An XPS Study on the Interaction at the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ Boundary on the Surface of Composite Microspheres Prepared via a Shear-Compressive Mechanical Route†

Isao Saito and Mamoru Senna
Faculty of Science and Technology, Keio University*

Abstract

Composite microspheres of polystyrene or silica coated with a double layer of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ were prepared via mechanical routes using a shear – compressing type machine, specially designed for the purpose of surface coating. The binding energy of $\text{Fe}_{2p3/2}$ measured by XPS increased, while that of Si_{2p} decreased after composite formation. These synchronized shifts increased with increasing intensity of mechanical stress. After heat treatments, chemical interaction during mechanical treatment at the $\text{Fe}_3\text{O}_4/\text{SiO}_2$ interlayer in a composite particle was verified. The fine structure of the interlayer boundary was also examined in detail by electron microscopy.

1. Introduction

Formation or synthesis of composite particles via mechanical routes is increasingly studied with the development of hard wares for those purposes¹⁻⁶⁾. Apart from the relatively simple procedure not involving the use of any solvents, the mechanochemical effects at the interfaces of the host/guest or between a multiple of guests are unique for the synthesis via a mechanical route⁷⁾. This kind of mechanochemical effects is not always particularly significant immediately after mechanical treatment, but often turns out to be important after subsequent thermal treatments. In other words, precursors of the products are formed due to mechanochemical effects, leading to a promotion of the subsequent solid state reactions on heating^{8,9)}. However, using spherical particles of tens of micrometers as host particles in the case of complex formation by a shear-centrifuge apparatus, the combination for the mechanochemical solid state reaction is quite restricted.

Double-layered composites can circumvent this limitation. During double coating, the reaction elements are successively attached on the surface, i.e., by coating the second component on the particles already coated with the first component. Since the choice of the first and the second components is almost unlimited, eventually every kind of solid state reaction can be induced in the confined area of the composite particles.

In contrast to the conventional reaction mixture, where the contact points of dissimilar particles are distributed throughout the mass of the reactant mixture, the contact points of the dissimilar particles are restricted to the interlayer boundaries in the case of a double-layered composite. This enables, for one thing, elucidation of the chemical interaction from the topochemical point of view, and for the other, preparation of a composite where the extent of chemical interaction at the interface is brought under control.

The purpose of the present study is to elucidate the chemical interaction at the boundary of two different guest layers with detailed structure development of fine structure.

2. Experimental methods

2.1 Preparation of composite particles

A commercial apparatus for fabricating complex particles following the principle of shear-compression (Ang-Mill Mechanofusion System, AM-15F, Hosokawa Micron) was used for the preparation of double layered composite particles. The materials employed as host and guest particles are listed in **Table 1**. The operational conditions are summarized in **Table 2**. The net operation time excludes the time for acceleration

Table 1 Starting materials

Abbreviation	Material	Manufacturer	Trade name	Av. particle size (μm)
Sb	Silica	San-ai Chem.	No.1061	9.3
P	Polystyrene	Soken Chem.	SGP-70C	15.6
Sa	Silica	Degussa	Aerosil 200	0.014
F	Magnetite	Toda Kogyo	SSP-9115	0.011

* 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223 JAPAN

† This report was originally printed in *J. Soc. Powder Technology, Japan*, **31**, 18 (1994) in Japanese, before being translated into English with the permission of the editorial committee of the Soc. Powder Technology, Japan.

Table 2 Composite particles and their preparation conditions

Symbol	Host (g)	Guest (g)	Net operation time (min)	Number of revolution (rpm)
F·Sb-1	Sb/54.75	F/0.36	30	1200
F·Sb-2	Sb/54.75	F/0.36	60	1200
F·Sb-3	Sb/54.75	F/0.36	30	2400
F·Sb-4	Sb/54.75	F/0.36	60	2400
Sa·P-1	P/23.67	Sa/5.87	30	1200
F·Sa·P-1	Sa·P-1/29.47	F/0.18	30	1200
F·Sa·P-2	Sa·P-1/29.47	F/0.18	60	1200
F·Sa·P-3	Sa·P-1/29.47	F/0.18	30	2400
F·Sa·P-4	Sa·P-1/29.47	F/0.18	60	2400

and deceleration for the initiation and termination of the machine operation.

