

COMPOSITE REACTANTS OF CALCIUM CHLORIDE COMBINED WITH FUNCTIONAL CARBON MATERIALS FOR CHEMICAL HEAT PUMPS

Keiko Fujioka¹, Kensuke Hatanaka², Yushi Hirata²

¹Shinsei Cooling Water System Co., Ltd.
501 Toa bldg., 1-3-22 Kyomatibori, Nishi-ku, Osaka 550-0003, Japan
Tel +81-6-6445-5433 / Fax +81-6-6445-5452 ; kfujioka@shinsei-uwtb.co.jp

²Division of Chemical Engineering
Graduate School of Osaka University
Toyonaka 560-8531, Japan
Tel +81-6-6850-6275 / Fax +81-6-6850-6277 ; hirata@cheng.es.osaka-u.ac.jp

Abstract

Enhancement of heat transfer in the reactor bed is one of the most important subjects for developing gas-solid chemical heat pumps. We have developed composite reactants combining calcium chloride with expanded graphite (EG) and activated carbon fiber (ACF) to promote the reaction between calcium chloride and working fluid of methanol and measured variations of effective thermal conductivity as well as volume and void fraction during reaction cycles for the beds packed with these composite reactants. Effective thermal conductivity of the EG composite bed was larger than 60 % that of untreated calcium chloride bed. Because of the bulky structure of expanded graphite, the overall void fraction of EG composite was larger than 0.8 for the bed packed freely without compression. When the overall void fraction was reduced below 0.78 by compression, the effective thermal conductivity was sharply increased up to 10 times higher than that of untreated calcium chloride bed. On the contrary, the effective thermal conductivity of ACF composite bed was slightly smaller than that of calcium chloride bed and no remarkable change was brought about by compression. The volume and overall void fraction of these composite particle beds varied only slightly with the amount of methanol reacted, while those of calcium chloride bed were largely influenced by reaction.

KEYWORDS

Heat transfer enhancement, Effective thermal conductivity, Expanded graphite, Activated carbon fiber.

INTRODUCTION

The final goal of our study is to develop chemical heat pumps for refrigeration or air conditioning by utilizing the reaction of calcium chloride with water, methanol, methylamine or ammonia. In order to achieve a high performance reactor bed driving the reaction at a rate desired for commercial use, it is required that the reactive particles should have high thermal conductivity, large specific area and high permeability. To this aim, we have developed two composite reactants combining calcium chloride with carbon materials; one is a composite of calcium chloride and expanded graphite and the other is that of calcium chloride and activated carbon fiber. These composite reactants are expected to have high thermal conductivity without reducing gas permeability because fine grains of calcium chloride are deposited inside and outside the carbon matrix.

The effective thermal conductivities of these composite particle beds were measured for the case where the following forward or backward reaction has been halted or completed,



Variations of the bed void fraction with reaction progress, which affect the heat transfer in it, were also measured. The thermal conductivity and the void fraction of the composite particle bed are compared to those of untreated calcium chloride bed and the effect of carbon material content on heat transfer enhancement will be discussed.

PREVIOUS WORKS

Various techniques for enhancing heat transfer and effective thermal conductivity

Heat transfer in a bed packed with reactive particles for chemical heat pumps is very poor. The effective thermal conductivity of the beds, which depends on the materials used in it and the reaction

system driving the heat pump, is generally in the range of 0.1 – 0.2 W/(mK). Therefore, enhancement of heat transfer in the reactor bed is one of the most important subjects to improve the overall reaction rate, and various methods have been developed for this purpose. They can be classified roughly into three categories: (a) forming a composite reactant of salt or adsorbent combined with heat transfer promoter with high thermal conductivity, (b) insertion of metals or carbon fibers into a bed, (c) integration of reactant into a heat exchanger. Some of them are summarized in Table 1 according to the kind of heat transfer promoter.

