Some Mechanochemical Considerations on the Numbers of Spins Induced by Ultraviolet Light

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The number of spins/g (NOS) generated in a binary powder of glycolic acid and silica-alumina (SA) increased during ultraviolet (UV) irradiation. After stopping illumination, the NOS value was found to decrease up to a constant number of sping/g (CNS), which was remarkably greater than the NOS value obtained before UV irradiation. The CNS values, thus obtained, were influenced not only by the calcination temperature of SA (T_{ca}) and by the atmosphere of storage, but also by the duration of UV irradiation (DI). The values of CNS obtained at a low T_{ca} (below 400 °C) were also influenced by the time interval between stopping shaking and the start of UV irradiation (t_i). Values of NOS having attained CNS remained unchanged for a long period, but finally began to decrease. The duration of CNS (DCNS) was also affected by T_{ca}, the atmosphere of storage, DI, and t_i. DCNS decreased when CNS increased, and became unchanged when CNS reached a constant value. Values of CNS and DCNS induced by UV light were also influenced by the size of SA particles and by the mechanical energy given by shaking or compressing. Such mechanochemical effects are available, at least for studying the generation mechanism of UV-induced surface activity, for an improvement of the reproducibility of physicochemical data obtained during or after UV irradiation, and for the method of obtaining materials of constant efficiency.

Mechanochemistry is concerned with changes in the properties of materials due to the mechanical forces applied to organic or inorganic solids and powders. Specifically, the effects of sintering, lubrication, wear, adsorption, wetting, structural changes, chemical reactions, such as oxidation, reduction, decomposition, polymerization, and corrosion have recently been investigated.[1] These transformations are usually preceded by a variation in surface structures, the ejection of electrons, the formation of ion pairs, the cleavage of covalent bonding, or the local formation of high energy sites, due to the energy or the heat evolved in the materials during the course of the mechanical processes.[1] Mechanochemical changes can also be caused by exposing materials to γ-rays, X-rays, light, or ultrasonic waves.[1]

We have already observed the formation of radicals in binary powders of a saccharide and a metal oxide,[2,3] and of a metal oxide and an organic compound[4] by means of electron spin resonance (ESR) spectroscopy. Subsequently, the effects of mechanical energy given by shaking or compressing on the number of spins (NOS) generated in a binary powder of glycolic acid (GA) and silica-alumina (SA) were examined.[5] A mixed powder of GA and SA may be taken as a model not only for studying the reactivity of a contact reaction occurring on the surface of a solid-acid catalyst, but also in considering the effects of mechanical forces on the solid acidity of an aluminosilicate when utilized as an antacid. Such mechanochemical effects on the transformation of physicochemical properties would provide a method for manufacturing antacids or catalysts possessing constant physicochemical properties, or a method of forcing drugs or catalysts to exhibit constant efficiency. Under these circumstances, the time-courses of NOS for periods of up to 5 years after mixing were considered mechanochemically.[6,7] We reported therein that NOS increased initially, remained at a maximal value for a long period, and finally began to decrease from the maximum.

Recently, we observed the characteristic behaviors of NOS induced by ultraviolet (UV) light with a binary mixture of GA and SA. New mechanochemical factors, such as the duration of UV irradiation (DI) and the time interval between the stop of shaking and the start of UV irradiation (t_i), were found to affect NOS induced by UV light significantly. Then, the object of this paper was to describe the influences of DI or t_i on the behavior of NOS, followed by some consideration of the reproducibility of physicochemical properties induced by UV light and on the induction of spin-generating sites.

Experimental

Materials. Commercial GR-grade GA was used after being recrystallized from water and dried in vacuo. Nikki Kagaku N631-L Type SA was calcined for 5 h at 200, 400, or 600 °C.

