Reaction in supercritical CO_2; an intercalation of 4-phenylazoaniline between layers of montmorillonite pillared with tetramethylammonium ions

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The intercalation reaction of 4-phenylazoaniline into montmorillonite pillared with tetramethylammonium ions has been performed successfully in supercritical CO_2 (SCC) at $T = 313$ K ($P = 15$ MPa), demonstrating that SCC is a better medium than organic solutions for intercalating large amounts of guest molecules into a host compound without the contamination of solvent.

The host–guest chemistry of intercalation systems have attracted attention for synthesis strategies for nanostructured functional materials.[1] These syntheses are usually achieved by promoting the intercalation reaction in the liquid phase. However, the solvent molecules inevitably participate in diffusion and adsorption of solutes in the reaction. A supercritical fluid (SCF) has several advantages for such an adsorption reaction with porous materials. First, solute transfer through the solid–SCF interface is smooth because of the low surface tension of SCF as well as its low viscosity. Second, the adsorption amount can be varied by controlling the dissolving power for the solute *via* the temperature and the pressure of the SCF. Third, the competitive adsorption of the solvent on the porous material is rare because of the weaker interactions between the solid surface and solvent molecules in a supercritical state than in the interaction in the liquid state. For material processing, these advantages lead us to anticipate the development of composite materials containing a large amount of functional adsorbate in the pores, but little contaminant by solvent molecules. Here we present a new intercalation technique using supercritical CO_2 (SCC) as the reaction medium. 4-Phenylazoaniline (PAA) was used as the intercalating molecule and montmorillonite (Mnt) pillared with tetramethyl ammonium (TMA) ions as the layered host (TMA-Mnt). This composite material is of interest as a candidate for photo-functional molecular devices.[2]

Gray colored TMA-Mnt was synthesized *via* the ion exchange method reported by J.-F. Lee *et. al.*[3] using tetramethylammonium chloride (Tokyo Kasei Co., purity : > 98%) and montmorillonite (Kunimine Industries Co., cation exchange capacity: 119 mequiv per 100 g). Chemical analysis of the nitrogen and carbon in TMA-Mnt indicated that 80 ± 3% of Na^+ ions were replaced by TMA ions. XRD analysis showed a layered structure for TMA-Mnt with basal spacing of 1.387 nm. The N_2 adsorption at 77.4 K indicated the presence of slit-shaped pores with a BET surface area of 180 $m^2 g^{-1}$ and a pore volume of 0.068 $cm^3 g^{-1}$.

The intercalation of PAA into TMA-Mnt was performed using a critical point dryer (HCP-2, Hitachi Koki Co.). After batches of TMA-Mnt (400 mg) and PAA (100 mg) were placed separately in the high pressure cell of the apparatus, CO_2 gas was supplied and then liquefied in the cell at 263 K. The liquid CO_2 was gradually heated to 313 K (pressure: 15.0 ± 0.5 MPa), at which point the CO_2 ($T_c = 304.21$ K, $P_c = 7.13$ MPa) was in a supercritical state. Separate batches were maintained in this state for 1, 6, 12, 24, 48 and 72 h, respectively. The cell temperature was then cooled to 293 K and the CO_2 liquid vented. The samples after SCC treatment were washed once with 50 cm^3 n-hexane to remove the residual PAA from the surface. Total nitrogen (TN) and total carbon (TC) contents of the SCC treated samples were determined by GC with a SUMIGRAPH GCT-12N (Sumika Bunseki Center Co.). The PAA uptake by TMA-Mnt in each sample was evaluated from the TN value by subtracting that due to TMA ions. The solubility of PAA in the SCC phase was roughly determined from the weight loss of PAA solid by SCC treatment in the absence of TMA-Mnt. The solubility was estimated as 0.3 mg cm^{-3}, considered reasonable since Hildebrand's solubility parameter of SCC at $T = 313$ K and $P = 15$ MPa is similar to that of n-hexane, which shows saturated solubility of 1.8 mg cm^{-3}.[4]

Yellowish samples were obtained by the SCF treatment. The PAA contents estimated from the TN values are listed in Table 1. The CO_2 residue was found to be negligible since the ratios of TN uptake to TC uptake were between 0.20 and 0.25; these are close to the TN to TC ratio (0.25) of PAA molecules. The PAA content increases rapidly during the first 24 h of treatment and is then almost constant from 24 to 72 h. The adsorption rate is relatively slow compared to the conventional dissolution rate of solute in SCF media.[5] The relatively slow rate may be caused by the slow diffusion of PAA molecules through the internal pores of TMA-Mnt. Since the pore size is near the lower limit for PAA diffusion, the intraparticle diffusion of PAA molecules may be the rate determining step in the present case, rather than the PAA transfer through the SCC–solid interface. The N_2 adsorption isotherms are analyzed with V_l *vs.* t plots, using the t values of Lecloux and Pirard[6] and C constants determined by BET plots, as shown in Fig.1. The V_l *vs.* t plot for the untreated TMA-Mnt shows a downward deviation from the straight line at $t > 0.4$ nm, indicating the presence of micropores around 0.4 nm in width. The downward deviation is not observed for the samples treated with SCC for 6 h or more. This demonstrates that the micropores disappear with the increase in the PAA uptake. The BET surface area, micropore volume, and the basal spacing determined by XRD analysis are given for the SCC-treated samples in Table 1. The specific surface area and the micropore volume decrease significantly with the PAA content.