Table 1. Methods for enhancing heat transfer in reactor bed for chemical heat pumps

Heat transfer promoter	Preparation technique	Reaction couple
Expanded graphite	Simple mixing	CaCl ₂ /NH ₃ [1]
	Impregnation of aqueous solution of salt into EG, dehydration and calcination	CaCl ₂ /CH ₃ OH [2] CaCl ₂ /CH ₃ NH ₂ [3]
	Impregnation of aqueous solution of salt into compressed EG, dehydration and calcination	CaCl ₂ /CH ₃ NH ₂ [4] MnCl ₂ /NH ₃ [4, 5] CaCl ₂ /NH ₃ [5] □ BaCl ₂ /NH ₃ [5]
	Mixing activated carbon with compressed and blocked EG using resin as a binder	Activated carbon/CO ₂ [6]
Carbon fiber	Impregnation of aqueous solution of salt into fiber and dehydrate	CoCl ₂ /NH ₃ [7]
	Insertion of carbon fiber brush into bed	MgO/H ₂ O [8]
	Formation of an intercalation compound	MnCl ₂ /HN ₃ [9]
Metal foam (Cu, Ni)	Impregnation of a suspension of salt, compression and calcination	Zeolite/H ₂ O [10] Activated carbon/CH ₃ OH [10]
Resin (Polyanilin)	Coating particles with resin network	Zeolite/H ₂ O [11]
Aluminum hydroxide	Mixing, compression and calcination	Zeolite/H ₂ O [12]
Metal fin or tube	Insertion of fins into bed	CaO/H ₂ O [13]
	Integration of reactant with heat exchanger by coating fin tubes with an adsorbent layer	Silica gel/H ₂ O [14] Zeolite/ H ₂ O [15]

In method (a), expanded graphite is normally used as a material for promoting heat transfer. The common preparation procedure is to impregnate an aqueous solution of inorganic salt into expanded graphite particles, dry and calcine to deposit its salt inside the pores of expanded graphite [2]. Using this method one can prepare a reactor bed whose effective thermal conductivity is several to 10 times larger than that of the bed packed with untreated salt particles [3]. Expanded graphite is a very bulky material, and its effective thermal conductivity can be improved remarkably by compression. For example, some researchers adopted a method to compress and mold expanded graphite before impregnation of the salt solution and attained extremely high thermal conductivity [4, 5]. In case of adsorbents like activated carbon that is insoluble in water, resin is used as a binder to bond the adsorbent with expanded graphite [6].

As for the examples of method (b), insertion of fins with a small void fraction of 0.01 into a packed bed increased its thermal conductivity by 6 times [13] and insertion of carbon fiber brush with volume fraction of 0.05 increased it by 4 times [8]. In the study of method (c), it was reported that reactors integrated with adsorbent layers packed between fins of heat exchanger were developed and reaction cycle time was reduced to almost 1/10 [14, 15].

Several values of the effective thermal conductivity, λ_{eff} , are plotted against the content or weight fraction of heat transfer promoter in composite reactor bed in Fig. 1. Although the data in each case were obtained for different materials, reaction couples, density, temperature or pressure, the effective thermal

conductivity increases remarkably to the weight fraction of heat transfer promoter in the bed. In the compressed and molded beds with high content of heat transfer promoter shown by open keys have extremely high effective thermal conductivity above 10 W/mK, which is several hundred times larger than the original packed bed.

