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# Analytical investigation of specific adsorption kinetics of CO<sub>2</sub> gas on dendrimer loaded in organoclays



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# Kinjal J. Shah<sup>a</sup>, Toyoko Imae<sup>a,b,\*</sup>

<sup>a</sup> Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan, ROC <sup>b</sup> Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan, ROC

#### HIGHLIGHTS

- Time-course CO<sub>2</sub> gas adsorption on dendrimer-loaded organoclays is
- analyzed.
  CO<sub>2</sub> adsorption follows the Langmuir monolayer adsorption kinetics.
- The adsorption sites are on clay surfaces, clay interlayers and dendrimers.
- Amine-terminated dendrimer on clays displays the preferable CO<sub>2</sub> adsorption.

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# G R A P H I C A L A B S T R A C T



# ABSTRACT

The time-course  $CO_2$  gas adsorption on pristine clays and dendrimer-loaded organoclays was analyzed by the computer simulation. Observed data of  $CO_2$  adsorption followed the Langmuir monolayer adsorption kinetics, when two and three adsorption sites were taken account for pristine clays and organoclays, respectively. The sites are on clay surfaces, clay interlayers and dendrimers. Amine-terminated dendrimer-loaded cation-exchange clays (laponite and sericite) displayed preferable adsorption of  $CO_2$ on dendrimer as well as on clay surface and interlayers. However, carboxylate-terminated dendrimerloaded anion-exchange clay (hydrotalcite) reduced the  $CO_2$  adsorption in comparison with pristine clay because of less affinity of  $CO_2$  with carboxylate-terminals. This quantitative study suggests the new insights for the selective adsorption of  $CO_2$  molecules on solid adsorbents of amine-terminated organoclays.

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# 1. Introduction

Nowadays, the release of pollutant gases like greenhouse gases from emission sources such as energy industries and transportation sectors is increasing in the world [1,2]. Therefore, the separation and storage equipment of gases are demanded to decrease the growing amount of such pollutant gases [3]. Adsorption is one of the most widely applied techniques for pollutant removal from contaminated atmosphere [4]. When the adsorption is concerned, the thermodynamic and kinetic aspects should be involved to notice more details about the performance of gases on adsorbents [5]. Many porous materials such as aluminosilicates [6], mesoporous silica [7], zeolites [8], metal oxides [9], carbons [10] and clays [11] were explored as adsorbents. Especially, the



<sup>\*</sup> Corresponding author at: Graduate Institute of Applied Science and Technology, National Taiwan University of Science and Technology, 43 Section 4, Keelung Road, Taipei 10607, Taiwan, ROC

E-mail address: imae@mail.ntust.edu.tw (T. Imae).

clay mineral group has large varieties of specific surfaces for adsorption, depending on sizes, shapes and components. Moreover, clays treated with functional molecules can possess the multiple selectivity of gas adsorption different from the pristine clays [12].

The analysis of adsorption kinetics allows the determination of rate constants and adsorption amounts on the completion of adsorption process. Over the years, a wide variety of adsorption kinetics models such as a Lagergren pseudo-first-order rate model, a pseudo-second-order rate model, an Elovich's model, a secondorder rate model, an intraparticle diffusion model, a Banghams pore diffusion model, a Langmuir adsorption kinetics model etc. have been proposed [5,13-16]. The adsorption capacity and selectivity of adsorbents are the principal properties relevant to adsorptive amounts, which depend on pressure, temperature, nature of the adsorbates, and nature of the pores in the adsorbents [17]. Adsorption of amphiphilic molecules on polar solid surfaces can give rise to the formation of the closely packed monolaver film [18]. Then the adsorption of pollutant gas molecules on the adsorbent surfaces may be interpreted by a simple Langmuir (monolayer) adsorption kinetics. The formation of Langmuir monolayer on solid substrate has been reported for adsorption of surfactants and dendrimers, and their kinetics behaviors was discussed based on the Langmuir adsorption kinetics [19-21].

