

# Changes in the Basicity and Species on the Surface of $Me(OH)_2-SiO_2$ ( $Me = Ca, Mg, Sr$ ) Mixtures Due to Mechanical Activation

Tomoyuki Watanabe, Jiefan Liao,<sup>1</sup> and Mamoru Senna<sup>2</sup>

Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223, Japan

Received May 12, 1994; in revised form August 18, 1994; accepted August 19, 1994

Mechanical activation increased the surface basicity of the alkaline earth hydroxides in the order  $Sr(OH)_2 > Ca(OH)_2 > Mg(OH)_2$ , as determined by titration, temperature-programmed, desorption, and FT-IR. The increase and the difference in the basicity between the hydroxides became more significant in the case of grinding  $Me(OH)_2-SiO_2$  mixtures, as a result of mechanochemical interactions between the ingredients. Bidentate adsorption of  $CO_2$ , found exclusively on the ground mixture with  $SiO_2$ , is only explained by the formation of new  $-Me-O-Si-$  bonding. This indicates the incipient formation of alkaline earth silicates as a result of charge transfer during grinding. © 1995 Academic Press, Inc.

## 1. INTRODUCTION

During the grinding of a mixture of solids like oxides or hydroxides, a variety of mechanochemical reactions take place (1). The surface acidic or basic properties of solids may play an important role in such a mechanochemical reaction (2–4). Increase in the surface basicity or acidity of some solids after mechanical activation is attributed to the surface defects (5, 6) or the change in the surface species as a result of ion exchange or charge transfer at the contact point of dissimilar solids [7].

The Avvakumov group found that mechanical activation of  $CaO$  produces  $Ca^{2+}$  and  $O^{2-}$  (4). They generalized that the relative mechanochemical reactivity of mixtures containing hydroxyl groups parallels the relative difference in the substance-specific basicity or acidity between the reactants (4). They did not refer, however, the change in these properties during grinding. In actual fact, the relative reactivity strongly depends on the state and structure of the starting materials and their change during the course of interaction. Compared with the studies on thermally induced changes in the surface properties (8–10),

however, those on mechanically induced ones are quite insufficient (5–7).

The purpose of the present study is to examine the changes of surface basicity of  $Me(OH)_2$  ( $Me = Mg, Ca, Sr$ ) due to grinding, to compare those on the  $Me(OH)_2-SiO_2$  mixtures and to elucidate their relationship with the fast mechanochemical reaction of  $Me(OH)_2-SiO_2$  systems (11). Not only the overall intensity but also the intensity distribution of such active centers are to be examined.

## 2. EXPERIMENTAL

The starting materials,  $Mg(OH)_2$ ,  $Ca(OH)_2$ , and  $SiO_2$ , were the same as those used in our previous study (10), while  $Sr(OH)_2$  was prepared from  $Sr(OH)_2 \cdot 8H_2O$  (guaranteed grade, Kanto Chemical) by dehydration at  $400^\circ C$  for 4 hr. One gram of hydroxide or a mixture of  $Me(OH)_2$  and  $SiO_2$  in a molar ratio 3 : 4 was put into a PTFE cylindrical vessel ( $26.1 \text{ cm}^3$ ) with eight nylon-coated iron balls of 9.8 mm diameter and vibro-milled. The method was given in detail elsewhere (13). The ground samples of  $Me(OH)_2-SiO_2$  were named as  $MeS-t$ , where  $t$  denotes the grinding time in hours. Similarly, the separately ground samples of  $Me(OH)_2$  were denoted  $Me-t$ .

