaldehyde. The spectra of the sample which was evacuated at 200° for 30 min to remove the physically adsorbed molecules showed a similar band, but when evacuated at 300° for 30 min, a shoulder of the band began to appear at 3740 cm^{-1} and a new

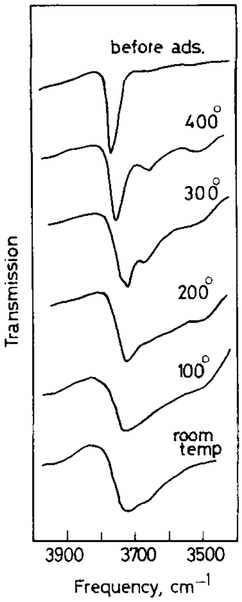

FIG. 3. Infrared spectra of benzaldehyde adsorbed on CaO calcined at 500° *in vacuo* and evacuated at various temperatures.

band at 3670 cm^{-1} as shown in Fig. 3. In the sample evacuated further at 400° for 30 min, the peak at 3740 cm^{-1} shifted to 3760 cm^{-1}, the band becoming sharp and the band at 3670 cm^{-1} shifted to 3650 cm^{-1} and became clearer.

In the case of isopropyl alcohol adsorption, the band at 3765 cm^{-1} is hidden by broad band at around 3700 cm^{-1}, but when the sample is evacuated at 300° for 30 min, the sharp band begins to appear and the bands at 3720 and 3640 cm^{-1} to be observed, as shown in Fig. 4. The spectrum of the sample evacuated further at 400° showed a broad band at 3640 cm^{-1} and the band of OH group which coincided with that before adsorption.

The spectra of adsorbed chloroform are different from those of benzaldehyde and isopropyl alcohol, no shift of 3765–3770 cm^{-1} band being observed, as shown in Fig. 5. A broad band of OH group appears at around 3640 cm^{-1} and it separates completely from the band at 3765–3770 cm^{-1} by evacuation at 170°. In the spectra of adsorbed toluene, the band at 3765 cm^{-1} becomes broad only a little and no bands at

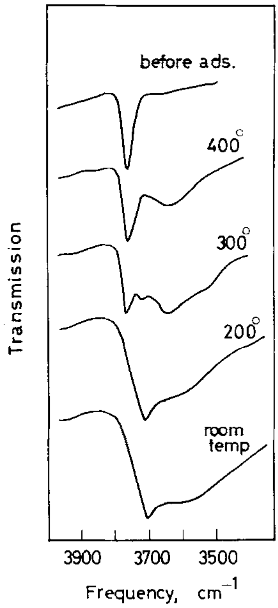

FIG. 4. Infrared spectra of isopropyl alcohol adsorbed on CaO calcined at 500° *in vacuo* and evacuated at various temperatures.

3650 cm^{-1} appear when evacuated at room temperature. The spectra of the sample evacuated at 170° for 30 min was the same as that before adsorption.

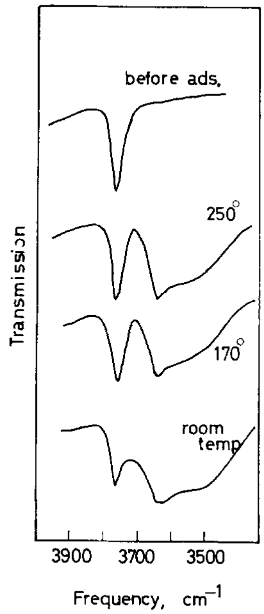

FIG. 5. Infrared spectra of chloroform adsorbed on CaO calcined at 500° *in vacuo* and evacuated at various temperatures.

Correlation of Basic Property with Catalytic Activity

The first order rate constants per unit surface area of catalyst of the esterification reaction of benzaldehyde plotted against calcination temperatures are demonstrated in Fig. 6, where the basicity change per unit surface area measured by using bromothymol blue is also shown by dotted lines. There was found a very good correlation between the basicity and the catalytic activity. Schächter and Pines reported that the catalytic activity per gram of calcium oxide catalysts for the isomerization of olefins is largest when the catalyst was calcined at 500°C and low when calcined at lower or higher temperature (*1*). The catalytic activity seems to correlate with the observed basicity per unit gram of calcium oxide shown in Fig. 1.