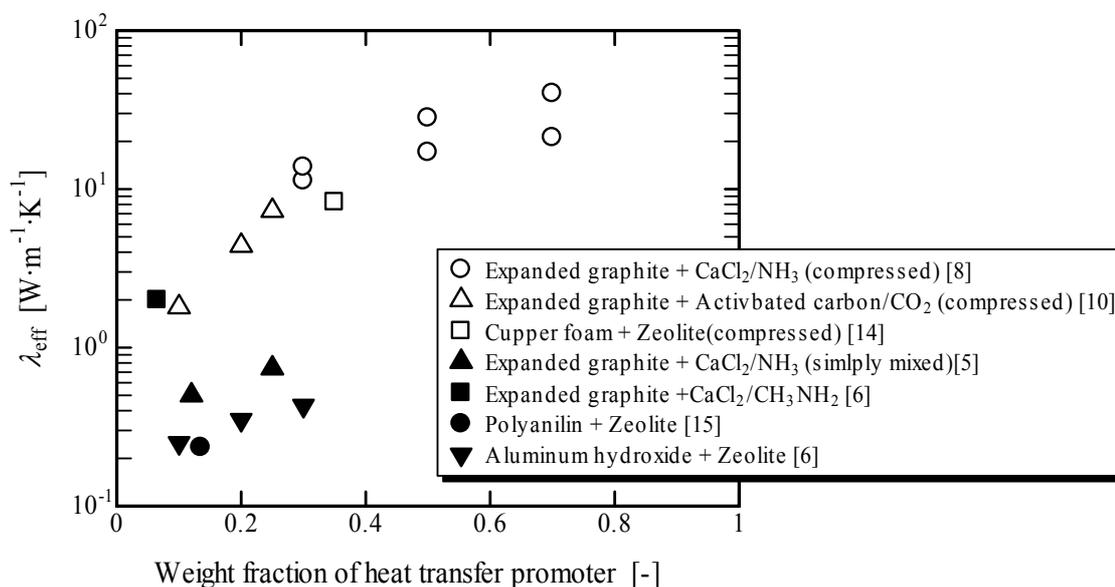


Fig.1. Relation between effective thermal conductivity and weight fraction of heat transfer promoter

Effect of heat transfer enhancement on reaction rate

Effects of improvement in the effective thermal conductivity on the overall reaction rate will be discussed here using the results of simulation analysis in our previous study. The simulation was performed for the CaCl_2 and CH_3NH_2 reaction couple [16]. Kunii-Smith equation for packed bed [17] was modified so that it could be extended to a bed packed with composite particles of CaCl_2 and expanded graphite. The reaction progress was calculated using the effective thermal conductivity estimated by the extended Kunii-Smith equation and the rate parameters obtained from experimental results. The average reaction rate in the process from $X = 0$ to $X = 0.44$ was adopted as a measure to evaluate the reaction promoting effect, since the reaction in this period progresses relatively fast and is applicable to driving chemical heat pumps. For each weight fraction of expanded graphite, the reaction time required for reaching conversion $X = 0.44$ was obtained from the simulated reaction progress, from which the moles of CaCl_2 reacted with CH_3NH_2 per unit time and unit volume, N_r , was obtained as shown in Fig.2. For each bed height H , N_r increased with the effective thermal conductivity, but the increasing rate gradually slows down as the effective thermal conductivity becomes larger.

Similar results were reported for the experiments of the reaction of composite reactant of CaCl_2 and expanded graphite with CH_3NH_2 . When the effective thermal conductivity increased from 0.46 to 1.02 W/mK the output of the reactor increased by 2.5 times, but when λ_{eff} increased to about 30 W/(mK) the output was only 1.5 times larger

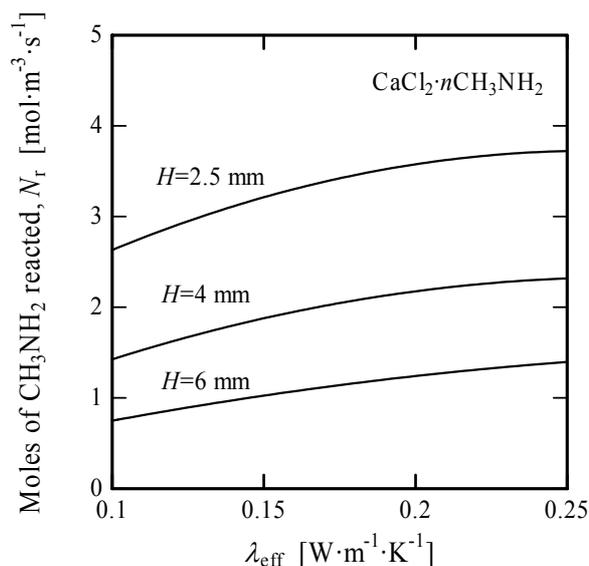


Fig.2. Effect of thermal conductivity on average reaction rate simulated for $\text{CaCl}_2/\text{CH}_3\text{NH}_2$

millimeters in length.