The surface basicity was determined by titration with phenolphthalein,  $pK_a = 9.8$  (6). Results are expressed by the mole equivalent of the titrant required per unit BET surface area of the sample. The temperature-programmed desorption analysis, TPD, was carried out with a thermal conductivity detector, TCD, in a stream of  $He$  ( $40 \text{ cm}^3 \text{ min}^{-1}$ ) by heating at  $10 \text{ k} \cdot \text{min}^{-1}$  to  $500^\circ C$ .  $CO_2$  was chosen as a probe gas, as it chemisorbs selectively on the basic sites. The simultaneous mass spectroscopic analysis of the evolved gas was carried out (TG-MS, MAC Science 2020/VG, PC-300D) for some of the samples.

After preliminary desorption and exposure to  $CO_2$  under the same conditions as in TPD, the samples were subjected to FT-IR measurement (FTS-40V BIO-RAD) by using a self-supporting disk (12), without exposing to

<sup>1</sup> Present address: Nara Machinery Co., Ltd., 2-5-7 Jonanjima, Otaku, Tokyo 143, Japan.

<sup>2</sup> To whom correspondence should be addressed.

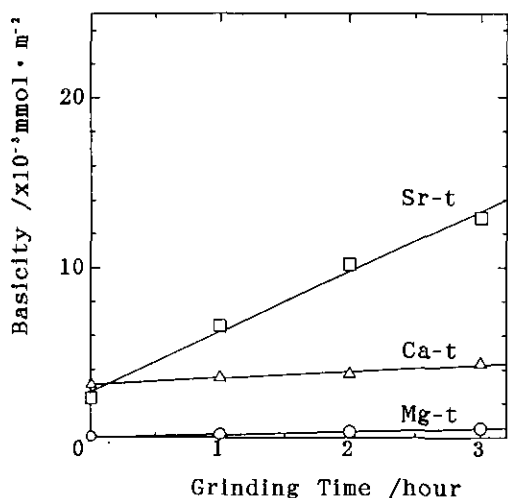


FIG. 1. Changes in the surface basicity of  $Me(OH)_2$  ( $Me = Sr, Ca,$  and  $Mg$ ) due to mechanical activation.

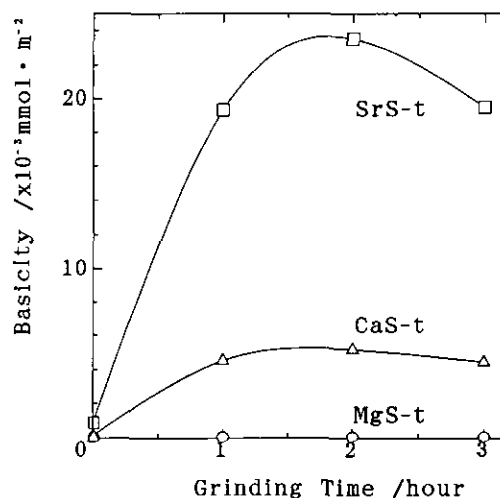


FIG. 2. Changes in the surface basicity of  $Me(OH)_2$ - $SiO_2$  mixtures due to mechanical activation.

the ambient atmosphere. Specific surface area was measured by a BET method using  $N_2$  at 77 K (Sibata, SA-1000). Structural change of the sample was characterized by XRD (Rigaku, CN2103).

### 3. RESULTS AND DISCUSSION

#### 3.1. Changes in the Overall Basicity on Grinding

The overall surface basicity of the vibro-milled hydroxides of Sr, Ca, and Mg is shown in Fig. 1, as a function of grinding time. The basicity increased linearly with time. This is partly attributed to the local dehydration reaction, and resulted in  $O^{2-}$  serving as a basic site. It is also possible that the increase in the basicity is attributed to the increased polarization of OH groups as a result of increased lattice imperfection on the surface.

The rate of basicity increase was the highest for  $Sr(OH)_2$ , followed by  $Ca(OH)_2$  and  $Mg(OH)_2$ . The observed order of basicity strength was the same as that for oxides, i.e.,  $Sr > Ca > Mg$  (11, 13, 14). A relatively fast increase in the surface basicity of  $Sr(OH)_2$  might be related to the higher structure sensitivity of seven-coordinated  $Sr(OH)_2$  as compared to the more stable, six-coordinated hydroxides of Mg and Ca.