Dendrimers are explicitly branched macromolecules with repeating functional units of branching groups, which have versatility, great potentiality, high selectivity and their promising ability for storage [22,23]. Due to wide range of processing possibilities, dendrimer-loaded organoclays [24–26] will provide preferential selectivity among all organoclays. We have developed the advanced organoclay adsorbents with effective capture and storage abilities of gas, which possess binding sites for  $CO_2$  adsorption on clays and poly(amide amine) (PAMAM) dendrimers [26]. It has been elucidated that the cation-exchange laponite can load amine-terminated PAMAM dendrimer and become a valuable solid adsorbent with a selective capture capacity for  $CO_2$ .

The aim of this investigation is to analyze adsorption kinetics using the time-course data of CO<sub>2</sub> adsorption obtained in previous paper [26], where adsorption experiments were carried out at the time-course up to 300 min on a thermogravimetric analysis instrument under the N<sub>2</sub> gas flow (balance chamber, 40 mL min<sup>-1</sup>) and the CO<sub>2</sub> (pure) gas flow (sample chamber, 60 mL min<sup>-1</sup>) at room temperature. To the best of our knowledge, there are no investigations that report quantitative analysis of CO<sub>2</sub> adsorption on individual binding site on organoclays. In the current analysis, we derive appropriate analytical equations based on Langmuir monolayer adsorption kinetics. The computer simulations are carried out for analyzing kinetics data of CO<sub>2</sub> adsorption on clays and organoclays. The estimated adsorption kinetics models and the evaluated kinetics parameters will give us new insights on the adsorption sites for CO<sub>2</sub>, which are possible on and between clay layers and on dendrimer.

## 2. Adsorption kinetics of CO<sub>2</sub> on clays

The time-course  $CO_2$  adsorption on clays (cation-exchange clays of laponite and sericite and an anion-exchange clay of hydrotalcite, named Lap0.0, Ser0.0 and Hyd0.0) has been performed and obtained previously ([26], Fig. S2). As seen in Fig. 1, the experimental data of  $CO_2$  adsorption on pristine laponite and sericite increased with time and approached to the saturation at long period like 300 min. This behavior seems like Langmuir monolayer adsorption [27,28]. Although the  $CO_2$  absorption on hydrotalcite still proceeded even after 300 min, this behavior should be interpreted to be the initial stage of Langmuir monolayer adsorption. Therefore, the  $CO_2$  adsorption kinetics data were first analyzed based on the kinetics equation of Langmuir monolayer adsorption.

Scheme 1(1) shows the schematic representation of the Langmuir adsorption mechanism. Supposing that adsorption sites are all equivalent and they are independent of the occupation of neighboring sites, the kinetics of Langmuir monolayer adsorption is described by Eq. (1).

$$A + S_1 \rightleftharpoons A - S_1, \tag{1}$$

where  $k_{1a}$  and  $k_{1d}$  are the intrinsic rate constants of adsorption and desorption, respectively, of an adsorbate *A* on the site  $S_1$ . The surface coverage varies depending on the concentration *C* of adsorbate *A* and the numbers of occupied and nonoccupied adsorption sites,  $N_{1ad}$  and  $(N_1-N_{1ad})$ , respectively, where  $N_1$  is the total number of adsorption sites. Then the rate equation at a finite time *t* is described by

$$\frac{dN_{1ad}}{dt} = k_{1a}C(N_1 - N_{1ad}) - k_{1d}N_{1ad}.$$
 (2)

When Eq. (2) was integrated,

$$N_{1ad} = N_1 I_1 \{ 1 - \exp(-k_{1obs}t) \}, I_1 = \frac{k_{1a}C}{k_{1obs}},$$
(3)

and  $K_{1obs} = k_{1a}C + k_{1d}$ .