2.2 Structural characterization

Transmission electron microscopy (TEM) was predominantly used for this purpose. An ultrathin specimen sliced by an ultramicrotome was subjected to local elemental analysis by using an energy dispersive spectrometer (EDS), installed in a transmission electron microscope (TEM) with an electron beam of 25nm. 5 to 7 points along the diametral direction were chosen to determine the atomic ratio of Fe/Si to determine the distribution of the iron transferred from the second guest, magnetite, in the first guest, SiO_2 . Distribution of Fe and Si was further elucidated by an electron probe microanalyzer (EPMA).

2.3 Chemical interaction

Two methods were used to evaluate the extent of chemical interaction between the host and guest particles or between two guest species. The extent of dissolution of iron was estimated. The sample containing nominally 3.0mg Fe in total, was put into 100cm³ 1N aqueous solution of HCl. Concentration of Fe was analyzed by a phenanthroline method.

For the purpose of examining the direct chemical interaction between magnetite and silica, X-ray photoelectron spectroscopy (XPS) was employed and it observed whether and to what extent the chemical shift of Fe_{2p} and Si_{2p} peaks took place. A 0.05g composite sample was pelletized in a mold of 11mm in diameter under 400MPa. With the aid of a calibration reference to the $Au_{4f7/2}$ signal at 83.8eV, the maximum possible error of the chemical shift was reduced to less than $\pm 0.1eV$.

3. Results and discussion

3.1 Surface structure of the composite particles

The BET specific surface area of the host silica

beads was 155m²g⁻¹. The surface of the composite sample Sb-1, where guest silica beads were top-coated by magnetite of ca. 0.3 μm , magnetite microparticles were smoothed with increasing net operation time and rate of revolution of the machine. This tallies well with the results obtained by Naito *et al*⁽¹⁰⁾ which indicated that the apparent specific surface area of the composite decreases with increasing stress and duration.

On the surface of silica microspheres (Sa)-coating on the polystyrene host particles, Sa·P-1, silica particles were densely deposited, as shown in **Figure 1 (a)**. The top coat, Fe_3O_4 , was also visible on the magnetite/silica double-coated polystyrene, F·Sa·P-1, as shown in **Figure 1 (b)**. With increasing rate of revolution during coating, the surface roughness increased, as shown in **Figures 1 (c)** and **(d)** for samples F·Sa·P-3 and 4, respectively. This kind of surface roughening by severe stress during coating was already suggested previously, when the substrate host particles are relatively deformable⁷⁾.

Fig. 1 Scanning electron micrographs of the composite microspheres: a: Sa·P-1; b: F·Sa·P-2; c: F·Sa·P-3; d: F·Sa·P-4.

3.2 Cross-sectional structure

The cross-section of the doubly coated composite particles, F·Sa·P-1 was subjected to EPMA line analysis. As shown in **Figure 2**, a distinct existence of two different species, Si and Fe , is detected.

In order to analyze the structure of the guest layer and the mechanism of such complex formation, further analysis was also carried out by transmission electron microscope (TEM). As shown in **Figures 3 (a)** and **(b)**, a double-layer as a whole was uniform in thickness, ca. 3 μm , in the case of the sample F·Sa·P-1. The thickness cannot be considered as being representative of the entire composite particles, since there is no guarantee of being cut through an equator. For the samples F·Sa·P-3 and F·Sa·P-4, two different

Fig. 2 EPMA line analysis of the F·Sa·P-1 cross-section

sections of the guest layer were obtained, i.e., with a relatively uniform thickness and a wavy layer with varying thickness, in accordance with the surface observation by SEM, shown in **Figure 1**.

Energy dispersive spectrometry was carried out with a beam spot diameter of 25nm to obtain the local elemental composition of the guest layer. Variation of the atomic ratio, Fe/Si along the thickness of the guest layer is shown in **Figure 4**. Fe is concentrated on the outermost layer for samples F·Sa·P-1 and F·Sa·P-2. In contrast, the maximum value of Fe concentration was found 0.27 μm inward from the outermost surface

for the sample F·Sa·P-4, which was subjected to severer stressing during preparation. The thin dark layer shown in **Figure 3 (f)** corresponds to this magnetite deposits. This indicates that the migration of the outermost layer during coating is also possible when the rate of revolution during the shear compression is high enough. In other words, the first and second guest species are partly mixed during mechanical stressing. It is to be noted that the thin dark layer is not a continuous circle. Fe maximum at the outermost surface was also observed depending on the spot, where local elemental analysis was carried out.