At the beginning of mixed-grinding, a much higher rate of increase in the basicity was found for  $Sr(OH)_2$  than those of separate grinding, as shown in Fig. 2. For the samples of  $SrS-t$  and  $CaS-t$ , maxima were observed, while no appreciable basicity,  $pK_a$  larger than 9.3, was detected for  $MgS-t$ . With the presence of  $SiO_2$ , basicity can increase by the enhancement of dehydration, but can also decrease by consumption due to solid state neutralization. The mechanism will be discussed in detail later.

#### 3.2 Thermal Behavior of Ground Samples

Two TPD peaks below  $200^\circ\text{C}$  from the intact  $Ca(OH)_2$ , as shown in Fig. 3, are attributed to the dehydration, as confirmed by TG-MS analysis. Thermal dehydration of  $Ca(OH)_2$  from the bulk began at about  $340^\circ\text{C}$ . After mechanical activation, two weak peaks appeared at about  $290$  and  $340^\circ\text{C}$ , which were related with the desorption of

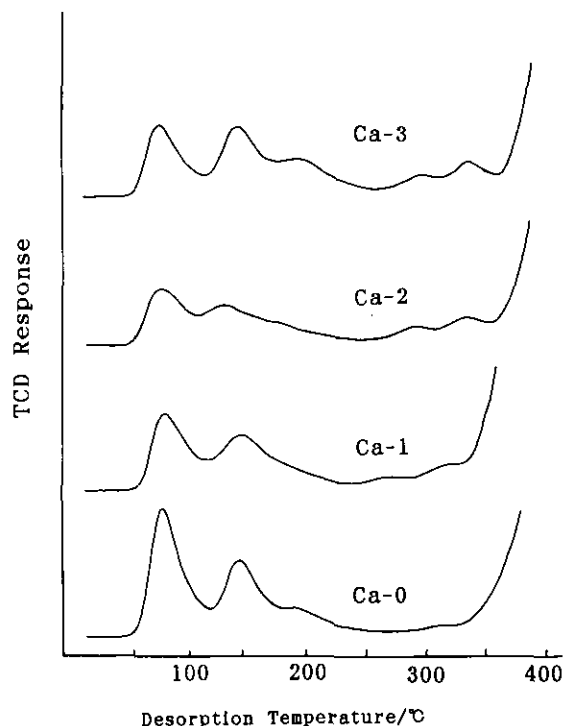


FIG. 3. TPD spectra of  $Ca-t$  with different grinding times.

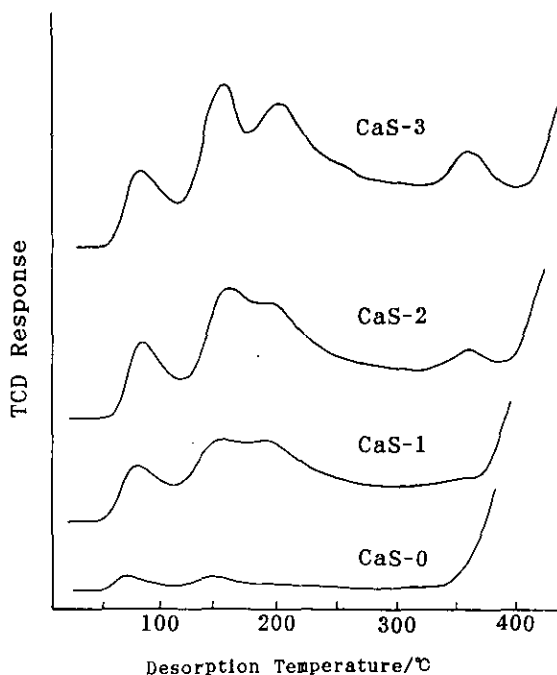


FIG. 4. TPD spectra of CaS-*t* samples ground for different times.