Eq. (3) is the typical Langmuir adsorption kinetics equation [21]. Since the adsorption kinetics were observed as an adsorbed amount of CO<sub>2</sub> on clay (CO<sub>2</sub>/clay (mg/g)  $\equiv W_{CO_2}$ ) as a function of time *t*, the adsorption kinetics can be described as Eq. (4).

$$W_{1CO_2} = W_{1CO_2\infty} \{ 1 - \exp(-k_{1obs}t) \}.$$
(4)

where  $W_{CO_{2\infty}}$  is the adsorbed amount of  $CO_2$  at  $t = \infty$ .

The computer-simulation was carried out based on Eq. (4), and the results were compared to experimental data of  $CO_2$  adsorption on pristine laponite, sericite and hydrotalcite clays [26]. Utilized parameters were listed in Table 1, and the fitting curves were drawn in Fig. 1. The calculated kinetics curves did not fit to all the experimental data. This indicates that the simple Langmuir monolayer adsorption mechanism, namely, a single adsorption site model is not available for  $CO_2$  adsorption on clays, but another binding site (the second adsorption site) must be provided. If the

**Fig. 1.** Computer simulation based on one-site Langmuir monolayer adsorption model for CO<sub>2</sub> adsorption on pristine laponite, hydrotalcite and sericite clays. The corresponding parameters are listed in Table 1. Red: parameter 1; blue: parameter 2; black: experimental data ([26], Fig. S2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)





**Scheme 1.** Schematic representation of adsorption mechanism of gas molecule (A) on three individual sites (Sn, n = 1, 2 and 3).  $N_n$  and  $N_{nad}$  are total numbers of adsorption sites and occupied sites, respectively, at site n.  $k_{an}$  and  $k_{dn}$  are adsorption and desorption rates, respectively on site n.

site  $S_2$  is independent of the first adsorption site  $S_1$ , the adsorption kinetics are described by

$$A + S_2 \rightleftharpoons A - S_2$$

$$k_{2d}$$
(5)

and the number of occupied adsorption sites  $N_{2ad}$  is described alike.

$$N_{2ad} = N_2 I_2 \{ 1 - \exp(-k_{2obs} t) \}, \tag{6}$$

$$I_2 = \frac{k_{2aC}}{k_{2obs}}$$

k.

and  $k_{2obs} = k_{2a}C + k_{2d}$ , where  $N_2$  is the total number of second adsorption site, and  $k_{2a}$  and  $k_{2d}$  are the intrinsic rate constants of adsorption and desorption, respectively, on the second binding site of the clay (Scheme 1(2)). Thus, the total number of occupied sites by adsorption is:

$$N_{ad} = N_{1ad} + N_{2ad}$$
  
=  $N_1 I_1 \{1 - \exp(-k_{1obs}t)\} + N_2 I_2 \{1 - \exp(-k_{2obs}t)\},$  (7)

On the description as a total adsorbed amount of CO2 on clay,

$$W_{\rm CO_2} = W_{\rm 1CO_2\infty} \{1 - \exp(-k_{\rm 1obs}t)\} + W_{\rm 2CO_2\infty} \{1 - \exp(-k_{\rm 2obs}t)\}.$$
 (8)

Fig. 2(A)(a) shows a profile of the adsorption kinetics of CO<sub>2</sub> on pristine laponite, which computed based on Eq. (8) with parameters of  $k_{1obs} = 0.150$  and  $k_{2obs} = 0.008$ . The calculation fitted very well (with  $r^2 = 0.9994$ ) to the observed one. The results revealed that while the fast monolayer formation on the site 1 was saturated at an early stage of adsorption, the adsorption on the second site increased slowly with adsorption time. Curve fitting simulation was carried out even for a case of hydrotalcite (Fig. 2(A)(b)) and sericite (Fig. 2(A)(c)). The CO<sub>2</sub> adsorption on two sites of hydrotalcite occurred at the same time but one was fast but another was slow. The situation was different for the case of sericite: The slow adsorption started late from the fast adsorption. Then the Eq. (9) had to be applied.

$$\begin{split} W_{\rm CO_2} &= W_{\rm 1CO_2\infty} \{1 - \exp(-k_{\rm 1obs} t)\} \\ &+ W_{\rm 2CO_2\infty} \{1 - \exp(-k_{\rm 2obs} (t-t_0))\}, t-t_0 \leq 0. \end{split} \tag{9}$$

 Table 1

 Parameters adopted on computer simulation in Fig. 1.

