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Solid State Radical Recombination and Charge Transfer across the Boundary between Indomethacin and Silica under Mechanical Stress

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A composite of indomethacin (IM) and SiO_2 was prepared in a solid state by cogrinding. Dehydration was observed as a consequence of a chemical reaction between silanol groups of SiO_2 and carboxyl groups of IM. Several specific radical species found on separately ground SiO_2 disappeared preferentially after cogrinding as a result of their recombination. These chemical interactions under mechanical stress bring about a charge transfer, as confirmed by X-ray photoelectron spectroscopy, leading to Si–O–C bridging bond formation at the IM/SiO_2 interface.

Key Words: **silica composite; mechanochemical; mechanoradical; charge transfer; electronegativity equalization.**

1. INTRODUCTION

We have elucidated the mechanisms of mechanochemical synthesis for inorganic–inorganic systems (1–3), and proposed a general scheme (4). Mechanochemical routes are widely studied in pharmaceutical research as well. In order to control pharmaceutical properties such as a dissolution process or stabilization of an amorphous drug, elucidation of the interaction between a drug and a carrier is indispensable. The interactions between a drug and a carrier are quite diverse. However, most of the analytical techniques established for inorganic solid state systems could also be useful to elucidate the nature of the interaction between a drug and a carrier.

Taylor and Zografi (5) reported, by using FT-IR and FT-Raman spectroscopy, that the interaction between indomethacin (IM) and polyvinylpyrrolidone (PVP) in an amorphous solid dispersion is attributed to hydrogen bonding between the amide carbonyl of PVP and the carboxylic acid hydroxyl of IM. Although many researchers claim that hydrogen bonds are responsible for the interaction between a drug and a carrier (6, 7), the chemical interactions have rarely been studied from the viewpoint of formation of new bonds other than hydrogen bonds. We revealed by X-ray photoelectron spectroscopy (XPS) that mechanical activation induces interaction between $Ca(OH)_2$ and SiO_2 to form Ca–O–Si bridging bonds at the interface (1). Since XPS gives preferentially information at the particle surface, we consider XPS to be useful to examine the interaction in a solid dispersed system as well.

The existence of a mechanically induced radical, i.e., a mechanoradical, is widely known for inorganic substances (8, 9). Concentrations of E' centers ($\equiv$ Si·) in silica- (8) and oxygen-related radicals, e.g., the F^+ center and O^-, in MgO increase by grinding (9). In our previous report on the system $Ca(OH)_2$–SiO_2 (2), oxygen vacancies such as E' centers were observed on the surface of separately ground SiO_2. These active sites, in turn, react with other radical species during cogrinding with $Ca(OH)_2$. Electron spin resonance (ESR) spectroscopy is used to examine these mechanoradicals.

By using the analytical tools mentioned above, we focus in this study on elucidating what happens at the interface between IM and SiO_2 when the mixture is subjected to grinding. Emphasis is placed on (1) the changes in the surface hydroxyl groups, (2) the role of the radical species in the drug–carrier, and (3) the mechanism of charge transfer at the drug–silica interface.

2. EXPERIMENTAL

A commercial reagent (Sigma Chemical Co.) was used as the source of indomethacin (IM, γ-indomethacin: 1-(*p*-chlorobenzoyl)-5-methoxy-2-methylindole-3-acetic acid). As a carrier, fumed SiO_2 powder (Areosil 200; Nippon

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Aerosil Co.) was used. Specific surface areas of the sieved IM and SiO_2 were 0.84 $m^2 g^{-1}$ and 191 $m^2 g^{-1}$, respectively, as determined by a BET method with N_2 gas adsorption (Quantasorb, Quantachrome Co.). They are the same as those used in our previous study (10).