Reducing Property

When nitrobenzene was adsorbed on calcium oxide calcined above 500°, the color of the oxide surface became gray-greenish and the absorption band at 530–550 mμ in visible spectra as well as ESR absorption were observed. The band in visible spectra is in agreement with that of anion radical of nitrobenzene observed by Ishitani *et al.* (*5*). The ESR spectra changing with time passed after introduction of nitrobenzene are shown in Fig. 7. Since vapor pressure of nitrobenzene is below 0.2 mm Hg at room temperature, the rate of adsorption is slow. The spectra show first a hyperfine structure of triplet due to ^{14}N and as adsorption proceeds, the signal intensity increases and the line width becomes larger. The spectrum becomes almost singlet after 1-day adsorption. Peaks due to Mn^{2+} included as impurity are observed, but they do not much change on heat treatment. A relation of line width with length of adsorption time is shown in Fig. 8. On the other hand, when adsorbed nitrobenzene was evacuated by heating, the line width as well as the signal intensity decreased. This seems to indicate that, as the adsorbed amount of

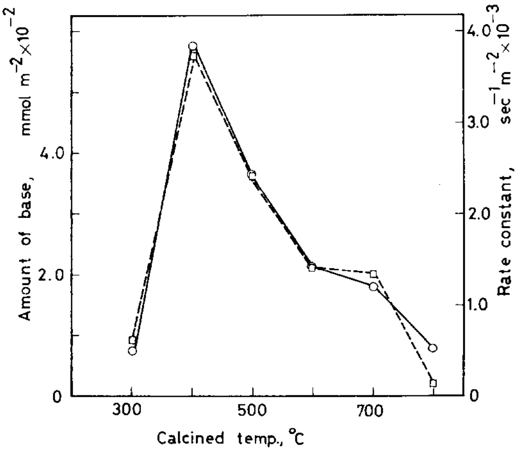

FIG. 6. Correlation of basicity of CaO with catalytic activity for esterification of benzaldehyde: (○—) activity; (□--) basicity.

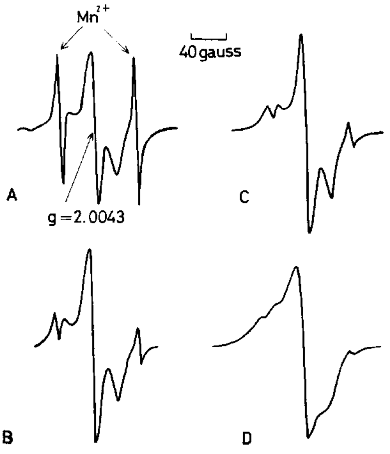

FIG. 7. Time change in ESR signal of nitrobenzene adsorbed on CaO: (A) immediately after adsorption; (B) 10 min after adsorption; (C) 30 min; (D) 1 day.

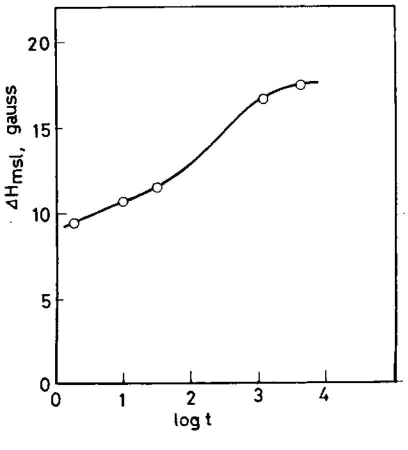

FIG. 8. Line width vs adsorption time (min).

nitrobenzene increases, the anion radicals approach to increase the dipole–dipole interaction, which causes broadening of the line width. In other words, the spin–spin relaxation time is considered to be a main factor contributing to the line width, although there are various factors affecting the line width of the ESR spectrum. If spin–lattice relaxation time is effective for the increase in line width, the change in line width with the change in adsorbed amount should not be observed. The fact that no change of line width was observed at the temperatures ranging from 77 to 373°K at the same adsorbed amount also indicates that any factors other than spin–spin interaction do not affect the line width. Assuming that the increase in line width is due to dipole–dipole interaction, the mean distance between anion radicals was calculated to be 13.0 Å, according to Van Vleck's equation (*6*) given below.

$$\langle \Delta H^2 \rangle = \tfrac{3}{5} S(S + 1) g^2 \beta^2 \sum_j \gamma_{jk}^{-6},$$

where ΔH denotes secondary moment of line width; S, the spin quantum number (½); g, the g value of radical; β, the Bohr magneton; and γ_{jk}, the distance between radicals. In calculation, the contribution from the nearest neighbor was taken account as the first approximation.

The concentrations of the anion radicals formed on calcium oxides calcined in air and in vacuum are shown in Fig. 9(A). The dependency of the radical concentration of the sample treated in air on calcination temperature is quite different from that of basicity shown in Fig. 1. The basicity maximum was observed at 500°, while the maximum amount of anion radicals at 700°. The radicals were found even at 900°, whereas little basicity at the same temperature.