Clay	$W_{1{\rm CO}_{2\infty}}$ (mg/g)		k <sub>1obs</sub> (mi	$k_{1 \text{obs}} (\text{min}^{-1})$		r <sup>2</sup>	
Parameter	1	2	1	2	1	2	
Lap0.0	11.530	11.456	0.0080	0.0060	0.8885	0.8657	
Hyd0.0	8.053	8.039	0.0015	0.0011	0.8638	0.8781	
Ser0.0	3.037	3.033	0.0015	0.0012	0.8087	0.8123	

where  $t_0$  is the delay time. The curve fitting included in Fig. 2(A) indicates that CO<sub>2</sub> gas adsorption happens at two different sites on each clay. In common, the fast adsorption reaches the high adsorption amount, and the adsorption amount of the slow adsorption is low. Since the possible adsorption sites of clays are on the outer surfaces and in the interlayers, the fast adsorption may abundantly occur on the clay surfaces and the slow one should poorly arise in the clay interlayers. It should be noted that the slow adsorption on sericite showed the time delay (50 min) (see Fig. 2(A)(c)). Sericite clay with low cation exchange capacity [29] has resulted in the replacement of small amounts of cations by dendrimer molecules [26]. Thus, because clay sheets are tightly bound by bigger K<sup>+</sup> than Na<sup>+</sup> and Ca<sup>2+</sup> in laponite [30], the penetration of CO<sub>2</sub> between interlayers of clays is rather hard to arise the time-delay.

Table 2 lists the parameters obtained for clavs. The high  $r^2$  values mean the well-made curve fitting and the adequate modeling. The  $W_{1CO_{2}\infty}$  and  $W_{2CO_{2}\infty}$  depend on the total number of adsorption sites, the rate constants and the concentration of adsorbate, and the  $k_{1obs}$  and  $k_{2obs}$  values relate to only the rate constants and the concentration of adsorbate. The numerical values of  $W_{CO_{2}\infty}$ were always largest for laponite, medium for hydrotalcite and lowest for sericite, although the order of  $k_{obs}$  values was different, namely the values of hydrotalcite were smallest. Moreover,  $W_{CO_{2}\infty}$ and  $k_{obs}$  were always larger for site 1 than for site 2. Since the order of  $W_{CO_{2^{\infty}}}$  values for laponite, hydrotalcite and sericite is same as that of their surface area [26], mainly the number of binding sites depending on the surface area can contribute  $W_{CO_{2}\infty}$ . From the similar concept, the larger  $W_{CO_{2^{\infty}}}$  values for site 1 than for site 2 may come from the larger number of binding site for site 1 than for site 2.

Since CO<sub>2</sub> molecules have higher collision frequency on the outer surface than in the interlayer, the  $k_{1obs}$  may be always larger than  $k_{2obs}$  because of less space for CO<sub>2</sub> to pass though in interlayer. Small numerical values of  $k_{obs}$  indicate that the adsorbed CO<sub>2</sub> molecules are less attracted by binding sites and easy remove on it. On the other hand, negative zeta potential, depending on surface charge, was higher for laponite than sericite, and hydrotalcite had positive zeta potential [26]. This indicates that the attraction of CO<sub>2</sub> on binding site should depend on the surface charge. Probably, it is stronger on the highly negative surface but lowest on the positive surface. It can be assumed that the counter ions are easier removable from outer surface rather than from interlayer due to the steric hindrance and the surface charge of outer surface will be large in comparison with that of interlayer, raising the smaller  $k_{2obs}$ . Incidentally, since both laponite and sericite clays have the similar values of d-spacing [26], the penetration of CO<sub>2</sub> inside the clays will have similar probability and thus the  $k_{2obs}$  values are similar.