The bulk temperature of the specimen never exceeded 67°C, so that the migration of iron-containing species by thermal diffusion is not conceivable, even if the local temperature were considerably higher than the observed mean temperature. Rather, it is more likely that some parts of the second guest layer have been destroyed, detached together with a part of the first layer and reattached somewhere else. This also explains the discontinuity of the dark layer with enriched iron mentioned above. When the shear-compression stress is large enough, this kind of fall-off and reattachment must have been repeated.

3.3 Dissolution of guest species from composite guest layer

The extent of dissolution of iron-containing species was evaluated and is shown in **Figure 5**. The vertical

Fig. 3 Transmission electron micrographs of thin slices of the composite microspheres: a and b : F·Sa·P-1; c and d : F·Sa·P-2; e and f : F·Sa·P-4

Fig. 4 Variation of the local atomic ratio, Fe/Si with the distance from the composite particle surface

axis in Figure 5 denotes the fractional dissolution, with respect to the total iron content calculated from the overall concentration of magnetite in the overall composite particles. The lower fractional dissolution means the larger fraction of magnetite remaining in the composite, in spite of the immersion of the sample into 1N HCl at 30°C for 48h, where bare magnetite can be completely dissolved. As shown in Figure 5, the fractional dissolution was smaller at a higher rate of revolution and longer retention time. One of the reasons for incomplete dissolution is obviously the geometrical factor, i.e., some part of magnetite was buried in the first guest layer, silica, preventing its contact with the acidic solution.

We have therefore tried to crush the guest layer in a ball mill in the presence of HCl solution and let it dissolve *in situ*. As shown by triangles in Figure 5, the fractional dissolution increased to some extent with additional ball milling *in situ*. Nevertheless, the fractional dissolution never reached unity. This might suggest that magnetite was chemically stabilized by virtue of mechanochemical reaction, although persisting geometrical factors, i.e., hard coating of magnetite particles by silica microspheres are not to be ruled out.

3.4 Chemical shift of XPS spectra

In order to examine directly whether and to what extent silica and magnetite mechanochemically inter-

Fig. 5 Variation of fractional dissolution of Fe with net operation time for composite preparation

acted, X-ray photoelectron spectroscopy was carried out. The binding energies of inner electrons, Fe_{2p} , Fe_{3p} and Si_{2p} were examined. As shown in Figure 6, the binding energy of Fe_{2p} is shifted consistently toward a higher energy compared to that of the intact magnetite, 710.8eV, for the series of $F·Sb$ samples, where magnetite was coated directly on the host silica beads. A similar tendency is also observed for the series of $F·Sa·P$, i.e., silica/magnetite double layered composite, coated on polystyrene beads, although the extent of the chemical shift was smaller than that for $F·Sb$, as shown in Figure 7. The binding energies of Fe_{3p} (not shown in the figure) showed a similar behavior.

As for the binding energy of Si_{2p} , the extent of chemical shift is much smaller, due mainly to its larger amount compared with magnetite. Nevertheless, the chemical shift in the direction opposite to that of the case of Fe_{2p} , i.e., toward the lower energy side, was observed, as shown in Figures 8 and 9.

3.5 Chemical interaction between guests or guest and host

From the chemical shifts of XPS spectra as well as the depression of iron dissolution, chemical interaction between magnetite and silica during a complex formation by shear-compression stressing has been indicated. Similar phenomena were reported for the chemical shift of V_{2p} electrons toward higher energy as a result of interaction with silica for supported catalyst of V_2O_5 ^{11,12).}

Fig. 6 Fe_{2p} XPS profiles for F·Sb composites. Vertical line corresponds to $Fe_{2p3/2}$ for untreated magnetite.

Fig. 7 Fe_{2p} XPS profiles for F·Sa·P composites with double guest layers. Vertical line corresponds to $Fe_{2p3/2}$ for untreated magnetite.

Fig. 8 Si_{2p} XPS profiles F·Sb composites. Vertical line corresponds to Si_{2p} for untreated silica.

The chemical shift of Fe_{2p} , Fe_{3p} can also take place by a simple oxidation from its ferrous state to a ferric state. Therefore, we examined the XPS peaks for hematite, obtained by calcining magnetite in air at 1100°C, with and without the coexistence of silica. As shown in **Figure 10**, commercial hematite and calcined magnetite without silica show the same chemical shift. However, when magnetite was calcined with silica microspheres (Silica a) and silica beads (Silica b), the chemical shifts observed were still higher by 0.4eV and 0.3eV, respectively. The chemical shifts to a value higher than the highest possible oxidation number of Fe, i.e. 3, can only be explained by a chemical interaction with silica. When incipient chemical bonding $Fe-O-Si$ is formed at the magnetite/silica interface, the electron density of silica is increased due to the higher electron affinity of Si than that of Fe, leading to a decrease in the binding energy of the electrons bound to silicon atoms. The reverse is the case for iron, i.e., the interaction with silicon brings about a decrease in the electron density, causing an increase in the binding energy. These are exactly what we observed in **Figures 6** through **9**.

