DEVELOPMENT AND EVALUATION OF NOVEL RADICAL-TRAPPING SHEETS COMPOSED MAINLY OF CLAY

KAZUNORI KAWASAKI*, KAZUHISA SAKAKIBARA, FUJIO MIZUKAMI and TAKEO EBINA*

* Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan
b Department of Applied Chemistry, Graduate School of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

(Received April 16, 2008. Accepted June 3, 2008)

ABSTRACT

The authors produced novel radical-trapping sheets mainly from an environmentally friendly material, natural bentonite clay. Using two identical radical-trapping reagents, their effectiveness was confirmed for high performance in active radical trapping. Radical-trapping sheets were prepared using casting from dispersion pastes including clay and radical-trapping reagents. Purified natural bentonite clay that had been treated by quaternary ammonium ions was used along with one of two radical-trapping reagents, a spin-trap reagent (α-phenyl-N-tert-butyl nitrone; PBN) or a radical-scavenging reagent (4-Oxo-2,2,6,6-tetramethylpiperidine 1-Oxyl; 4-Oxo-TEMPO), yielding 40-μm-thick flexible self-standing sheets. The sheets' radical-trapping performance was investigated using electron spin resonance (ESR). Results confirmed the radical-trapping sheets' capability for capturing active radical species that were observed neither in the original radical trap reagents nor in the clay. The PBN spin-trapping sheet trapped hydroxyl radicals and hydroxyethyl radicals. The sheet provides long-term stabilization of radical species. The trapped radicals remained active more than one month after the trapping experiment. The 4-Oxo-TEMPO radical scavenging sheet also trapped both radicals. New basal-plane reflection was observed in the X-ray diffraction (XRD) pattern of the radical-trapping sheets, suggesting intercalation of radical-trapping reagents between the clay platelet crystals. These radical-trapping sheets might be applicable to packaging, catalytic sheets for radical reactions, and environmental analyses.

Key words: Clay, Intercalation, Radical trapping, Environmental analysis

INTRODUCTION

Clay, which has been widely used as a filler in polymer composites, is an excellent material in terms of its heat-resistance, chemical resistance, harmlessness, and economic efficiency. Recently, clay-based films have been developed (Ebina and Mizukami, 2007; Tetsuka et al., 2007). They are useful as a freestanding film that is non-combustible, heat-resistant, and flexible, with excellent high gas barrier properties. Moreover, clay has interstitial spaces among molecules between clay layers. For that reason, it is possible to intercalate and functionalize various chemical compounds between the clay layers (Grim, 1953; Whittingham and Jacobson, 1982). Functionalization of clay-based films is possible using these characteristics.

Although radicals are short-lived, the reactivity of active radical species is higher than that of other radical species. They also participate in and originate various reactions such as degradation and fading of plastics, generation of photochemical smog by air pollution, and putrefaction of food. Especially, spin trapping and radical scavenging are used as methods for stabilizing radicals (Schemes 1, 2) (Fuji et al., 2005; Janzen, 1971). Spin trapping is a useful method to capture short-lived reactive radicals and to convert them to stable diamagnetic compounds for identifying radical species. However, the half lives of the hydroxyl radical spin adducts are actually about 90 s (Janzen et al., 1992). Consequently, an ESR signal that shows the generation of the hydroxyl radical spin adducts cannot be observed using a typical ESR measurement. Sufficient analysis for the capture of radical species identification is not possible during such a short lifetime. Although several examples of observation of the solution state are available, observations aside from those of the solution state are few.
Recently, a few studies combining clays with radical-trapping reagents have been carried out. Mostly, experiments have been done using dispersions (Alain et al., 2006; Gournis et al., 2002). Trapping performance and long-term stabilization of the radical species have not been evaluated.

For use in this study, we produced two types of clay-based radical-trapping sheets using either a intercalating spin trap reagent (Janzen and Blackburn, 1968 and 1969) or a radical scavenging reagent (Wright and English, 2003). The sheet characteristics were investigated using electron spin resonance (ESR), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared microspectroscopy (FT-IR microspectroscopy), thermogravimetry–differential thermal analysis (TG-DTA), and electron impact (EI) mass spectroscopic analyses. Results confirmed that the novel radical-trapping sheets maintained the stability of the captured radicals for more than one month after the radical trapping.