ESR Measurement. The spectrometer, the instrumental settings, and the method of the determination of NOS were described previously.[5,6]

Procedure. GA (10%) was mixed with SA (100—150, 150—200, 200—250, or 250—325 mesh) in nitrogen, dry air, or humid air and was shaken by a Taiyo SR-II type reciproshaker for 15 min. This mixed powder was stored in a desiccator or an ESR cell in nitrogen, dry air, or humid air for a given period (t_i) at 25 °C in the dark. The mixed powder was then irradiated with UV light for a given duration (DI) and left as such at 25 °C for a suitable period; then an ESR spectrum was finally measured at 25 °C. A JEOL ES-05 H-type UV irradiation unit fitted with a 500-W mercury lamp was used for illumination.

The method to determine the duration of constant number of spins/g (DCNS) was as follows: SA was mixed with a small amount (less than 1%) of GA, left for a period of t_i, irradiated with UV light for a period of DI, and then mixed again with GA (10%) immediately after the NOS value of the irradiated mixture started to decrease from a constant number of spins/g (CNS). The DCNS value is defined by the time interval between the end of the second mixing with GA and the start of the second decrease in NOS.[7]

A method for obtaining dry or humid air,[8] and that of applying compressive stress[5] were described previously.

Results and Discussion

Characterization of Spins. The ESR spectra of GA-SA mixtures were demonstrated in a previous paper.[6] ESR signals obtained with a binary powder of GA and SA comprised two components: 2,2′-oxydiacetic acid radicals, and electrons or holes trapped in SA.[6]

Time-Courses of NOS. A) Increase in NOS during UV Irradiation. In the first place, the time-courses of NOS during UV irradiation were exmined with a binary system of GA (10%) and SA (150—200 mesh) at a constant shaking duration (15 min) and constant t_i (170 h). An ESR spectrum was measured under UV irradiation from immediately after the start of illumination. Some examples of the time-courses of NOS are shown in Fig. 1. The NOS value at T_{ca}=600 °C in nitrogen rapidly increases for a period of up to 2 h after the start of UV irradiation; it then increases very slowly, and finally reaches an entirely constant value (75×10^{15} spins/g) at ca. 70 h after the start of the illumination. A similar time-course of NOS is observed at a T_{ca} of 400 or 200 °C in nitrogen. However, NOS at T_{ca}=400 or 200 °C increases remarkably for a period of up to ca. 8 or 30 h, respectively, and reaches an entirely constant NOS (68 or 56×10^{15} spins/g, respectively) at ca. 100 or 300 h, respectively, after the start of UV irradiation. The values of NOS, time-courses of NOS, and the dependences of the time-courses of NOS on T_{ca} in dry air were identical with those in nitrogen. Although the time-courses of NOS in humid air (relative humidity (RH)=60%) were analogous to those described above, their NOS values were smaller than those in nitrogen, while their variations in NOS continued for longer periods.

The ratio of entirely constant NOS obtained at DI=300 h to an NOS at DI=0 h decreased with an increase in T_{ca}. Moreover, the NOS ratio obtained in nitrogen was identical with that in dry air, but was considerably smaller than that obtained in humid air.

B) Decrease in NOS after the Stop of UV Irradiation. Figure 2 depicts the time-courses of NOS after stopping UV irradiation for a binary powder of GA (10%) and SA (150—200 mesh). The experimental conditions were: shaking duration, 15 min; t_i, 170 h; DI, 32 h. NOS values were measured from immediately after the stop of UV irradiation. As shown in Fig. 2, NOS is greatest immediately after stopping UV irradiation, gradually decreasing, and finally reaching a constant number of spins/g (CNS). In an atmosphere of nitrogen, the CNS value increases with an increase in T_{ca}, while the time required for attaining a constant number of spins/g (t_{CNS}) decreases. The values of CNS and t_{CNS} in dry air were almost identical with those in nitrogen. However, in humid air, the CNS values were smaller, and the t_{CNS} values were greater than those in nitrogen (e. g., CNS in humid air at T_{ca}=200, 400, or 600 °C was 26, 41, or 47×10^{15} spins/g, respectively, and the corresponding t_{CNS} was ca. 48, 24, or 3 h, respectively).