IM and SiO_2 were mixed in a mortar with a weight ratio of 1:1 to obtain a physical mixture, which showed no interaction between IM and SiO_2. Grinding conditions for IM, SiO_2, and their mixture are given elsewhere (10). For ESR measurements, grinding was carried out in He to avoid possible hazards from the gaseous species in an ambient atmosphere. The physical mixture was prepared in a dry box filled with He, and was put into a sealed cylindrical vessel for grinding in the box. The resultant mass was put into a quartz tube for ESR measurement without being exposed to air.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT, Bio-Rad, FTS-175) was carried out to characterize silanol groups on the SiO_2 and carboxyl groups of IM particles. The spectra are obtained at 2 cm^{-1} resolution by signal-averaging 128 scans. ^1H solid state nuclear magnetic resonance (NMR) analysis was made using a high-resolution solid state unit (Chemagnetics Inc., CMX-300) by the method of combined rotation and multiple pulse (CRAMPS) NMR spectroscopy under the following conditions: pulse delay, 5 s; spinning rate, 1.5 kHz; spectral width, 9.3 kHz; and acquisition time, 32.4 ms. Silicon rubber was used as a secondary standard with a chemical shift of 0.12 ppm from tetramethylsilane. Samples were put into a quartz tube for ESR measurement without being exposed to air. Spectra were measured by using an X-band spectrometer (JEOL JSX-RE3X) at room temperature. A microwave power saturation method was also used for the assignment of overlapping complex ESR signals. Changes in the radical concentration after grinding were determined with the aid of the radical standard, TEMPOL (4-hydroxy-2,2,6,6-tetramethyl-1-piperidine-1-oxyl). The samples and the standard were measured under the same conditions, and the concentrations were determined by comparison with their second-order integrated spectra. Charge transfer at the mechanically activated interface between IM and SiO_2 was examined by XPS (JEOL JPS-90SX) from the O1*s*, C1*s*, and Si2*p* electronic states of the solid dispersions. The binding energy of $Au4f_{7/2}$ was used as a standard for the charge-up calibration.

3. RESULTS AND DISCUSSION

3.1. Changes in the Brønsted Acidity on SiO_2 Surface

The changes in the DRIFT spectra by grinding are shown in Fig. 1. DRIFT preferentially detects the silanol groups on the surface of SiO_2. The bands at 3747 cm^{-1} for free surface silanol groups (11, 12) and those at 3377 cm^{-1} for surface OH groups from the carboxylic groups of IM (5) disappear by dehydration after cogrinding for only 10 min (Fig. 1, curve b). The former band was assigned to isolated or geminal hydroxyl groups on the surface of SiO_2 (12). Separate grinding of SiO_2 does not bring about dehydroxylation, as shown in Fig. 1. Dehydration due to a mechanochemical reaction is called mechanochemical dehydration. Liao and Senna (13) reported that immediate mechanochemical dehydration occurred between alkali earth hydroxides and SiO_2. They found that such dehydration plays a crucial role in the mechanochemical synthesis of a complex oxide precursor.

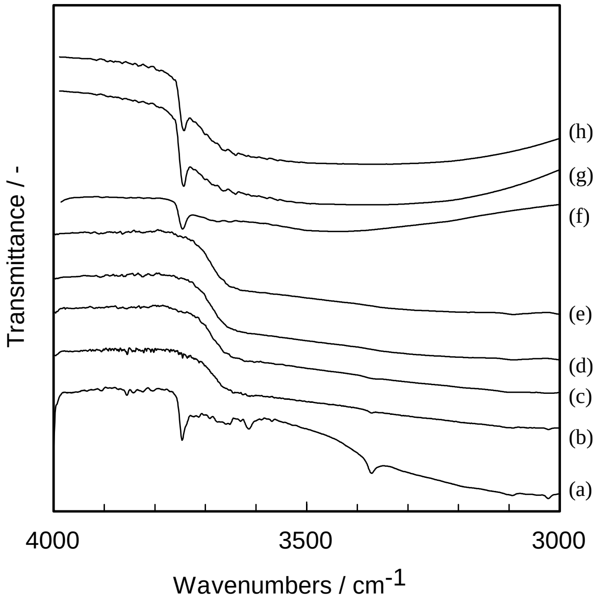

FIG. 1. DRIFT spectra of the OH stretching region for (a) physical mixture, (b) coground for 10 min, (c) coground for 30 min, (d) coground for 60 min (e) coground for 180 min, (f) SiO_2 intact, (g) SiO_2 ground for 30 min, and (h) SiO_2 ground for 180 min.