### 3. Adsorption kinetics of CO<sub>2</sub> on organoclays

Organoclays (termed as Lapn, Hydn and Sern, where *n* indicates the weight proportion of dendrimer against clay) have been synthesized by means of hydrothermal reaction of clays with PAMAM dendrimers under the acidic condition, and the time-course  $CO_2$ adsorption has been performed on them ([26], Fig. S2). Cation exchange clays (laponite and sericite) were reacted with amineterminated fourth generation (G4.0) PAMAM dendrimer, and anion exchange clay (hydrotalcite) loaded carboxylate-terminated G4.5 PAMAM dendrimer. The adsorption of  $CO_2$  gas on organoclays took place similarly to the adsorption on pristine clays, that is, it initially increased fast and gradually saturated (see Fig. 2(B)). Moreover, the adsorption amounts of  $CO_2$  on organoclays of laponite and sericite increased with increasing dendrimer/clay ratio on preparation [26]. These results indicate the existence of the adsorption site



**Fig. 2.** Computer simulation based on the multi-site Langmuir monolayer adsorption model for  $CO_2$  adsorption on (A) pristine clays and (B) organoclays of (a) (d) laponite, (b) (e) hydrotalcite and (c) (f) sericite. The corresponding parameters are listed in Table 2. Red: site 1; blue: site 2; green; site 3; pink: fitting curve; black: experimental data ([26], Fig. S2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

# Table 2Parameters adopted on computer simulation in Figs. 2 and 3.

Clay	$W_{1{\rm CO}_{2\infty}}$ (mg/g)	$k_{1 \text{obs}} (\text{min}^{-1})$	$W_{2{ m CO}_2\infty}~({ m mg/g})$	$k_{2 \mathrm{obs}} (\mathrm{min}^{-1})$	$W_{3{ m CO}_{2\infty}}$ (mg/g)	$k_{3 { m obs}} ({ m min}^{-1})$	$r^2$
Lap0.0	8.132	0.1505	3.034	0.0080			0.9994
Lap0.1	8.233	0.1555	3.034	0.0080	2.900	0.1000	0.9973
Lap0.2	7.350	0.1604	3.093	0.0085	5.800	0.1004	1.0000
Lap0.3	7.105	0.1678	3.093	0.0085	8.000	0.1003	0.9978
Lap0.4	6.500	0.1770	3.550	0.0100	9.250	0.1070	1.0000
Lap0.5	6.000	0.1770	3.820	0.0125	10.030	0.1251	0.9984
Lap0.6	6.000	0.1804	3.880	0.0168	10.055	0.1350	0.9945
Lap0.7	6.000	0.1802	3.880	0.0170	10.801	0.1372	0.9995
Hyd0.0	5.767	0.0101	2.356	0.0030			0.9985
Hyd0.1	3.600	0.0094	1.500	0.0025	1.007	0.0010	0.9998
Hyd0.2	3.000	0.0078	1.350	0.0030	1.000	0.0007	1.0000
Hyd0.3	0.980	0.0091	1.300	0.0074	0.984	0.0007	0.9996
Hyd0.4	0.551	0.0085	0.900	0.0075	0.996	0.0007	0.9933
Hyd0.5	0.551	0.0085	0.850	0.0076	0.999	0.0007	0.9946
Hyd0.6	0.540	0.0084	0.850	0.0075	1.003	0.0007	0.9995
Ser0.0	2.265	0.0150	0.997	0.0071			0.9989
Ser0.1	2.201	0.0151	1.500	0.0100	3.282	0.0210	0.9997
Ser0.2	2.130	0.0171	1.900	0.0150	5.507	0.0211	0.9993
Ser0.3	2.000	0.0242	3.300	0.0260	8.002	0.0310	0.9992
Ser0.4	2.000	0.0240	3.700	0.0275	8.690	0.0334	0.9976
Ser0.5	2.143	0.0251	3.700	0.0275	8.760	0.0350	0.9985

on loaded dendrimer besides adsorption sites on surfaces and in interlayers of clays. On the other hands, since the adsorption amount of  $CO_2$  on hydrotalcite clay rather decreased with loading of dendrimer, carboxylate-terminated dendrimer does not adsorb  $CO_2$  gas or disturb the  $CO_2$  adsorption because of no affinity between them.