Correlation of Reducing Property with Catalytic Activity

The polymerization of styrene did not proceed over calcium hydroxide. Calcium oxide showed only a little activity for the polymerization when calcined in air, but did remarkable activity when calcined in a vacuum, as shown in Fig. 9B. The maximum activity was observed when the catalyst was calcined at 500° in a vacuum. The dependency of the catalytic activity on calcination temperature is in agreement with that of anion radical concentration of the sample treated in vacuum (compare Fig. 9B with A).

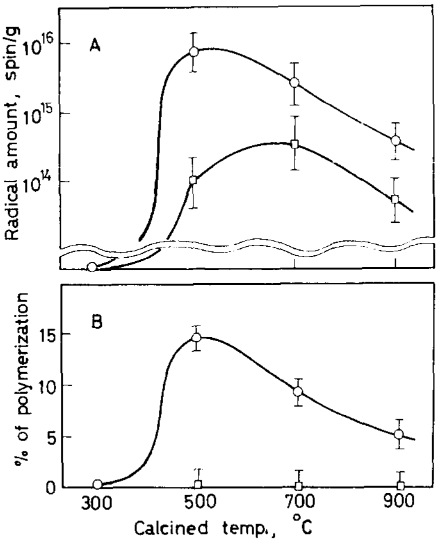

FIG. 9. (A) Amount of anion radical of nitrobenzene formed on CaO vs calcined temperature: (○) calcined in vacuum; (□) calcined in air. (B) Polyemrization activity in vacuum vs calcined temperature: (○) calcined in vacuum; (□) calcined in air.

It is interesting to note that when styrene was added in a vacuum to calcium oxide calcined in a vacuum, the color of adsorbed layer became yellow in the first stage and gradually changed to red purple, whose color did not disappear as long as the sample was not exposed to air. The absorption spectra in visible region is shown in Fig. 10. The absorption at 500 mμ does coincide with the absorption of benzyl anions (*7*) which is observed during the formation of a living polymer of styrene over sodium. Therefore, the living polymer is considered to be formed on calcium oxide surface.

Basic and Reducing Properties

As mentioned above, the basicity change of calcium oxides on heat treatment was different from the change in anion radical concentration (see Figs. 1 and 9A). Fur-

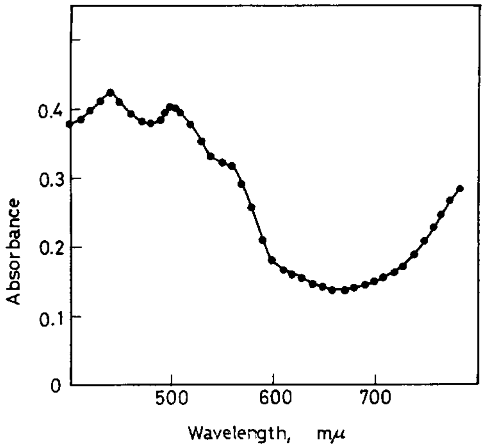

FIG. 10. Visible absorption spectra of styrene adsorbed on CaO calcined in vacuum.

thermore, the amount of the radicals is much smaller than that of basic sites (see also Figs. 1 and 9A). These facts suggest that the reducing site is different from the basic site, i.e., one site does not possess a dual function of single electron and electron pair donating actions. To study this point further, the following experiment was carried out. A large amount of phenolphthalein was adsorbed on calcium oxide calcined at 500° and the diffuse reflectance spectra was observed. After the sample was allowed to stand under nitrogen for 3 days, *m*-dinitrobenzene was adsorbed and the spectra was similarly observed. As shown in Fig. 11, the spectra at 570 mμ of adsorbed phenolphthalein is that of basic form of the indicator and the absorptions at 550 and 680 mμ are due to the anion radical of *m*-dinitrobenzene. This indicates that the sites for anion radical formation (reducing sites) are not poisoned by the adsorption of acidic indicator having electron pair accepting property, confirming that two kinds of sites exist separately on the surface of calcium oxide.

Pore Size Distribution

Figure 12 shows pore size distribution of calcium oxides calcined at 300, 500, and 700° in air for 3 hr and evacuated further at 200, 400, and 600° for 1 hr. A large part of surface area is occupied by pores of relatively smaller size between 30 and 100 Å in the case of calcium oxide calcined at 500°, but about a half of surface area by pores of relatively larger size between 100 and 300 Å when calcined at 300°.