^1H-CRAMPS-NMR profiles are shown in Fig. 2 for SiO_2 ground separately for 30 to 180 min. A resonance peak at about 4–5 ppm is attributed to the silanolic proton (14). The peak top chemical shift increases with grinding. The peak shift toward a higher field by separate grinding of SiO_2 suggests an increase in the acidity of Si–OH (15, 16). Formation of an acidic site is associated with a decrease in the coordination number for Si and, in turn, with increased polarization of –OH. For the physical mixture, the peaks from the silanolic proton (4–5 ppm) of SiO_2 and the carboxylic proton (13 ppm) of IM are detected, as shown in Fig. 3. These peaks are absent from the mixture coground for 180 min. We therefore presume that the protons were consumed by the acid–base reaction during cogrinding. The peak of carboxylic proton persisted with a decrease in their intensity on the mixture ground for 30 min. The remaining peak in the ^1H-CRAMPS-NMR spectra, in contrast with the DRIFT as mentioned above, is presumably attributed to

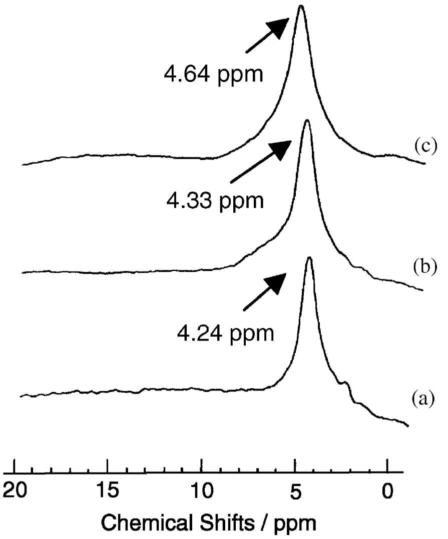

FIG. 2. ^{1}H-CRAMPS-NMR spectra of (a) physical mixture, (b) SiO_2 separately ground for 30 min, and (c) ground for 180 min.

the contribution of protons not only on the surface but also in the bulk of IM. A mechanochemical dehydration reaction releases H_2O (13). In our previous report on the $Ca(OH)_2$–SiO_2 system (1), dissociative adsorption of water which was generated by mechanochemical dehydration took place on the separately ground $Ca(OH)_2$, but not in the case of the ground $Ca(OH)_2$–SiO_2 mixture because of the consumption of juxtaposed acid–base sites on $Ca(OH)_2$ due to the formation of Si–O–Ca bonds. Based on the absences of the IR bands or NMR peaks derived from hydroxyl groups on the coground mixture, as shown in Figs. 1 and 2, released water by cogrinding dose not chemically adsorb on the coground mixture.

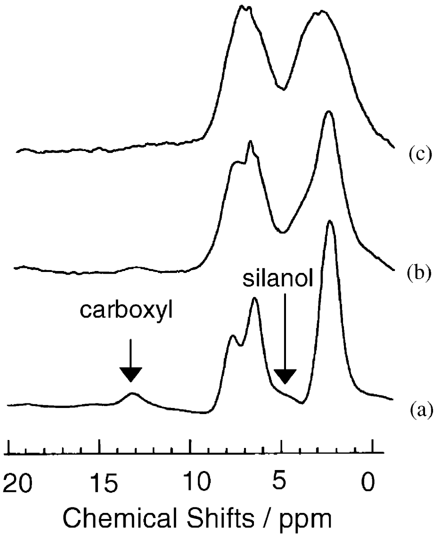

FIG. 3. ^{1}H-CRAMPS-NMR spectra of (a) physical mixture, (b) IM/SiO_2 coground for 30 min, and (c) coground for 180 min.