CO<sub>2</sub> and H<sub>2</sub>O, respectively, as also detected by TG-MS. According to Aymes *et al.* (15), Ca(OH)<sub>2</sub> is mechanochemically stable, showing no significant structural change during grinding (6). However, the change in the TPD spectra of Ca(OH)<sub>2</sub> suggests a significant change in its surface properties by mechanical activation. This should be associated with surface defects generating basic or acidic sites. These are not specific to the substance but are highly sensitive to the real structure.

The TPD spectra of the CaS-*t* samples are shown in Fig. 4. The spectrum of CaS-0 was similar to that of Ca-0, although the intensity of these two peaks at low temperature was much smaller for CaS-0 than those for Ca-0. However, the change in the TPD spectra due to mechanical activation of the mixtures was significantly different from those of separately ground samples. Strong desorption peaks appeared at ca. 360 and 200°C in the mixture, in addition to those found in separately ground samples.

### 3.3. Change in the Surface Species

Change in the state of the species associated with CO<sub>2</sub> and H<sub>2</sub>O once adsorbed on the basic sites, was monitored by FT-IR spectra after heating at various temperatures. As shown in Fig. 5, the band at 1236 cm<sup>-1</sup> due to HCO<sub>3</sub><sup>-</sup> (16, 17) was observed on the sample Ca-3. This peak is considered to come from the adsorbed CO<sub>2</sub> on the surface basic sites of *Me*-OH type (8). The intensity of this peak decreased quickly at lower temperature range

and disappeared completely after heating to 355°C. The basicity due to the surface OH groups is, therefore, relatively weak (18). The band at 1160 cm<sup>-1</sup> is presumably due to the vibration of the water adsorbed on the Lewis acidic sites, caused by Ca<sup>2+</sup>, changing into the Brønsted acidic sites. The intensity of this kind of Lewis acidic site increases when the *Me*-O-*Me* link is distorted (18). Two strong bands at 1400–1500 and 860 cm<sup>-1</sup> are due to the vibration of chemisorbed CO<sub>2</sub> to form a unidentate complex (16, 17). They remained even after heating to 440°C.

By comparing Fig. 4 with Fig. 3, it is clear that the two peaks appeared at about 290 and 340°C on the TPD spectrum of Ca-3 are due to the desorption of CO<sub>2</sub> adsorbed in the form of HCO<sub>3</sub><sup>-</sup>, and water, respectively, once adsorbed on the active sites induced by mechanical activation.

FT-IR spectra of CaS-3 heated at different temperatures are shown in Fig. 6. The bands at 1700 cm<sup>-1</sup> are unique for the Ca(OH)<sub>2</sub>-SiO<sub>2</sub> mixture, irrespective of whether or not they have been ground. This peak remained unchanged even after heating up to 800°C. It must therefore be attributed to the adsorbed species on the surface of SiO<sub>2</sub>, i.e., -OH of the silanol.

It is also noteworthy that an adsorption band was observed at 1270 cm<sup>-1</sup> due to the bidentate adsorption of CO<sub>2</sub> (16, 17). This peak showed a chemical shift to the

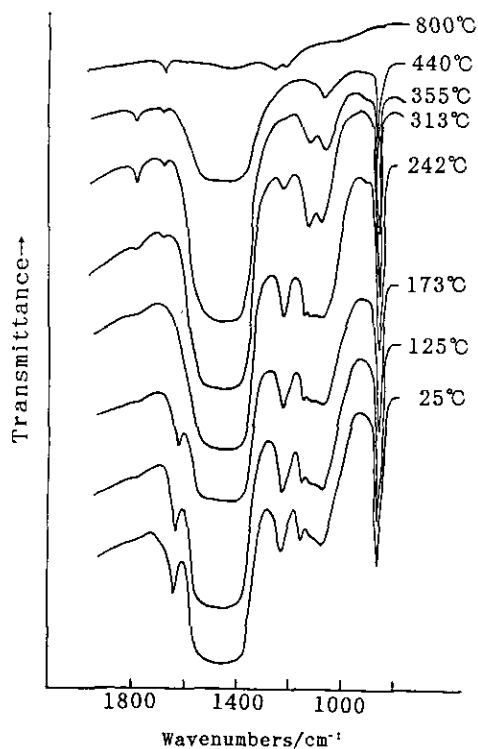


FIG. 5. FT-IR spectra of Ca-3 after thermal treatment at different temperatures.