The preparation procedure is common to both composite reactants as follows:

1. Soak and rinse the carbon material in methanol.
2. Rinse it with water and mix it in a calcium chloride aqueous solution in a beaker.
3. Set the beaker in a vacuum desiccator to concentrate the solution.
4. Generate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ particles by evaporating the concentrated solution in a drier at 333K for 30 minutes.
5. Calcine and dehydrate $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ particles in an electric furnace at 573K for one hour.

The mass ratio of CaCl_2 to ACF of the ACF composite is 15:1, 7.5:1, 3.8:1, 1.9:1 or 0.9:1. That for EG composite is 15:1, which has been confirmed to have the largest specific surface area in our previous study [2].

Structure of composite reactants

SEM photographs of composite reactants are shown in Fig.4. In the ACF composite with the mass ratio of 15:1, membranous coating CaCl_2 is formed on the surface of ACF and lumps of CaCl_2 deposited between ACF fibers (Fig.4 (a), (b)). Similar aspect has been observed in the ACF composite with mass ratio of 7.5:1. Few such lumps of CaCl_2 are seen in the ACF composite with the mass ratio of 3.8:1, 1.9:1, and 0.9:1, whose surface is covered with fine grains of CaCl_2 . (Fig.4 (c), (d)). In the EG composite, CaCl_2 grains have been deposited in the pores of expanded graphite (Fig.4 (e), (f)). Comparing these SEM photographs in Fig.4 with each other, it can be seen that there is a clear difference in the state of CaCl_2 grains in the reactant; in the EG composite aggregates of CaCl_2 grains deposited in the pores are surrounded by graphite walls and in the ACF composite CaCl_2 grains has deposited outside the graphite fiber. In the heat transfer experiments, ACF composite with mass ratio of 3.8:1 as well as EG composite with that of 15:1 was used for further investigation.

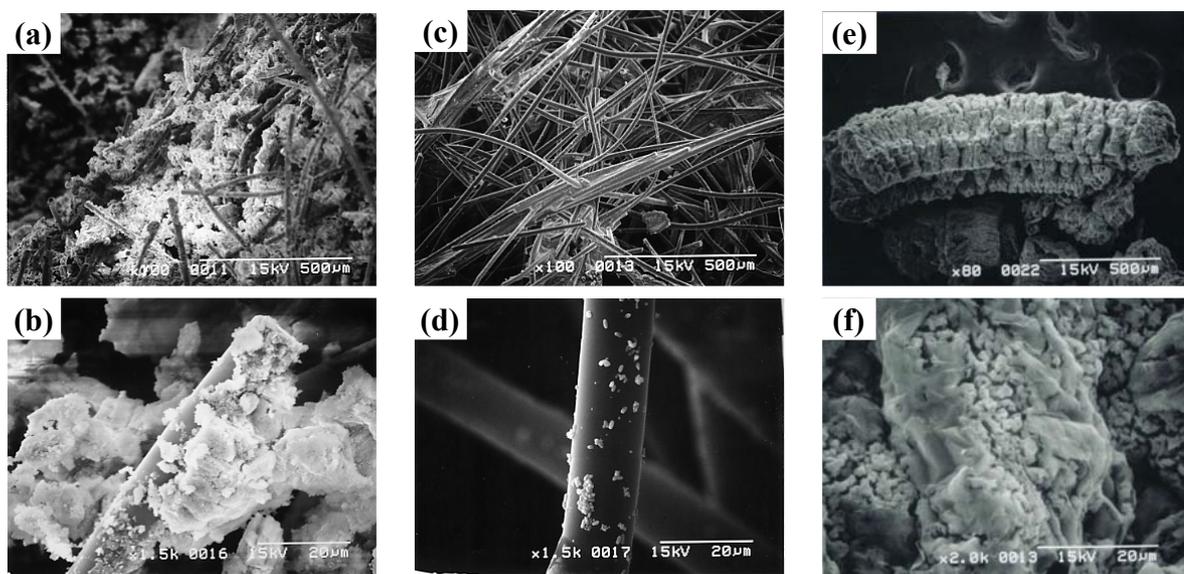


Fig.4. SEM photographs of ACF composite with mass ratio of 15:1(a, b), ACF composite with mass ratio of 1.9:1 (c, d) and EG composite with mass ratio of 15:1 (e, f)