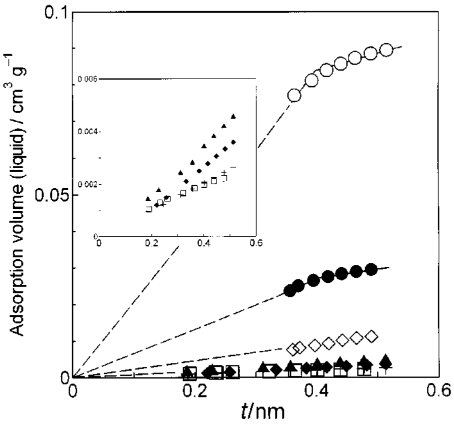

Fig. 1 V_l *vs.* t plots of TMA-Mnt and PAA-TMA-Mnt composites: (○) untreated TMA-Mnt, and SCC treatment for (●) 1, (◇) 6, (□) 12, (▲) 24, (◆) 48 and (+) 72 h

Table 1 PAA content, basal spacing, BET surface area and micropore volume of PAA-TMA-Mnt composites produced with SCC as a medium

Reaction time/h	PAA content/ mg g^{-1}	Basal spacing/ nm	BET surface area/m^2 g^{-1}	Pore volume/ cm^3 g^{-1}
0	0	1.38(7)	180	0.068
1	8.6	1.39(6)	60	0.018
6	29	1.40(7)	22	n.d.[a]
12	38	1.41(3)	5	n.d.
24	70	1.43(6)	7	n.d.
48	75	1.43(9)	6	n.d.
72	80	1.43(9)	4	n.d.

[a] n.d. = Values not determined.

In addition, the basal spacing, which corresponds to the interlayer distance of the PAA-TMA-Mnt composite, increases slightly with an increase in the adsorbed amount. These results clearly indicate that most of the PAA molecules are intercalated in the interlayer of TMA-Mnt. The equilibrium PAA uptake is evaluated as 75 mg g^{-1} (0.38 mmol g^{-1}) from the time courses of PAA adsorption in Table 1. The intercalation capacity is calculated as 124 mg g^{-1} from the micropore volume of TMA-Mnt and the geometric volume of a PAA molecule (1.2 × 0.5 × 0.3 nm). The PAA uptake reached 60% of the intercalation capacity, indicating that SCC is an efficient intercalation medium as compared with PAA uptakes in the solution stated below.

Liquid-phase intercalation reactions at 313 K for 48 h with acetone and n-hexane were investigated for comparison with the reaction in SCC phase. We confirmed that the liquid-phase reactions attain equilibrium after treatment for 48 h. The adsorption isotherms of PAA in the organic solutions are given in Fig. 2 together with the PAA uptake in the SCC system. The PAA adsorptivity is much higher in the SCC phase than those in the organic systems at the same PAA concentration. The PAA uptake (31 mg g^{-1}) in n-hexane solution is less than half that (80 mg g^{-1}) in the SCC phase at a PAA concentration of 0.3 mg cm^{-3}. The PAA uptake is estimated to be negligible in acetone solution at the same PAA concentration. The difference in PAA adsorptivity can be explained by considering two factors; the dissolving power of the solvent for the solute and the influence of competitive adsorption of solvent on the intercalation site. The lower dissolving power of SCC makes the PAA molecules unstable in the fluid phase, driving the migration of solutes from the fluid to the TMA-Mnt phase. Also, competitive adsorption may not occur in the SCC system, since the kinetic energy of CO_2 molecules is higher than the interaction energy between CO_2 and the pore wall.[7] On the other hand, TMA-Mnt shows high adsorptivity (more than 50 mg g^{-1}) for hydrocarbon and organic solvents at 323 K.[8] The competitive adsorption of solvent molecules causes a decrease of PAA uptake, depending on PAA concentration. These two factors are likely to be responsible for the higher PAA adsorptivity in the SCC system.

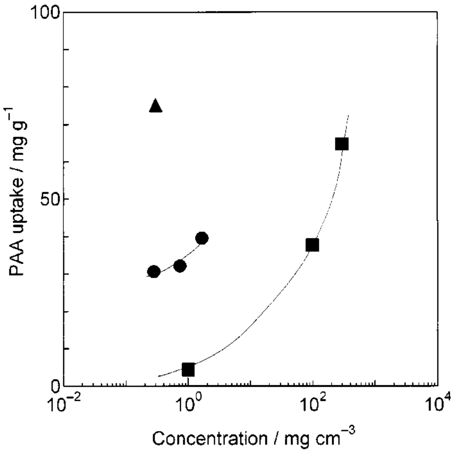

Fig. 2 PAA uptakes into TMA-Mnt in (●) n-hexane, (■) acetone and (▲) SCC

In conclusion, we have successfully intercalated PAA into TMA-Mnt using SCC as a medium. The resultant PAA-TMA-Mnt composite has relatively large amounts of PAA without CO_2 contamination. This demonstrates that SCC is a highly suitable medium for the intercalation reaction. The SCF technique can be expected to find application as a unique method for the synthesis of the nanostructural functional materials.

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Notes and References

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