Comparing the time-courses shown in Fig. 1 with those shown in Fig. 2, NOS varies hysteretically. That is, CNS at DI=32 h (CNS_{32}), for example, is less than NOS during illumination, but is greater than NOS just before UV irradiation (NOS_0). The CNS_{32}/NOS_0 ratio in dry air was small at T_{ca}=600 °C (1.06), but

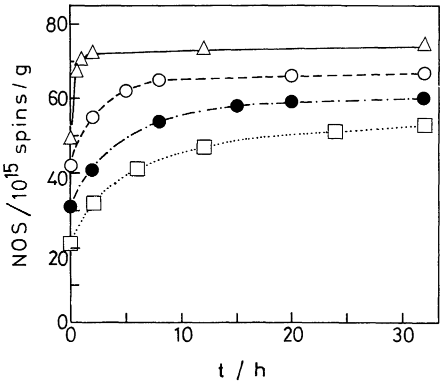

Fig. 1. Time-courses of NOS during UV irradiation for the binary system of GA and SA. Experimental conditions were: T_{ca}=200 °C in nitrogen (□), T_{ca}=400 °C in nitrogen (○), T_{ca}=600 °C in nitrogen (△), or T_{ca}=400 °C in humid air (RH=60%) (●).

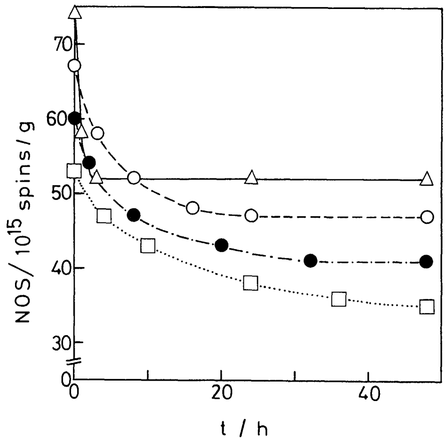

Fig. 2. Time-courses of NOS after the stop of UV irradiation for the binary mixture of GA and SA. Symbols are the same as those in Fig. 1.

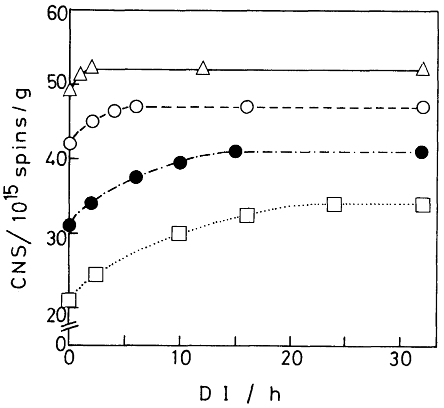

Fig. 3. Dependences of CNS on DI for the binary powder of GA and SA. Symbols are identical with those in Fig. 1.

increased at a decreased T_{ca} (1.12 or 1.62, respectively, at a T_{ca} of 400 or 200 °C). The CNS_{32}/NOS_0 ratio in nitrogen was identical with that in dry air, but was smaller than that in humid air (1.18, 1.32, or 1.86, respectively, at a T_{ca} of 600, 400, or 200 °C).

Dependences of CNS on the Conditions of UV Irradiation. A) Effects of DI on CNS. Next, the nature of CNS was examined. First, CNS was found to be influenced by DI. The values of CNS obtained with a binary powder of GA (10%) and SA (150—200 mesh) at a constant shaking duration (15 min), and constant t_i (170 h) are dependent on DI in the manner demonstrated in Figure 3. As can be seen from Fig. 3, CNS increases with an increase in DI, decreases its increase, and finally reaches a plateau at a saturated CNS (SCNS). The dependences of SCNS (obtained at DI=32 h) on T_{ca} and on the atmosphere of storage have already been described (Fig. 2). Unsaturated CNS values obtained at a decreased DI were, of course, less than SCNS, but varied with T_{ca} or with the atmosphere of storage in a manner similar to SCNS values.