As reported previously on the $Ca(OH)_2$–SiO_2 system (1), we confirmed that the silanol groups served as acidic sites against the basic hydroxide, $Ca(OH)_2$. Two kinds of mechanochemical dehydration paths are possible in the present IM/SiO_2 system. Intact and separately ground SiO_2 can adsorb methyl red ($pK_a = +4.8$) to give a characteristic red color. On the other hand, the pK_a of IM due to carboxyl groups is reported to be $+4.5$ (17). The pK_a values of SiO_2 and IM are very close to each other. Therefore, a silanol group becomes amphoteric to behave either as a Brønsted acid or as a Brønsted base in the present mechanochemical reaction.

3.2. *The Role of Mechanoradicals*

In the previous section, we discussed the IM/SiO_2 interaction from the viewpoint of acid–base reaction, i.e., the changes in the states of the electron pair. It is well known that radicals also play an important role in a mechanochemical reaction (2, 8, 9). In order to further examine whether and to what extent a radical reaction is concerned, ESR spectroscopy was employed. Figure 4 shows

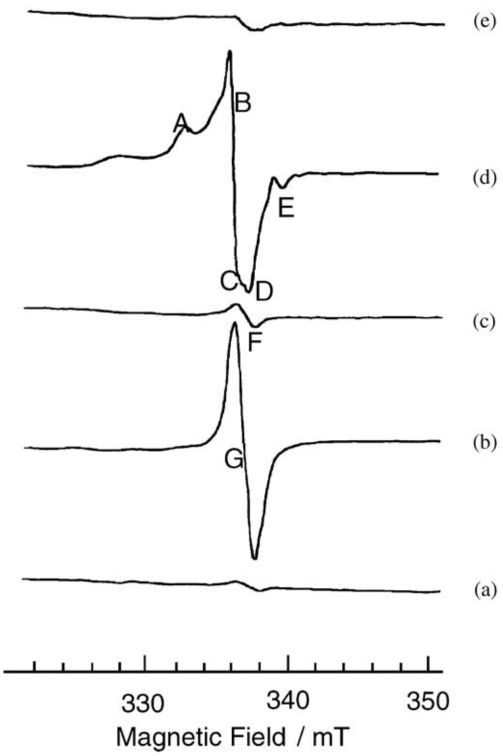

FIG. 4. ESR spectra of (a) physical mixture, (b) ground mixture in He, (c) ground IM in He, (d) ground SiO_2 in He, and (e) ground SiO_2 in ambient air. The *g*-values are B, 2.009; C, 2.002; D, 2.001; F, 2.001; and G, 2.001.

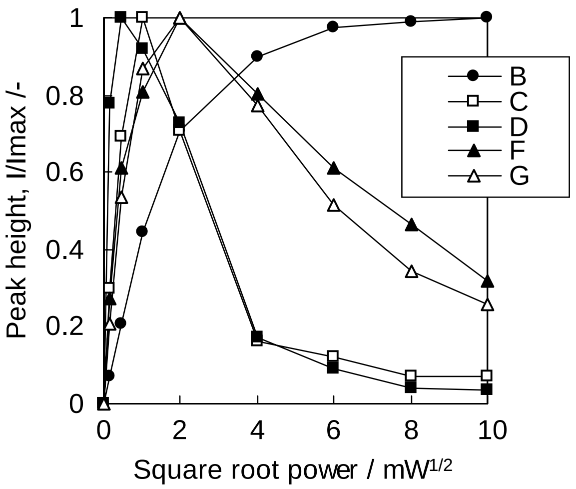

FIG. 5. Peak heights of signals B, C, D, F, and G (Fig. 4) in arbitrary units versus the square of the microwave.