When the behavior of the  $CO_2$  adsorption on organoclays is quantitatively evaluated, the necessary consideration is the additional binding site on dendrimer. If this third adsorption site (Scheme 1(3)) is not involved in the first and second adsorption sites, the total number of occupied sites by adsorption is

$$N_{ad} = N_{01} + N_{02} + N_{03}$$
  
=  $N_1 I_1 \{1 - \exp(-k_{1obs}t)\} + N_2 I_2 \{1 - \exp(-k_{2obs}t)\}$   
+  $N_3 I_3 \{1 - \exp(-k_{3obs}t)\}$  (10)

Alternatively, a total adsorbed amount of CO<sub>2</sub> on clay is

$$W_{CO_2} = W_{1CO_2\infty} \{1 - \exp(-k_{1obs}t)\} + W_{2CO_2\infty} \{1 - \exp(-k_{2obs}t)\} + W_{3CO_2\infty} \{1 - \exp(-k_{3obs}t)\}.$$
(11)

As shown in Fig. 3(A), the good agreement of the calculated curves with the observed curves were obtained, when three types of monolayer formation in organo laponite clays was supposed according to Eq. (11). Similar good fitting was achieved even organo hydrotalcite and organo sericite clays, as seen in Fig. 3 (B) and (C). These results indicate that there is an additional site on organoclays compared with pristine clays. The optimum parameters of  $W_{CO_{2\infty}}$  and  $k_{obs}$  for the good fitting with higher  $r^2$  values are listed for each site in Table 2, and the numerical values for three organoclays were plotted in Fig. 4 as a function of dendrimer/clay value.

The  $W_{1CO_{2\infty}}$  (Fig. 4(a)) of organoclays of laponite and hydrotalcite decreased with increasing dendrimer content, while the  $W_{1CO_{2\infty}}$  of sericite decreased scarcely. These results indicate the decrease of binding sites on surfaces of laponite and hydrotalcite clays because of large amount of dendrimer adsorption on them against less adsorption on sericite [26]. On the other hand, the  $k_{1obs}$  values (Fig. 4(b)) of laponite and sericite organoclays slightly increased with dendrimer content and these of hydrotalcite was not changed, indicating few or no variation of the rate constants, although the rate constant of laponite was larger than those of sericite and hydrotalcite. These results suggest that the rate constant of CO<sub>2</sub> is not strongly affected by the loading of dendrimer.

In the case of internal binding site,  $W_{2CO_{2\infty}}$  and  $k_{2obs}$  (see Fig. 4 (c) and (d)) of laponite and sericite organoclays increased with dendrimer content, because the intercalation of dendrimer increases free volume in clay interlayers to adsorb CO<sub>2</sub>. However,  $W_{2CO_{2\infty}}$  and  $k_{2obs}$  of hydrotalcite decreased and slightly increased, respectively. These different behaviors between cationic and anionic clays may depend on the character of dendrimer as describe below.

The  $W_{3CO_{2\infty}}$  and  $k_{3obs}$  values (see Fig. 4(e) and (f)) always increased in the case of laponite and sericite organoclays, since the binding site of dendrimer and the rate constant of CO<sub>2</sub> adsorption on dendrimer site increased with increasing dendrimer content. In contrast, the  $W_{3CO_{2\infty}}$  and  $k_{3obs}$  values of hydrotalcite organoclay were independent of dendrimer content and lower than those of laponite and sericite organoclays. These results indicate that CO<sub>2</sub> gas scarcely adsorbs on dendrimer site on hydrotalcite organoclays. Since cationic dendrimer was adsorbed on cation-exchange clays and anionic dendrimer was used for anion-exchange clay, the affinity of CO<sub>2</sub> with dendrimer should occur the different behaviors on two kinds of organoclays. Namely, CO<sub>2</sub> is affiliative to amine-terminated dendrimer but not to carboxylate-terminated dendrimer.