MEASUREMENT OF EFFECTIVE THERMAL CONDUCTIVITY

Experimental apparatus and procedure

The reactor vessel used for thermal conductivity measurement is shown in Fig. 5. The experimental apparatus consists of a gas supply line and two water baths. The gas supply line was equipped with a nitrogen gas-cylinder and a container of liquid methanol. The reactor vessel of pressure glass with 27 mm in inner diameter and 250 mm in height with a stainless steel flange was connected to the gas supply line. Inside the vessel, five thermocouples of 0.5 mm in sheath diameter were placed in such an arrangement that the radial distance from the center to each position, r^2 , was equally spaced.

Samples used for measurement were composite reactants and untreated CaCl_2 particles. The amount of initially packed in the vessel was 23.1g for EG composite, 13.9 g for ACF composite and 27.8 g for untreated CaCl_2 . Each sample was kept at 523 K for 5 hours to remove water and then charged into the vessel. The vessel was connected to the vacuum line and evacuated. Then methanol gas was introduced into the vessel to promote the absorption reaction. After the absorption reaction was completed, the vessel was evacuated while it was heated at 373 K to promote desorption reaction. The moles of methanol reacted with CaCl_2 was obtained from the difference between the weight of the reactive solid and that of initial sample packed in the reactor. After the reactor vessel was shaken so as to make the packed state uniform in the bed and tapped for several times, the bed height was measured. The reactor vessel was connected to the line again and kept at a constant temperature T_1 (273 K) in water bath 1. Then it was quickly transferred to water bath 2 at a different temperature T_2 (293 K). From that time on, the outputs of thermocouples and pressure gauge were recorded at intervals of two seconds. The gas phase in the vessel was nitrogen at 101.3 kPa in all the measurements.

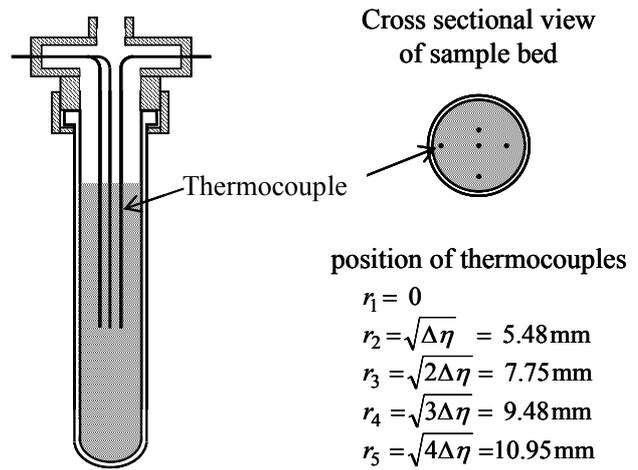


Fig. 5. Reactor vessel and configuration of thermocouples

Data reduction

The effective thermal diffusivity of bed was obtained from the unsteady temperature profiles. Since the bed height is large enough compared with the bed radius, the heat transfer in the middle of the bed where the tips of thermocouples have been placed can be assumed to take place only in the radial direction. Assuming that the heat capacity of the gas phase can be neglected, the unsteady heat balance in the bed is expressed by

$$\frac{\partial}{\partial \theta} \int_0^r 2\pi r [(1-\varepsilon)\rho C_p] T dr = 2\pi r \lambda_{\text{eff}} \left. \frac{dT}{dr} \right|_r \quad (2)$$