**EXPERIMENTAL METHODS**

The novel radical-trapping sheets were prepared as follows. First, natural bentonite clay, Kunipia G (Kunimine Industries Co. Ltd.), was treated using tetradecyl trimethylammonium bromide, yielding an organoclay. This organoclay and one of the two kinds of radical-trapping reagents—PBN or 4-Oxo-TEMPO—was added to toluene at a fixed ratio. Uniform dispersion was achieved by shaking. The solid-liquid ratio of the dispersion was 4%. Loading of the radical-trapping reagent was 5–20% by weight. The sheets’ crystal structure was characterized using X-ray diffraction (XRD) (MXP18; Mac Science Ltd.) with a Cu Kα source under an applied voltage of 40 kV and a current of 250 mA for diffraction angles 1°≤θ≤70°, step width 0.02, and counting time 1 s.

The radical-trapping tests were carried out as follows. First the hydroxyl radical was produced by the reaction of 1.00×10⁻⁴ mol H₂O₂ with 1.00×10⁻⁴ mol FeSO₄ on a Petri dish (Fenton reaction) (Goldstein et al., 1993). Next 1 cm×1 cm radical-trapping sheets were soaked in the reactive solution until the Fenton reaction was completed. Finally, the radical-trapping sheets were introduced into an ESR sample tube after drying. Then, the existence of the radical in the radical-trapping sheets was analyzed using ESR. The ESR spectra were obtained using a spectrometer (JES-FE1XG; JEOL). The spectra were recorded at room temperature.

TG-DTA was carried out using a thermogravimeter apparatus (Thermoplus TG8120; Rigaku Corp.). In addition, the structural characterization of radical-trapping sheets was carried out using FT-IR microspectroscopy as a transmission method. The spectra were recorded (Spectrum100; PerkinElmer) using AUTOIMAGE, then cooled at 77 K, the spectral range was 4000–700 cm⁻¹. Each spectrum was obtained after 16 scans and was signal-averaged at a resolution of 4 cm⁻¹ and an aperture setting of ca. 100 μm×100 μm. A background spectroscopic image was collected from an area that was free of the sample. The mapping steps were equal to the aperture size. The XPS measurements were performed using a spectrometer (S601ci; Ulvac PHI Inc.) with MgKa radiation source (150 μm×100 μm). A background spectroscopic image was collected from an area that was free of the sample. The mapping steps were equal to the aperture size. The XPS measurements were performed using a spectrometer (JFE-600; JEOL) with the direct inlet probe method.
RESULTS AND DISCUSSION

Structural analysis of radical-trapping sheets.

First, X-ray diffraction (XRD) was carried out on each radical-trapping sheet. Sharp basal plane peaks were observed in PBN radical-trapping sheets with and without the PBN intercalation, suggesting highly oriented layer-by-layer stacking of the clay crystals. Figure 1 shows that new peaks were observed at 2.41 nm after the PBN intercalation. As indicated by this result, PBN spin-trapping sheets are inferred to contain a main component with layer spacing of 3.22 nm and a subcomponent with layer spacing of 2.41 nm. The former component is shown in both cases with or without PBN. The layer spacing resembles that of a typical organoclay sheet (Baldassari et al., 2006; Mackintosh et al., 1971). The latter component appeared in the PBN sheet, suggesting that it includes more PBN molecules. Similar XRD results were observed for the 4-Oxo-TEMPO scavenging sheet. The new peak near 2.45 nm appeared in the case with 4-Oxo-TEMPO, which indicates that the 4-Oxo-TEMPO scavenging sheet has main component layer spacing of 3.57 nm and the subcomponent, presumably the 4-Oxo-TEMPO condensed component, has layer spacing at 2.45 nm.

Although the newly observed peaks from the subcomponents intensified concomitantly with the increase in each radical trap reagent, no change was observed in layer spacing (Fig. 2). Each radical trap reagent molecule can be arranged perpendicular. Especially the molecule length of PBN, about 1.2 nm, is consistent with interlayer spacing obtained from XRD, considering that the basal plane interval of clay alone is about 1 nm. Because the regular arrangement of molecules is maintained using the van der Waals interaction among radical trap reagents, the interlayer spacing of subcomponents is determined. It is consequently presumed that few long-chain ammonium ions exist: subcomponents are considered to be components of low layer charge, or components in which alkaline ions unexchanged by long-chain ammonium ions remain to some degree. Because (001) reflection peaks sharpen and intensify with the increase in radical trap reagents, the radical trap reagents are assumed to form orientated layers that are more dense and regular between layers. In contrast, a downward tendency in the layer spacing of main components was identified with increased radical trap reagents. This result is interpreted as follows. Because the volume of radical trap reagent molecules is about half that of long chain alkylammonium, it is considered that the former can enter between layers even after long-chain alkylammonium occupies spaces between layers equivalent to the layer charge.