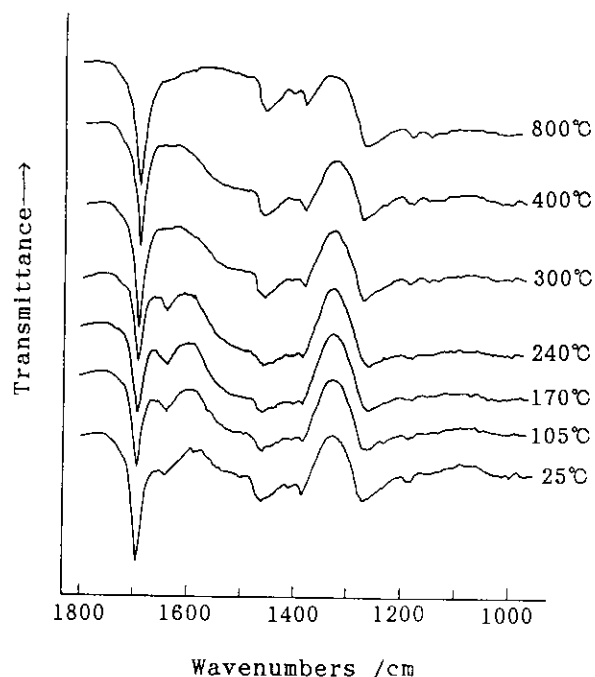


FIG. 6. FT-IR spectra of CaS-3 samples with thermal treatment at different temperatures.

higher wave number after heating above 300°C. Changes in the adsorption bands at 1620 and 1400–1500  $cm^{-1}$  due to grinding were similar to the case of Ca-3. It is also to be noted that the adsorption band at 1236  $cm^{-1}$ , due to  $HCO_3^-$ , was entirely absent in the CaS-3 samples.

### 3.4. Mechanisms of Incipient Addition Reaction

Formation of a unidentate  $CO_2$ -substrate complex is accompanied by the transformation of Lewis acidic sites into Brønsted ones as a result of water adsorption. It was observed on both samples with and without  $SiO_2$ . In contrast, the adsorption band related to the  $CO_2$ -substrate bidentate complex was observed only on the mixed ground samples. The formation of paired acidic-basic sites,  $-Ca-O-$  bonding, is only possible when the Lewis acidic sites due to  $Ca^{2+}$  are not annihilated by the preadsorption of  $H_2O$ . The coexistence of  $SiO_2$  can well prevent the annihilation, since the affinity of  $SiO_2$  for  $H_2O$ , i.e., relative acidity, is much stronger than  $Ca^{2+}$ . This is supported by the fact that the adsorption bands at 1160  $cm^{-1}$  is weaker for mixed ground samples than for separately ground ones, as shown in Fig. 6.

It is clear that grinding  $Me(OH)_2-SiO_2$  brings about more than a simple solid state neutralization. Basic sites are consumed as a result of complex formation, as verified by the bidentate adsorption. This explains the appearance of the maxima of basicity on prolonged grinding of  $Sr(OH)_2$  or  $Ca(OH)_2$  with  $SiO_2$ , as shown in Fig. 2. Produc-

tion and consumption of surface basic sites are taking place simultaneously in a vessel during grinding. An apparent invariance of the basicity in the case of grinding  $Mg(OH)_2-SiO_2$  mixture would thus indicate the relatively higher rate of consumption of the basic sites.