the ESR spectra obtained at 4 mW microwave power. We observed only a very weak signal in the spectrum of the physical mixture (a) and SiO_2 ground for 30 min in air (e). However, the spectrum from SiO_2 ground in He (d) exhibits complex signals from several radical species. The signals A and E were derived from hyperfine structures (hfs) of ^{29}Si (18). In order to assign other signals, a power saturation method (19) was carried out. In Fig. 5, standardized peak heights of each ESR spectrum are plotted against the square root of the microwave power. Signals from ground SiO_2 are divided into two categories, i.e., (I) those that increase with saturation (signal B) and (II) those that exhibit a maximum (signals C and D). Knowing that the intensity of all the signals from SiO_2 ground in air changes (Fig. 4e), these signals must be attributed to surface defects and/or oxygen-related radicals. From their *g*-value and power saturation behavior, the signals of category (I) is assigned to the NBOHC (nonbridging oxygen hole center; $\equiv$Si–O·) (18, 20) and of (II) to the *E*′ center ($\equiv$Si·) (8, 19, 20) of SiO_2 particles, respectively. These radicals are formed under mechanical stress via a scheme:

$$\equiv\text{Si–O–Si}\equiv\text{(siloxane bond)} \xrightarrow{\text{Mechanical stress}} \equiv\text{Si–O}\cdot\text{(NBOHC)} + \equiv\text{Si}\cdot\ (E'\ \text{center}). \qquad [1]$$

An extra signal (signal F) was detected from IM ground in He. The corresponding *g*-value was close to that of the *E*′ center of SiO_2. However, its power saturation behavior was different from that of the *E*′ center, as shown in Fig. 5. Judging from its *g*-value, signal F was assigned to carboxyl radicals (21). The γ-IM crystal structure exhibits hydrogen bonding of the carboxylic acid groups around the centers of inversion to form molecular dimers (22). It is known that an IR peak for an asymmetric acid, e.g., ν C=O of a cyclic dimer, disappears during grinding (23). Since the ESR line intensity of carboxyl radicals decreases at higher acidity (21), an increase in the signal intensity for carboxyl radicals of ground IM implies uncoupling of the cyclic dimers. Radicals were found in the physical mixture, but the radical concentration was increased by cogrinding. The ESR spectrum of the coground mixture (Fig. 4b) shows only one signal, denoted as G. Judging from its *g*-value and the power saturation behavior, the radical species are not from SiO_2, but from a carboxyl radical of IM. We emphasize that both NBOHC and *E*′ radical species are consumed by cogrinding with IM.

Changes in the radical concentration after grinding of each component or cogrinding were determined with the aid of the radical standard. Table 1 shows that the carboxyl radical concentration of the ground mixture is more than 10–20 times higher than that of the physical mixture or separately ground IM. The ESR line intensity reflects the carboxyl radical concentration, and is associated with the deprotonated state, whose concentration depends on the ambient acidity. The carboxyl radical concentration reaches the maximum around pH 5 (21). Therefore, the deprotonation of a silanol group by grinding leads to an increase in the ambient acidity of IM, which, in turn, increases the carboxyl radical concentration.

Note that the radical concentration of the coground mixture is much lower than that of the separately ground SiO_2. We conclude that the dangling bonds, formed by grinding SiO_2 and ascribed to the *E*′ center or NBOHC, were consumed by entrapping oxygen of IM molecules. We revealed by ^{13}C CP/MAS NMR (10) that cogrinding brought about a chemical reaction between the siloxane bonds of SiO_2 and the oxygen atoms of methoxy and carbonyl groups in IM molecules. Based on these results, we conclude that the dangling bonds, formed by grinding SiO_2 and ascribed to the *E*′ center or NBOHC, entrap oxygen of the methoxy or carbonyl groups of IM molecules. We cannot distinguish between the methoxy radicals (24) and carbonyl radicals (25) since their *g*-values are very close to those of carboxyl radicals. However, unpaired electrons on SiO_2 formed by cogrinding may transfer to the methoxy or carbonyl groups in IM molecules since the electronegativity of carbon or

TABLE 1
Changes in the Radical Concentration by Grinding

	Physical mixture	IM ground for 30 min	SiO_2 ground for 30 min	Mixture ground for 30 min
Radical conc (10^{15} spin/g)	3.4	7.7	363.6	68.8

oxygen is higher than that of silicon. This charge transfer increases the radical concentration in IM, and decreases that of SiO_2 as a consequence of cogrinding.