The value of DI required for attaining SCNS (DI_{SCNS}) also depended on T_{ca} and on the atmosphere of storage. For example, a DI_{SCNS} value obtained in nitrogen at T_{ca}=200, 400, or 600 °C is ca. 24, 6, or 2 h, respectively. A DI_{SCNS} value in dry air (e.g., ca. 6 h at T_{ca}=400 °C) was identical with that in nitrogen, but was smaller than that in humid air (e.g., ca. 15 h at T_{ca}=400 °C).

B) Effects of t_i on CNS. Some CNS values were influenced by t_i. The effects of t_i on CNS were observed at T_{ca}=200 °C in nitrogen or in dry air, and at a T_{ca} below 400 °C in humid air. At a T_{ca} of 600 °C, the effects of t_i were not observed. Figure 4 demonstrates the relationship between CNS and t_i for the binary powder of GA (10%) and SA (150—200 mesh) at a constant shaking duration (15 min). As illustrated in Fig. 4, CNS is the greatest at t_i=0 h, decreases gradually, and reaches a constant value at a suitable t_i.

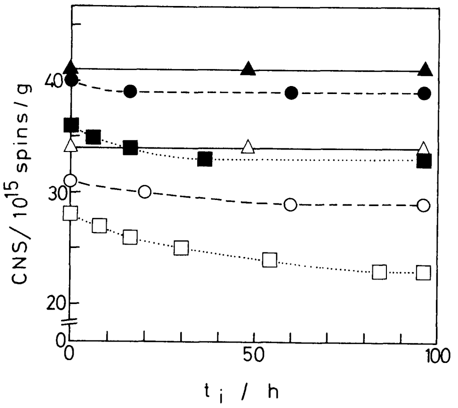

Fig. 4. Relationship between CNS and t_i for the GA-SA mixture obtained at T_{ca}=200 °C and at a DI of 1.0, (□), 8.0 (○), or 24 (△) h in nitrogen, or at T_{ca}=400 °C and at a DI of 1.0 (■), 8.0 (●), or 24 (▲) h in humid air.

The value of t_i required to reach constant CNS decreased with an increase in DI. That is, the ratio of CNS at t_i=0 h to the constant CNS independent of t_i decreased with an increase in DI and reduced to unity at a DI of greater than 30 h. In addition, this ratio obtained in humid air was greater than that in nitrogen or dry air. The dependences of CNS on t_i in dry air were identical with those in nitrogen.

Dependences of DCNS on the Conditions of UV Irradiation. A) Effects of DI on DCNS. As can be predicted by previous reports,[6,7] NOS values remained constant at CNS for a long period, but finally began to decrease. The time when NOS began to decrease agreed with the time when free GA molecules mixed with SA disappeared.[6,7] Then, DCNS may be a good measure of the rates of the contact reactions on the surface of SA.[6,7]

Figure 5 shows the effects of DI on the CNS (ordinate) vs. DCNS (abscissa) plots for the binary powder of GA (10%) and SA (150—200 mesh) at t_i=170 h. Although not shown in Fig. 5, DCNS in nitrogen obtained at T_{ca}=200 °C and at DI=0, 1.0, 3.0, or 32 h was ca. 1100, 1060, 1040, or 1020 d, respectively, while the corresponding value of CNS was the same as that in dry air (shown in Fig. 5). As can be seen from Fig. 5, DCNS is dependent on T_{ca}, on the atmosphere of storage, and on DI. DCNS decreased when CNS increased. On the contrary, when the slope of the decrease curve of CNS increased, the slope of the increase curve of DCNS increased. In addition, both CNS and DCNS reached constant values under identical experimental conditions.