**Fig. 3.** Computer simulation based on the three-site Langmuir monolayer adsorption model for  $CO_2$  adsorption on organoclays of (A) laponite, (B) hydrotalcite and (C) sericite. The corresponding parameters are listed in Table 2. Red: fitting curve; black: experimental data ([26], Fig. S2). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The analysis based on Eq. (11) indicates that  $CO_2$  gas adsorption happens at three different sites on the organoclays. The weight adsorption of  $CO_2$  at each site for clays with dendrimer content of 0.1 was calculated according to Eq. (11) and plotted in Fig. 2 (B) in comparison with the plot for pristine clay in Fig. 2(A). From the comparison, it is apparent that the adsorption of  $CO_2$  gas on binding sites of organoclays is taking place similar to that of pristine clays such as on outer surfaces of organoclays (site 1) and in interlayers of organoclays (site 2). However, additionally, den-



**Fig. 4.** Parameters used on computer simulation based on the multi-site Langmuir monolayer adsorption model for CO<sub>2</sub> adsorption on pristine clays and organoclays of laponite, hydrotalcite and sericite. (a)  $W_{1CO_2\infty}$ , (b)  $k_{1obs}$ , (c)  $W_{2CO_2\infty}$ , (d)  $k_{2obs}$ , (e)  $W_{3CO_2\infty}$  and (f)  $k_{3obs}$ .

drimer provides a binding site for  $CO_2$  gas adsorption in the case of organoclays (site 3).

In the case of laponite organoclay, while CO<sub>2</sub> adsorption on site 1 and site 3 sharply increased with time as well as on sites of pristine clay, the CO<sub>2</sub> adsorption on site 2 of organoclay was rather gradual (see Fig. 2(B)(d)). This indicates that the CO<sub>2</sub> adsorption on dendrimer happens easier than into clay interlayer and, in other words, the adsorption into interlayer is disturbed by intercalated dendrimer. In this view, the binding site on the surface of sericite organoclay is blocked by adsorbed dendrimers, since CO<sub>2</sub> adsorbs quickly on dendrimers. The different behavior from laponite organoclay may come from the CO<sub>2</sub> adsorption on dendrimers existing at different locations: Small amount of binding site (see Table 2) of sericite should be partly occupied by the adsorption of dendrimers. Then CO<sub>2</sub> is selectively adsorbed on dendrimers loaded on the surface of clay, while dendrimers intercalated into interlayers of clay are less as described above. In common between organoclays of laponite and sericite, it should be noted that CO<sub>2</sub> adsorption at site 1 and 2 on clays closed almost same amount as pristine clays at long adsorption period and the increase of total CO<sub>2</sub> adsorption on organoclays come from the increase of adsorption on site 3 (on dendrimer).

The adsorption behavior of CO<sub>2</sub> at site 1 and 2 on hydrotalcite organoclay was similar to that on pristine hydrotalcite clay but

the total amount of  $CO_2$  adsorption decreased (see Fig. 2(B)(e)). Meanwhile, the adsorption on dendrimer (site 3) was less, that is, anionic (carboxylate-terminated) dendrimer scarcely adsorb  $CO_2$  on anion-exchange clay because of the nonaffinity of carboxylate-terminal group to  $CO_2$  in contrast to the affinity of amine-terminated dendrimer to  $CO_2$ . This phenomenon limits even the  $CO_2$  adsorption on site 1 and 2 of clay, since loaded anionic dendrimer should occupy the sites (1 and 2) of clays and the terminal groups with nonaffinity disturb the approach of  $CO_2$  to site 1 and site 2 of clay.