3.3. Charge Transfer at the IM/SiO_2 Interface

We now examine by XPS whether and to what extent charge transfer occurs across the IM/SiO_2 interface, since the change in the electron binding energy reflects the change in the electron density. The results are shown in Fig. 6 for Si2*p* of the ground mixture and separately ground SiO_2. The changes in the Si2*p* binding energy by cogrinding are remarkable. One Si2*p* peak of the physical mixture (102 eV), typical for a Si–O bond on the SiO_2 surface (26), shifts toward both low- (100 eV) and high-energy (104 eV) sides by cogrinding. The shift in the Si2*p* spectra of the coground mixture is approximately 2 eV toward lower binding energy. No such shift is observed on separately ground SiO_2. This indicates that separate grinding does not bring about a change in the Si electron density because of the absence of the partner that interacts with SiO_2. Simon *et al.* reported that the binding energy for Si–O bonds shifted by approximately 1.5 eV to a lower binding energy in a poly(cyclopentadiene)–silica hybrid (27). Therefore, the shift strongly suggests formation of Si–O–C bridging bonds at the interface between IM and SiO_2. This is one of the consequences of the chemical reaction during cogrinding SiO_2 with IM. The signals at 102 eV and 100 eV are attributed to states similar to Si^{4+} and those like Si^{2+}, respectively (28). Therefore, it is highly likely that the formation of Si–O–C bonds brings about a charge transfer from the initial state of Si similar to Si^{4+} toward the final state similar to Si^{2+}. The shift of the Si2*p* peak toward highbinding energy indicates that the number of nearest-neighbor oxygen atoms increases under mechanical stress. As shown by the ESR spectra, the increase in the number of oxygen atoms coordinated to the Si atom results from the dangling bond formation to generate an *E*′ center and NBOHC, and to entrap oxygen of IM molecules.

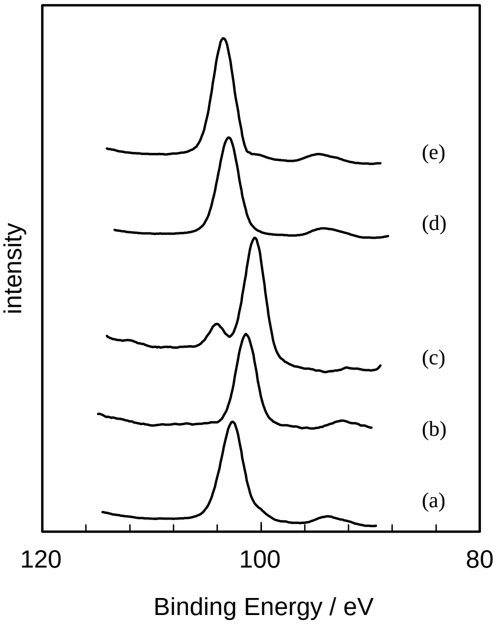

FIG. 6. Si2*p* X-ray photoelectron spectra of (a) physical mixture, (b) coground for 30 min, (c) coground for 180 min, (d) SiO_2 ground for 30 min, and (e) SiO_2 ground for 180 min.

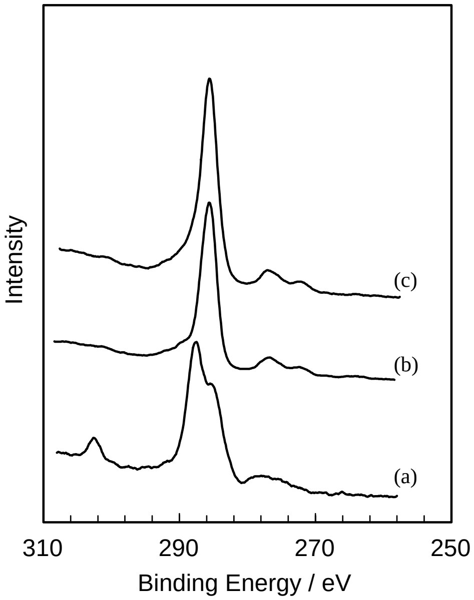

FIG. 7. C1*s* X-ray photoelectron spectra of (a) physical mixture, (b) IM/SiO_2 coground for 30 min, and (c) coground for 180 min.