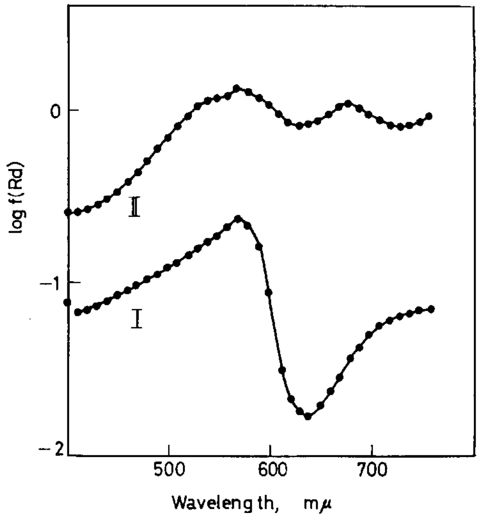

FIG. 11. Diffuse reflectance spectra of phenolphthalein and *m*-dinitrobenzene adsorbed on CaO: (I) adsorbed phenolphthalein; (II) adsorbed phenolphthalein plus adsorbed *m*-dinitrobenzene.

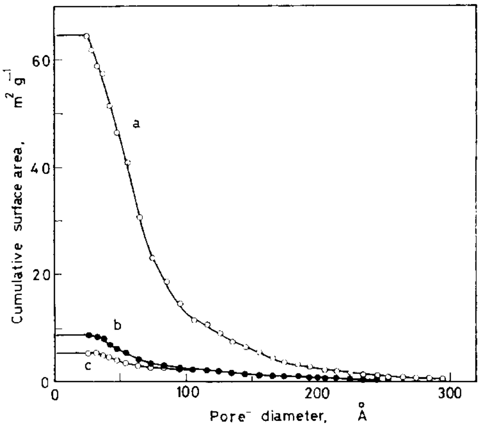

FIG. 12. Pore size distribution of CaO calcined at 300, 500, 700°, and evacuated at 200, 400, and 600° for 1 hr, respectively: (a) 500°; (b) 700°; (c) 300°.

DISCUSSION

We shall first discuss the nature of basic sites. The infrared absorption band at

3765–3770 cm^{-1} of calcium oxide which appeared by calcination at around 400° (see Fig. 2) shifted to lower frequency and became broad by the adsorption of benzaldehyde and isopropyl alcohol (Figs. 3 and 4). These facts indicate that the band is due to the isolated OH on the surface. Since the band appears at higher frequency than 3750 cm^{-1} at which the absorption of neutral OH group of silanol is usually observed, the nature of the isolated OH is considered to be basic.

This basic OH group is only a part of basic sites on dehydrated calcium oxide, because the amount of basic sites of the sample calcined at 500° is so large that titrated benzoic acid covers the surface almost competely, despite the fact that a large amount of water is dehydrated. Hence, a large part of basic sites is considered to be surface O^{2-}. The evidence that basic sites consist of surface O^{2-} and basic OH is provided by infrared study on adsorbed acidic molecules. As shown in Fig. 3, the calcium oxide shows a new band of OH at 3650 cm^{-1} which is considered to be formed by proton abstraction of surface O^{2-} from adsorbed benzaldehyde and also shows the band of weakly basic OH which is in considerably strong interaction with benzaldehyde. In the case of isopropyl alcohol, the interaction of basic OH with the adsorbate is not so strong, but the OH band at 3640 cm^{-1} which was formed by proton transfer from isopropyl alcohol to surface O^{2-} was mainly observed. On the other hand, the basic OH band does not change when chloroform was adsorbed and only the OH band formed by proton abstraction of surface O^{2-} was observed. The nature of basic sites for the above three acidic substances might be pictured as in Fig. 13.

In the case of the adsorption of very weakly acidic toluene ($pK_a \cong 35$), the observed little broadening of the band at 3765 cm^{-1} is due to the physical adsorption, indicating that the surface O^{2-} cannot accept a proton from such a weak acid. The fact that the newly formed OH band at 3640–3650 cm^{-1} observed in cases of benzaldehyde, isopropyl alcohol, and chloroform was not observed in this case does confirm that the OH was formed by proton transfer from adsorbates to surface O^{2-}, strongly basic site.