At the early stage of grinding, dehydration takes place, resulting in the Brønsted basic sites, as shown in Fig. 5. This, in turn, promotes the subsequent complex formation by the charge transfer between acidic and basic sites, leading to the formation of  $-Me-O-Si-$  new bonding. The latter is supported by the relatively weaker  $CO_3^{2-}$  band on IR on the mixed ground samples. Whether this charge transfer is dominated by electron transfer between Lewis acidic and basic sites or proton transfer between those of Brønsted type is still open to the further study.

## 4. CONCLUSION

While the unidentate adsorption of  $CO_2$  was observed on both separately and mixed ground samples, bidentate adsorption, for which the Lewis acidic site aside the  $O^{2-}$  basic site is indispensable, was only observed on the mixed ground samples. In the latter case, the dehydrated water molecule can be sustained by the strong acidic sites generated as a result of  $Me-O-Si$  complex formation. Consequently, the nearest Lewis acidic sites are survived, enabling the bidentate adsorption. Although indirectly, the complex formation between alkaline earth hydroxides and silica under mechanical stressing is thus verified.

## ACKNOWLEDGMENTS

We thank Professor M. Chikazawa, Dr. T. Takei, Dr. M. Fuji, and Dr. T. Isobe for helpful discussions, and MAC Science Co. for TG-MS measurements. We appreciate the financial support of the Iketani Science and Technology Foundation.

## REFERENCES

1. G. Heinicke, "Tribochemistry," p. 107. Akademie-Verlag, Berlin, 1984.
2. A. Zecchina, M. G. Lofthouse, and F. S. Stone. *J. Chem. Soc. Faraday Trans. 1* **71**, 1476 (1975).
3. F. S. Stone, E. Garrone, and A. Zecchina, *Mater. Chem. Phys.* **13**, 331 (1985).
4. V. A. Polubojarov, E. G. Avvakumov, O. V. Andrushkoba, V. V. Boldyrev, N. V. Kisiva, and V. D. Yumatov, *Sib. J. Chem.* **5**, 115 (1991).
5. Y. Arai, T. Yasue, and H. Miyake, *Nippon Kagaku Kaishi*, 547 (1972).
6. J. Liao and M. Senna, *Solid State Ionics* **66**, 313 (1993).
7. Y. Arai, T. Yasue, *Nippon Kagaku Kaishi*, 49 (1974).
8. ST. Malinowski, S. Szczepanska, A. Bielanski and J. Sloczynski, *J. Catal.* **4**, 324 (1965).
9. G. Zhang and H. Hattori, *Hyomen* **28**, 248 (1990).
10. R. N. Spitz, J. E. Barton, M. A. Barteau, R. H. Staley, and A. W. Sleight, *J. Phys. Chem.* **90**, 4067 (1986).

11. J. Liao and M. Senna, *Thermochim. Acta* **210**, 89 (1992).
12. E. P. Parry, *J. Catal.* **2**, 371 (1963).
13. A. Auroux and A. Gervasini, *J. Phys. Chem.* **94**, 6371 (1990).
14. E. Garrone, A. Zecchina, and F. S. Stone, *Philos. Mag. Part B* **42**, 683 (1980).
15. D. Aymes, J. C. Mutin, A. Nonat, and C. Sciora, in "Materials Science Monographs, Vol. 28, Reactivity of Solids" (P. Barret and L-C. Dufour, Eds.), p. 741. Elsevier, Amsterdam, 1985.
16. N. D. Parkyns, *J. Phys. Chem.* **75**, 526 (1971).
17. Y. Fukuda and K. Tanabe, *Bull. Chem. Soc. Jpn.* **46**, 1616 (1973).
18. ST. Malinowski, S. Szczepanska, A. Bielanski, and J. Sloczynski, *J. Catal.* **4**, 45 (1965).