Charge transfer due to cogrinding can also be visualized by the chemical shift of XPS for C1*s*, as shown in Fig. 7. In the spectrum of the physical mixture, C1*s* peaks from C–OH or C–O–C (286 eV), and C=O or COOH (289 eV) (27) are detected. We cannot distinguish whether the C1*s* peak at 286 eV is from the C–C or C–H bonds of the IM molecule. By cogrinding, the peak intensity at 289 eV remarkably decreases relative to that at 286 eV. This indicates that cogrinding brings about dehydration. Since a water molecule is formed from the carboxyl group of IM and the silanol group of SiO_2, an ether-like bond, Si–O–C, is left behind after dehydration.

The change in the O1*s* by grinding is shown in Fig. 8. The major peak in this figure is attributed to oxygen atoms from SiO_2 (26, 29). The absence of the O1*s* from IM might be due to the eventual coating of the IM surface by ultrafine SiO_2 particles. One O1*s* peak of the physical mixture (533 eV) shifts toward the low-energy (530 eV) side in the coground mixture. No such a shift is observed on separately ground SiO_2. Since an empirical proportionality between the

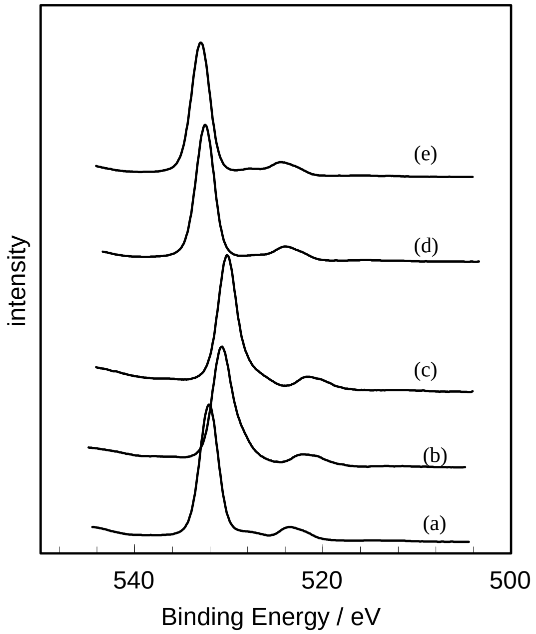

FIG. 8. O1*s* X-ray photoelectron spectra of (a) physical mixture, (b) coground for 30 min, (c) coground for 180 min, (d) SiO_2 ground for 30 min, and (e) SiO_2 ground for 180 min.

binding energy of the O1*s* core level and the Si valence state at the SiO_2/Si interface was reported (29), the shift toward low binding energy of O1*s* by cogrinding is the consequence of the reduction of Si atoms by charge transfer. Based on the above discussions, we propose a simple model of IM compounded with SiO_2, as shown in Fig. 9. The higher stability of amorphous IM compounded with SiO_2 was attained by prolonged cogrinding rather than by melt-quenching (10). Figure 9 illustrates two kinds of interactions between IM and SiO_2, which inhibit free rotation of IM molecules on SiO_2 and immobilize the indomethacin molecules to suppress recrystallization, and hence to increase the stability of the amorphous indomethacin.