Incipient chemical interaction or reaction during mechanical treatment can be explained by a mechanical diffusion, where migration of the atoms takes place at the contact point due to local plastic deformation, i.e., microscopic diffusion through the surface defects¹³⁾.

Fig. 9 Si_{2p} XPS profiles for F·Sa·P composites with double guest layers. Vertical line corresponds to Si_{2p} for untreated silica.

Fig. 10 Fe_{2p} XPS profiles for the samples after heating at 1100°C. Starting materials A: simple mixture of magnetite and silica (Sa); B: simple mixture of magnetite and silica beads (Sb); C: hematite without heating; D: magnetite; E: magnetite without heating. Vertical line corresponds to Fe_{2p} for untreated magnetite.

Fig. 11 Fe_{3p} XPS profiles for the samples after heating at 1100°C. Starting materials A: simple mixture of magnetite and silica (Sa); B: simple mixture of magnetite and silica beads (Sb); C: hematite without heating; D: magnetite; E: magnetite without heating. Vertical line corresponds to Fe_{3p} for untreated magnetite.

Formation of $Fe-O-Si$ chemical bonding during mechanical treatment shown above is compatible with the change in the dissolution behavior. The formation of $Fe-O-Si$ bonds provides the precursor of ferrosilicon compounds, in which iron is much stabler than in a simple iron oxide.

The effects shown above may not be caused exclusively by mechanical stress but by the result of combined thermo-mechanical effects. However, the dominant role is a mechanochemical one, since the XPS chemical shift of the mechanically treated samples was larger than that of the thermally treated ones.

4. Conclusion

With increasing rate of revolution during preparation of doubly coated spheres via a shear-compression mechanical route, a part of the second guest, magnetite, migrates into the first guest layer, silica, with simultaneous chemical interaction as confirmed by a retarded dissolution and, among others, by chemical shift of XPS analyses.

Acknowledgement

Financial support by Hosokawa Research Foundation of Powder Technology is sincerely appreciated.

References

- 1) Yokoyama, T., K. Urayama, M. Naito and T. Yokoyama: Kona, 5, 59 (1987)
- 2) Ono, K.: Kagakusouchi, 31, 40 (1989)
- 3) Alonso, M., M. Satoh and K. Miyanami: Powder Technol., 59, 45 (1989)
- 4) Tanno, K., T. Yokoyama and K. Urayama: J. Soc. Powd. Technol. Jpn., 27, 153 (1990)
- 5) Higashi, M., K. Terashita and K. Miyanami: Zairyou, 40, 417 (1991)
- 6) Kaga, H., Y. Taya, I. Shimotsuke and H. Katayama: Funtai oyobi Funmatsuyakin, 39, 546 (1992)
- 7) Mizota, K., S. Fujiwara and M. Senna: Mat. Sci. Eng., B10, 139 (1991)
- 8) Liao, J. and M. Senna: Thermochim. Acta., 197, 295 (1992)
- 9) Liao, J. and M. Senna: Thermochim. Acta., 210, 89 (1992)
- 10) Naito, M., M. Yoshikawa, T. Tanaka and H. Kondou: J. Soc. Powder Technol. Jpn., 29, 434 (1992)
- 11) Horvath, B., J. Strutz, J. Geyer-Lippman and E. G. Horvath: Z. Anorg. Allg. Chem., 483, 181 (1981)
- 12) Dillen and J. W. Geus: Appl. Catal., 40, 255 (1988)
- 13) Isobe, T., S. Komatsubara and M. Senna: J. Non-Cryst. Solid., 150, 144 (1992)

Author's short biography

Mamoru Senna, PhD

Graduated from Keio University, Graduate School in 1970, with a promotion to PhD. He has been a visiting scientist from 1972 to 1974 in Technische Hochschule Aachen and from 1980 to 1981 in Technische Universität in Karlsruhe. Since 1988, he is a professor in the Department of Applied Chemistry, Faculty of Science and Technology, Keio University. Enhancement of reactivity of solids by mechanical and irradiational strategy, including soft-mechanochemical synthesis center his research interests.