At a T_{ca} of 600 °C, DCNS values are almost inversely proportional to the corresponding CNS values. Therefore, NOS induced by UV light may increase directly the rates of contact reactions on the surface of SA. At a T_{ca} of 200 °C, however, CNS increases greatly

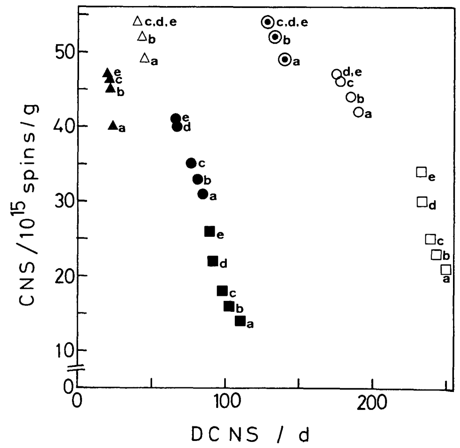

Fig. 5. Effects of DI on the CNS vs. DCNS plots for the binary powder of GA and SA at a constant t_i (170 h). Experimental conditions were: T_{ca}=600 °C in nitrogen (◉), T_{ca}=200 (☐), 400 (○), or 600 (△) °C in dry air, or T_{ca}=200 (■), 400 (●), or 600 (▲) °C in humid air. The DI values employed were: 0 (**a**), 1.0 (**b**), 3.0 (**c**), 10 (**d**), and 32 (**e**) h. The symbol **d**,**e**, for example, denotes that both CNS and DCNS values became unchanged at a DI value of above 10 h.

with an increase in DI, whereas the decrease in DCNS is much smaller than that expected from the inverse proportionality. Therefore, only part of spins produced by UV irradiation may increase the rates of the contact reactions. An intermediate relationship between CNS and DCNS is obtained at T_{ca}=400 °C.

B) Effects of t_i on DCNS. Figure 6 depicts the effects of t_i on the plots of CNS against DCNS for the binary powder of GA (10%) and SA (150—200 mesh) at a constant shaking duration (15 min) and constant DI (1.0 h). Although not shown in Fig. 6, DCNS obtained in nitrogen at T_{ca}=200 °C and at t_i=0, 8, 30, or 100 h was ca. 1030, 1040, 1050, or 1060 d, respectively, whereas the corresponding value of CNS was the same as that in dry air (shown in Fig. 6). The DCNS value was influenced by t_i at T_{ca}=200 °C in nitrogen or in dry air, and at a T_{ca} of below 400 °C in humid air. At a T_{ca} of 600 °C, the effects of t_i on DCNS were not observed. As can be seen from Fig. 6, a DCNS value is the smallest at t_i=0 h, increased with an increase in t_i and finally reached a constant value. Eventually, the DCNS value induced by t_i was dependent on T_{ca}, on the atmosphere of storage, and on DI. DCNS decreased when CNS increased, and became constant when CNS reached a constant value.

The DCNS values obtained at T_{ca}=400 °C in humid air are almost inversely proportional to the corresponding CNS, whereas those obtained at T_{ca}=200 °C are much smaller than those expected from the inverse proportionality. Therefore, only part of spins induced by t_i may increase the rates of contact reactions at a T_{ca} of 200 °C.

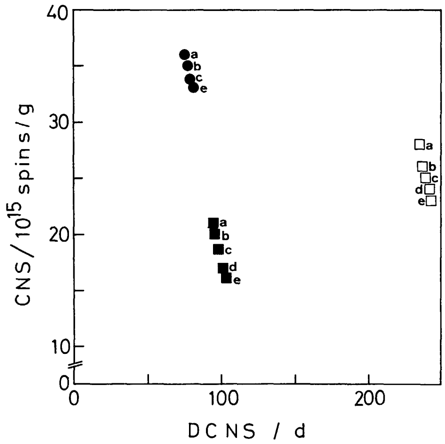

Fig. 6. Effects of t_i on the plots of CNS (ordinate) against DCNS (abscissa) for the binary system of GA and SA at DI=1.0 h. Experimental conditions were: T_{ca}=200 °C in dry air (☐), or T_{ca}=200 (■), or 400 (●) °C in humid air. The t_i values examined were: 0 (**a**), 8.0 (**b**), 30 (**c**), 60 (**d**), and 100 (**e**) h.

Effects of the Content of GA. Needless to say, DCNS increased with an increase in the content of GA. On the other hand, CNS and t_{CNS} were independent of the content of GA in the region of 0.1—30%.