The decrement on the TG curve in TG-DTA measurement from 150°C to near 350°C became more intense with the increase of radical trap reagents (Fig. 3). Furthermore, quantitative analysis of each radical trap reagent was performed with the intensity of peaks of radical trap reagent origin on the ultraviolet-visible spectral analysis. The result indicated that radical trap reagents equivalent to the initial addition were contained in the radical trap sheet.

Next, the state of the sheet surface was investigated using FT-IR and XPS, including the existence of exposition of radical trap reagents to the radical trap sheet surface and
the homogeneity of dispersion. Subsequent FT-IR analyses suggested that the two radical-trapping reagents were intercalated between the clay platelet crystals. The transmission FT-IR spectra of the PBN radical trapping and 4-Oxo-TEMPO-scavenging sheets are shown in Fig. 4 along with those for the Organoclay sheet. Regarding the measurement of each IR spectrum, most absorption peaks of Organoclay, PBN, and 4-Oxo-TEMPO overlap. However, the absorption peaks of N=O, N-O (Rintoul et al., 2006 and 2007), and C = O, which are keys to attribute PBN and 4-Oxo-TEMPO, are clearly identifiable and fully distinguishable. Therefore, in this study, we have identified the existence of each radical trap reagent according to attribution of these characteristic absorption peaks. On the other hand, when FT-IR spectra were measured using the ATR method, the peak of the radical-trapping reagents was not confirmed. This result shows that the radical trapping reagents rarely exist on each surface of the PBN spin-trapping sheet and the 4-Oxo-TEMPO scavenging sheet.

From results of XPS surface analysis, as described in a later part of this article, no change was apparent in the atomistic concentration of nitrogen on the surface of radical-trapping sheets and organoclay sheet. It follows that the radical-trapping reagents (PBN or 4-OxoTEMPO) were not present on the surface of the radical-trapping sheets.

We investigated the distribution of the radical species in the radical-trapping sheets using FT-IR spectrochemical imaging. We observed the bands at 1361 cm⁻¹ (NO group) for the PBN spin-trapping sheet and 1721 cm⁻¹ (carbonyl) for the 4-Oxo-TEMPO-scavenging sheet, respectively. Figures 5 and 6 present color imaging maps of functional groups of the organoclay sheet, PBN spin-trapping sheet, and the 4-Oxo-TEMPO-scavenging sheet. The analyzed area and single pixel area were, respectively, 1000 μm² and 100 μm². Using FT-IR spectrochemical imaging, the distribution and relative concentration of the chemical components associated with the radical-trapping reagents were mapped. Figure 5 shows that strong absorption under 1361 cm⁻¹, which is attributed to N→O bonding of PBN, is observed throughout the sheet surface quite uniformly, suggesting a uniform distribution of PBN along with the sheet surface. Similarly, the sheet including 4-Oxo-TEMPO• shows uniformly strong absorption under 1721 cm⁻¹, which is characteristic of C=O bonding of 4-OxoTEMPO•, and which suggests the uniform distribution of the reagent (Fig. 6). Using color mapping analysis, homogeneous distributions of PBN and 4-OxoTEMPO• along with the sheet surfaces were confirmed. Moreover, optical microscopic observation revealed many cracks on the surfaces of radical trap sheets (Fig. 7). This surface structure facilitates a radical trap sheet's collection of radicals, presumably because this characteristic surface structure allows radicals to penetrate into sheet depths through cracks, and to react easily with radical-trap reagents inside the sheet. Furthermore, a radical trapped inside a sheet prevents deactivation of the radical species, thereby extending the life span of radicals.

We carried out XPS analysis to verify in greater detail the existence of exposition of radical trap reagents on the sheet surface. Elemental analyses and bonding characterization of clay sheets were carried out using XPS. The XPS spectra of the organoclay sheet, PBN spin-trapping sheet, and 4-OxoTEMPO• scavenging sheet are presented in Fig. 8. Two nitrogen species with different chemical states exist (Kelemen et al., 2002; Liu and Tsai, 2003). A peak associated with the positively charged nitrogen species at 402.7 eV and the amine nitrogen at 400.0 eV were observed for all sheets, and the ratio of two peaks was almost identical. No change existed according to a radical-trapping reagent introduction, meaning
Development and evaluation of novel radical-trapping sheets composed mainly of clay

Organo Clay Sheet

FIG. 5. FT-IR spectrochemical imaging of the Organo clay sheet and PBN radical-trapping sheet. The color gradation reflects the intensity of the 1361 cm⁻¹ peak showing PBN concentration and distribution. The analysis area and the spatial resolution are, respectively, a 1000 μm × 1000 μm square and 100 mm.