The principle of electronegativity equalization (4, 30) is quite useful to explain this charge transfer. The heart of the principle is redistribution of the valence electrons until the atoms attain a common intermediate electronegativity when two atoms with different electronegativities react with each other. In order to explain the SiO_2/IM solid state interaction on the basis of this principle, local electronegativity must be taken into consideration. The local electronegativities of the silicon and oxygen atoms are expressed by the following equations (28),

$$X_{\mathrm{Si}} = [\chi_{\mathrm{Si}}\,\chi_1\,\chi_2\,\chi_3\,\chi_4]^{1/5} \qquad [2]$$

$$X_{\mathrm{O}} = [\chi_{\mathrm{O}}\,\chi_1\,\chi_2]^{1/3}, \qquad [3]$$

where χ_{Si} and χ_{O} are the electronegativities of silicon and oxygen atoms, respectively, and χ_n with $n = 1, 2, 3, 4$ expresses the number of nearest neighboring atoms. When we employ Pauling's electronegativity values (silicon, 1.8; oxygen, 3.5; and carbon, 2.5), the local electronegativities of oxygen of silanol groups (Si–O–H) and IM/SiO_2 bridging bonds (Si–O–C) are 2.37 and 2.51, respectively, from Eq. [3]. On the other hand, the electronegativity of COOH is reported to be 2.69 (31). The driving force toward a new bond is the difference in the electronegativities between the COOH of IM and Si–OH of SiO_2. When the electronegativities of the two functional groups remain unchanged, a large imbalance of the charge arises. In order to equalize the electronegativities between COOH and Si–OH to form a stable C–O–Si bridging bond, the valences have to change by charge transfer as in the following scheme,

$$\text{COOH (2.69)–Si–OH (2.37)} \rightarrow \text{Si–O–C (2.51)}. \qquad [4]$$

The local electronegativities of Si^{4+}, Si^{3+}, and Si^{2+} are 3.06, 2.68, and 2.34, respectively, from Eq. [2]. The formation of C–O–Si bridging bonds leads to the apparent reduction of silicon from the state similar to Si^{4+} to one like Si^{2+}. The closest valence state of Si to those calculated for the new bond is Si^{3+} or Si^{2+}. Actually, the mixture coground for 30 min shows a Si^{3+} peak at 101 eV, as shown in Fig. 6. Taking the valence electron of Si atom, i.e., two electrons in 3*s* and 3*p* orbitals, into account, Si^{2+} seems to be more stable than Si^{3+}. Thus, the apparent reduction of Si by cogrinding also justifies the formation of bridging bonds accompanied by a charge transfer.

4. CONCLUSION

Electron transfer from C to Si through the central oxygen of the hetero bridging bond, C–O–Si, was observed as a

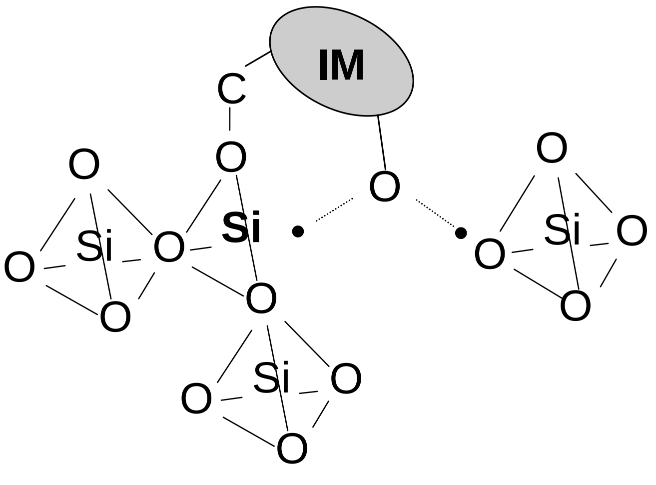

FIG. 9. Model of mechanically induced interaction between IM and SiO_2.

result of dehydration between silanol groups of SiO_2 and carboxyl groups of IM in the cogrinding process. The cogrinding process further brings about a specific interaction with an electron transfer. Oxygen atoms from the methoxy and carbonyl groups of IM interact with the mechanically induced dangling bonds on the surface of SiO_2. This charge transfer is in line with the principle of electronegativity equalization.

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