Results Obtained with Other Atmosphere of Storage. Values of CNS and t_{CNS} in dry oxygen were identical with those in nitrogen or dry air. On the other hand, CNS decreased, and t_{CNS} increased at an increased RH of the atmosphere used. Needless to say, DCNS values decreased with an increase in the content of oxygen or moisture of the atmosphere used. Although DCNS decreased, and CNS and the ratio of CNS to NOS before illumination increased with an increase in RH of the atmosphere used, CNS or DCNS was dependent on DI or t_i in a manner similar to that in a humid air of RH=60%.

Formation of Spins in a Binary Mixture Containing SA without Any Calcination. The NOS values in a binary mixture of GA and SA without any calcination were also affected by UV irradiation. The values of the NOS obtained during UV irradiation at DI=0, 10, 30, 100, or 300 h in nitrogen were determined to be 7.0, 16, 25, 29, or 31×10^{15} spins/g, respectively, while the corresponding CNS obtained after the end of the illumination was 7.0, 11, 16, 18, or 19×10^{15} spins/g respectively. DCNS values of this mixture were too great (>2000 d) to be measured.

NOS Generated in a Binary Mixture Containing SA Irradiated in Advance. SA calcined at 200 °C (150—200 mesh) was irradiated with UV light independently, and then mixed with GA (10%). The NOS value for this mixture was initially small, gradually increased, and reached a maximun. The maximal value in nitrogen at DI=0, 10, 30, 100, or 300 h, for example, was determined to be 21, 25, 27, 28, or 29×10^{15} spins/g, respectively, which indicated that SA illuminated in advance could induce spins after having been mixed with GA. The corresponding DCNS values (>2000 d) were too great to be measured. These facts suggest that the physicochemical properties of antacids or of solid-acid catalysts, for example, can be affected by the UV irradiation in advance to the powders of aluminosilicates.

Effects of the Particle Size of SA. Values of NOS or CNS obtained with GA-SA mixtures were found to increase with a decrease in the particle size of SA. Whereas, DCNS or t_{CNS} decreased with decrease in the size of SA particles in a manner similar to that described previously.[7] For a constant particle size of SA (100—150, 200—250, or 250—325 mesh), CNS, DCNS, or t_{CNS} showed almost the same dependences on T_{ca}, on the atmosphere of storage, on DI, or on t_i as those obtained with SA of 150—200 mesh described above. In every case, the value of CNS, the increment of CNS, the decrement of DCNS, and so forth became greatest when SA possessing of the smallest particle size (250—325 mesh) was used.

Effects of Shaking or Compressing. CNS, DCNS, t_{CNS}, and their dependences on DI and t_i were affected by the mechanical energy given by shaking or compressing. For example, the increments of CNS and the decrements of DCNS and of t_{CNS} with an increase in T_{ca} or DI, or with a decrease in t_i or the particle size of SA increased remarkably with an increase in shaking duration or in compressive stress in a manner similar to those described previously.[7]

NOS Generated in Binary Mixtures of SA and Other Organic Compounds or of GA and Other Aluminosilicates. The NOS values obtained with a binary system of SA and ascorbic acid, salicylic acid, acetic acid, indole, or glycerol, or with a binary mixture of GA and a zeolite, or an antacid (e.g., aluminum silicate, magnesium silicate, or magnesium aluminum silicate) were dependent on T_{ca}, the atmosphere of storage, DI, t_i, the particle size of SA, mechanical energy given by shaking or compressing, and so on in a manner similar to those obtained with GA-SA mixtures. Among the aluminosilicates examined, SA afforded the greatest NOS upon contact with an organic compound, probably due to its strong solid acidity (the acidity function $(H_0)<-8$).[9] DCNS obtained with a mixture containing ascorbic acid was too small, while that obtained with a mixed system containing acetic acid, or glycerol was too great for studying the time-courses of mechanically induced spins (e.g., CNS, DCNS, and t_{CNS}) in various atmospheres. Contact reactions of GA occurring on the surface of SA in nitrogen or dry air were found to be relatively simple.[6] Eventually, a GA-SA mixture was chosen as a convenient model of an antacid in contact with organic compounds and of a solid-acid catalyst used in some contact reactions.