PBN Spin Trapping Sheet

FIG. 6. Area under the 1721 cm⁻¹ peak showing 4-Oxo TEMPO concentration and distribution. The analysis area and the spatial resolution are, respectively, a 1000 μm × 1000 μm square and 100 mm.
that the radical-trapping reagents were not concentrated at the very surface, but at about 2–3 nm depth of the sheets. Therefore, intercalation of the radical between the clay layers was also verified through the analyses.

**Radical-trapping test**

These radical-trapping sheets are a new membrane material that brings long-term stabilization of the active radicals; we tried active radical trapping using the PBN spin-trapping sheet. An ESR signal peak appeared after the radical-trapping test, which resulted from the capture of the hydroxyl radical. In addition, Fig. 9 portrays a similar peak observed in the measurement after one month of the radical-trapping test. Generally, the half-life of hydroxyl radical spin adducts of PBN is about 90 s. However, we verified that the trapped hydroxyl radical was stable during one month in the radical-trapping sheet. Moreover, it is difficult for clays alone to adsorb the radical. Therefore, the long-term stabilization of radical species by this material is a new characteristic that is not observed in individual raw materials. Similarly, capture of the hydroxyethyl radical was attempted using the PBN spin-trapping sheet. Results indicate an ESR signal peak, which resulted from the capture of the hydroxyethyl radical. The radical-trapping capability arises from the newly prepared PBN spin-trapping sheet: it is not observed for bare PBN solids or liquids.
with difficulty. The radicals are naturally more stable if they clay platelets are fixed. Therefore recombination occurs only OH might facilitate their rapid movement. The bulky radical clay platelets; they are then captured. The small size of the the trapping reagents, which are intercalated between the species with larger molecular size intercalated between the penetration into sheet depths. Next, the radical species reach of a radical trap sheet with many cracks facilitates a radical' sheet through the edges or cracks of the sheet with the sol- stabilization mechanism. First, radical species seep into the sheet surface. These results support the following radical analyses show that the reagents are rarely exposed on the able fraction of the radical-trapping reagents is intercalated ing effects. Results of XRD analyses suggest that a consider- exmination is being conducted.

Finally, we sought to identify the captured radical species using electron impact (EI) mass spectrum analysis. Unfortunately, the acquired peaks of the OH-spin adduct and the OH-scavenging adduct were weak. Therefore, the unambiguous identification was not done. Identification and fixed quantities of the radical species are future tasks for which further examination is being conducted.

Long-term stabilization seems to be possible by the following effects. Results of XRD analyses suggest that a considerable fraction of the radical-trapping reagents is intercalated between the clay platelets. However, XPS and ATR FT-IR analyses show that the reagents are rarely exposed on the sheet surface. These results support the following radical stabilization mechanism. First, radical species seep into the sheet through the edges or cracks of the sheet with the solvent, presumably because this characteristic surface structure of a radical trap sheet with many cracks facilitates a radical' s penetration into sheet depths. Next, the radical species reach the trapping reagents, which are intercalated between the clay platelets; they are then captured. The small size of the OH might facilitate their rapid movement. The bulky radical species with larger molecular size intercalated between the clay platelets are fixed. Therefore recombination occurs only with difficulty. The radicals are naturally more stable if they are inside the sheet. Results show that long-term stability can be realized because the fixation of the radical-trapping reagents between the clay layers.

CONCLUSION

We manufactured radical-trapping sheets using an environmentally friendly material, natural bentonite clay, as a main component. It has two identical radical-trapping reagents. The flexible 40-μm-thick self-standing sheet has high performance in active radical trapping. The sheet enables long-term stabilization of the radical species. These novel radical-trapping sheets might be applicable to various fields such as packaging, catalytic sheets for use in radical reactions, and environmental analyses.

ACKNOWLEDGMENT

The authors thank Hiroyuki Tetsuka at the Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST) for measurement of XPS spectra.

REFERENCES