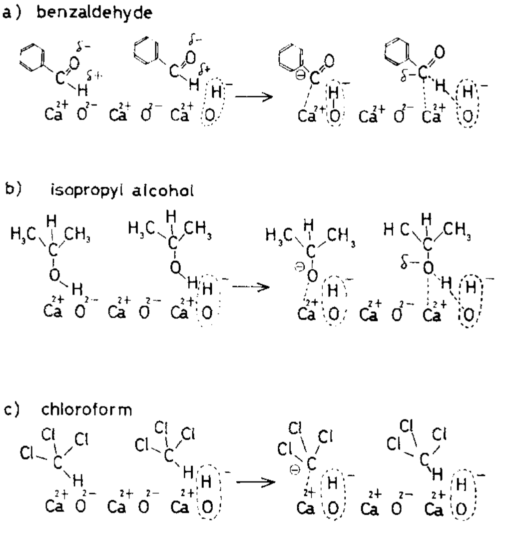

FIG. 13. Model of adsorption state of benzaldehyde, isopropyl alcohol and chloroform on CaO: OH^- in broken oval denotes surface hydroxide ion.

Krylov *et al.* (8) proposed the types of basic sites on the surface of partially dehydrated magnesium hydroxide on the basis of the study on adsorption and isotope exchange of carbon dioxide. Those are strongly basic O^{2-} sites, strongly basic sites derived from the O^{2-} ions adjacent to the surface OH groups, and surface OH groups constituting weakly basic sites. The present conclusion that the basic sites on calcium oxide consist of both surface O^{2-} and OH group is similar to their conclusion about those on magnesium oxide. However, the infrared study combined with basicity measurement in the present work reveals that a large part of the basic sites consist of strongly basic O^{2-} sites. Furthermore, the decrease in observed basicity at higher temperature of calcination seems to indicate that the basic sites are associated with unstable crystal structure of calcium oxide. Namely, the basicity decrease is considered due to the stabilization of the unstable structure.

The nature of reducing sites on calcium oxide is discussed next. Although the anion radical of tetracyanoethylene was reported recently to be formed on calcium oxide (*9*), the nature of reducing site is little known. The maximum amount of the anion radical of nitrobenzene which was formed on calcium oxide calcined at 500° in vacuum occupies only about 0.1% of the surface (cf. Figs. 1 and 9A). If we assume that the amount is homogeneously dispersed on the surface, the distance between the anion radicals should be several hundred angstroms. Since, however, the distance was calculated to be about 13 Å according to Van Vleck's equation, the site forming the anion radical (reducing site) is considered to be localized on the surface. The existence of the localized reducing site and the fact that the anion radical was not formed on commercial calcium oxide calcined at 500°, but formed when calcium hydroxide, which was made by adding water to the oxide, was heated at 500° seem to indicate that the reducing site is associated with the surface state after dehydration. A possible reducing site might be a terminal of dislocation or a point defect appearing on the surface by dehydration of the hydroxide. When edge dislocation or point defect occurs on the crystal of NaCl type like calcium oxide, anions become neighbor to each other, where electron density becomes very high (*10*). The anion radical is considered to be formed by the adsorption of electrophilic nitrobenzene on the site of the high electron density. The decrease in radical amount of calcium oxide which was observed when calcined at high temperature (see Fig. 9A) is considered due to the disappearance of point defect. The fact that the radical amount of the sample treated in air is smaller than that treated in vacuum is also considered due to the disappearance of point defect which may be accelerated by the presence of a small amount of moisture.

The polymerization of styrene over sodium metal (*11*) or by irradiation (*12*) was reported to proceed via the anion radical of styrene in initial stage of the reaction. In the polymerization over calcium oxide, the observed correlation between the polymer yield and the amount of anion radical and the fact that living polymer was formed similarly as in in the case of sodium metal catalyst led us to conclude that the polymerization occurs on the reducing sites. Since, however, the anion radical of styrene was not detected by ESR spectra, it is likely that the polymerization proceeds by a mechanism proposed by Szwarc *et al.* (*12*), in which an intermediate having two terminal benzyl anions which was formed by the bonding of two styrene anion radicals is involved, as shown in Fig. 14.

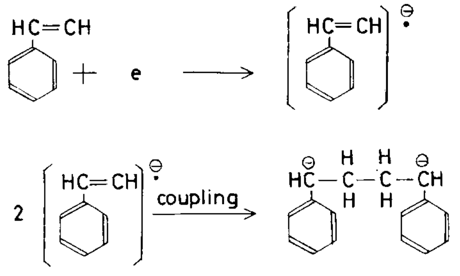

FIG. 14. Intermediate in styrene polymerization on CaO catalyst.

In conclusion, it should be emphasized again that two different kinds of active sites, basic and reducing sites, exist on the surface of calcium oxide and the number of their sites change characteristically with change of calcination temperature and that reducing sites are catalytically active for a reaction involving anion radical as intermediate, while basic sites are for a base-catalyzed reaction.

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