Reproducibility of NOS Induced by UV Light. Physicochemical properties (e.g., CNS, DCNS, or t_{CNS}) of mixed systems containing aluminosilicates were quite hard to reproduce the same phenomena constantly. As described above, mechanochemical considerations were important for a quantitative discussion of physicochemical properties.

In previous reports,[5—7] the effects of the storage temperature, humidity, atmosphere, T_{ca}, the size of SA particles, mixing duration, machines used for mixing, compressive stress on the behaviors of NOS were described using binary mixtures containing SA. In the present paper, we introduce some new factors available for considering the mechanochemical effects induced by UV light.

The effects of such new factors on NOS, CNS, DCNS, or t_{CNS} may be part of the important factors for explaining the lack of the reproducibility of the physicochemical properties of relatively complicated systems, and therefore may be useful for improving the degree of the reproducibility of the physicochemical data. Mechanochemical considerations may also provide a new method of supplying drugs or catalysts of constant efficiency.

Nature of the Spin-Generating Sites. An adsorption equilibrium for a mixture of an organic compound and an aluminosilicate is known to be attained 2 d or more after mixing.[9] Therefore, the state of the GA-SA mixture during or immediately after the application of mechanical energy might be regarded as being non-equilibrium. The results described in this paper seem to indicate that the NOS values induced by UV irradiation at a non-equilibrium state differed from those induced by the illumination at an equilibrium state. Especially, the difference became significant when illuminated at a non-equilibrium state remote from the equilibrium to be reached (t_i=0 h). We hope that the effects of DI and t_i on CNS and DCNS might be generalized for the dependences of many physicochemical properties on commonly employed mechanical processes.

Comparing again the time-courses shown in Fig. 1 with those shown in Fig. 2, the CNS values are smaller than NOS during UV irradiation, but are greater than NOS values before the illumination, indicating the occurrence of a hysteretical increase in NOS and a decrease in DCNS by UV irradiation, even for a very short period. Of course, no spin formation was observed in SA powder alone. However, as described above, spins are induced in a binary powder containing SA without any calcination or in a mixture containing SA illuminated independently in advance.

The active sites for the formation of spins on the surface of an aluminosilicate have been attributed to Lewis acid sites.[10] Lewis acid sites are known to be produced from Brönsted acid sites at an elevated T_{ca}

(over 500 °C).[10] However, the results described in this paper suggest that Lewis acid sites are formed even at a low T_{ca} (less than 200 °C) or in a humid condition. An increase in NOS in humid air during and after UV irradiation may then be explained by the gradual formation of weak Lewis acid sites, whereas a decrease in NOS at the final stage may be resulted from the gradual decay of Lewis acid sites, where strong Lewis acid site indicates an active site which induces spins relatively soon after mixing with an organic compound (e.g., the spin-generating site on the surface of SA calcined at 600 °C), while weak acid site means a mechanically induced spin-generating site exhibiting time and process dependences. Whether CNS is inversely proportional to DCNS or not (shown in Figs. 4 and 6) may have some significance on the induction mechanism of weak acid sites (mechanically induced Lewis acid sites). Further details will be presented in subsequent papers.

Conclusion

Mechanochemical considerations are of importance for understanding the lack of the reproducibility of the physicochemical properties of relatively complicated systems containing aluminosilicates. Therefore, they may also provide a method of supplying catalysts or drugs of constant efficiency. In the present work, we introduced some new factors, such as DI and t_i, which were available for mechanochemical considerations on the behaviors of spins, resulting in a further increase in the degree of reproducibility of physicochemical data. Mechanochemical considerations may also be useful for studying the induction mechanism of the surface activity (in particular, the generation mechanism of mechanically induced Lewis acid sites) of aluminosilicates, which suggest a new way of thinking of the induction mechanism of Lewis acid sites from comprehensive and correlative point of view.

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