Based on the results described above, the estimated adsorption of  $CO_2$  on sites of pristine clays and organoclays is represents schematically in Scheme 2. Site 1, 2 and 3 are on the surface of clays, between clay layers and on dendrimers, respectively, as described in Scheme 2. Cation-exchange and anion-exchange clays behave differently due to the difference of binding sites on them. In the case of cation-exchange clays, larger amount of  $CO_2$  is adsorbed on site 1 than site 2, because the penetration of  $CO_2$  between clay layers is not easy. When cationic dendrimers are loaded on clays,  $CO_2$  can adsorb even on dendrimer (site 3) and the adsorption is rather facile. Then  $CO_2$  adsorption is inhibited on site 2 for laponite organoclays and on site 1 for sericite as explained above. In the case of anion-exchange clay, the  $CO_2$  adsorption on site 1 is larger than on site 2 as well as the case of cation-exchange clays. When



Scheme 2. Schematic representation of estimated adsorption of CO<sub>2</sub> on sites of pristine clays and dendrimer-loaded organoclays of (A) cation-exchange and (B) anion-exchange clays.

anionic dendrimers are loaded on clay, less amount of  $CO_2$  gas is adsorbed on both sites, and the negligible amount of  $CO_2$  adsorption on dendrimer (site 3) results.

#### 4. Conclusions

In the present work, kinetics equations for Langmuir monolayer adsorption consisting of three independent adsorption sites were derived for analyzing adsorption of gas molecules on adsorbents, which are organoclays consisting of cation-exchange clays loaded cationic dendrimer and an anion-exchange clav loaded anionic dendrimer. Up to now, although many investigations based on Langmuir kinetics have been reported [19,21,31–36], this is the first report elucidated binding sites and the amount and rate constant of CO<sub>2</sub> adsorption at each binding site on clays and dendrimer-loaded organoclays. Clay layers have two binding sites of external binding unit and internal binding unit (site 1 and 2, respectively). Organoclays have an additional binding site on dendrimer (site 3). The variation of the amount and rate constant of adsorption as a function of dendrimer content differently behaved depending on cation-exchange clays (laponite and sericite) and anion-exchange clay (hydrotalcite), where amine-terminated and carboxylate-terminated dendrimers were loaded, respectively.

The adsorption amounts of  $CO_2$  on cation-exchange organoclays decreased or unchanged on site 1 and increased on site 2 and 3 with dendrimer content, but the rate constants for three sites increased with dendrimer content, although the rate constants were always higher on external binding site than on internal binding site. For the case of an anion-exchange organoclay, the adsorption amount on two sites of clay decreased but it on dendrimer and the rate constants for three sites do not change remarkably with dendrimer content.

Two binding sites on clay should be clearly distinguished, because the binding of  $CO_2$  on outer surface of clay is almost double to that in interlayers of clay. The amine-terminated dendrimer has been elucidated to act as a binding site for the adsorption of  $CO_2$  gas due to the high affinity with  $CO_2$ , although such action is absent for the case of carboxylate-terminated dendrimer due to less affinity. However, the adsorption of  $CO_2$  on clay slows down

after surface-covering by enough amount of dendrimer because of the hindrance by dendrimer loaded on clay.

Recently Chen et al. [37] have reported a review article relating to CO<sub>2</sub> capture by amine-functionalized nanoporous materials. Although collected numerical values of CO<sub>2</sub> adsorption capacity in the literature are higher than those of present clays, it may be due to the trapping of CO<sub>2</sub> into nanopores of nanoporous materials. However, if the CO<sub>2</sub> adsorption capacity of Lap0.7 ( $W_{3CO_{2\infty}} = 10.8 \text{ mg/g}$  (organolaponite), see Table 2) calculated on the basis of weight of organolaponite was recalculated on the basis of the dendrimer content (0.40 g/g (laponite), see Table 1 in [26]), the CO<sub>2</sub> adsorption capacity should be 36.4 mg/g (dendrimer). This value is comparable to the reported values in Table 1 in [37].

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