where T is temperature, λ_{eff} – effective thermal conductivity, θ – time, ρ – density, C_p – heat capacity and ε – void fraction. Since the temperature profiles in the radial direction in the bed are symmetrical with respect to the axis, the temperature profile $T(r)$ can be expressed by

$$T(r) = T_0 + a_1 r^2 + a_2 r^4 + \dots \quad (3)$$

Using $\eta = r^2$, Eq. (3) is rewritten as

$$T(\eta) = T_0 + a_1 \eta + a_2 \eta^2 + \dots \quad (4)$$

When the values of a_i with $i \geq 2$ are small compared with a_1 , T varies linearly with η . The measured temperature profiles of $T(\eta)$ become essentially linear to η for large θ . The linear relation between T and η reduces the error considerably in calculating the temperature gradient.

If the density, the heat capacity and the effective thermal conductivity are assumed to be constant, Eq. (2) is reduced to the following equation

$$\frac{\partial}{\partial \theta} \int_0^\eta T d\eta = \alpha_{\text{eff}} 4 \left. \frac{dT}{d\eta} \right|_\eta \quad (5)$$

where

$$\alpha_{\text{eff}} = \frac{\lambda_{\text{eff}}}{(1-\varepsilon)\rho C_p} \quad (6)$$

Integrating the temperature profile from $\eta = 0$ to η , and then differentiating it with respect to time θ , one can calculate the left hand side of Eq. (5). The value of $dT/d\eta|_\eta$ on the right hand side of Eq. (5) is obtained by differentiating temperature profile with respect to η . Then plotting the former value

against the latter one can obtain the effective thermal diffusivity α_{eff} through the relation of Eq. (5) An example of such a plot to obtain α_{eff} is shown in Fig. 6.

RESULTS AND DISCUSSION

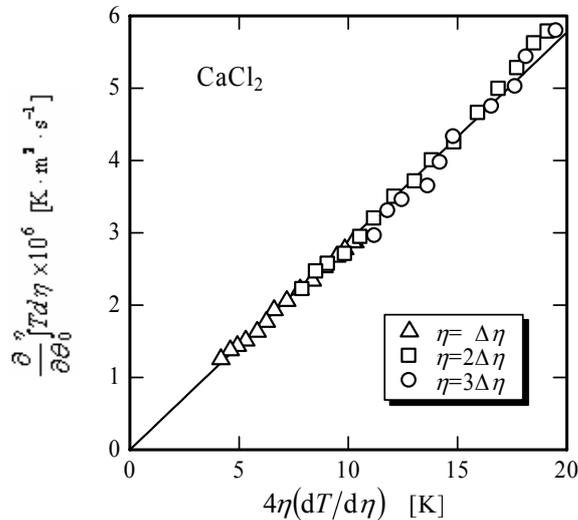


Fig.6. An example of plot based on Eq. (5)

CaCl_2 particle bed ε varied from 0.55 to 0.8, while it varied from 0.8 to 0.91 in the ACF composite bed and 0.75 to 0.9 in the EG composite bed. Because of the small changes in bed volume and void fraction, it is expected that a steady condition may be kept throughout the reaction for the bed of composite reactants.

Variations of volume and void fraction

In gas-solid reactions, the void fraction of a bed changes due to the expansion and contraction of reactive solid as it absorbs or desorbs reactive gas, which affects the heat transfer in bed. Figure 7(a) shows the variations of the ratio of bed volume V_b to the initial bed volume V_{b0} with n during the first three reaction cycles. The volume of bed packed with CaCl_2 particles expanded irreversibly in the first absorption reaction; it increased about two times as large as the initial volume. On the other hand, the volume of the ACF composite bed was kept almost constant during the first three reaction cycles. The bed volume of EG composite increased only slightly with the mole ratio, n , of methanol to CaCl_2 and repeated almost the same path. Corresponding to the bed volume, the overall void fraction, ε , also varied with n as shown in Fig.7(b). The bed volume increased with n but an increase in solid content with n causes a decrease in ε . In the

Effective thermal diffusivity and effective thermal conductivity

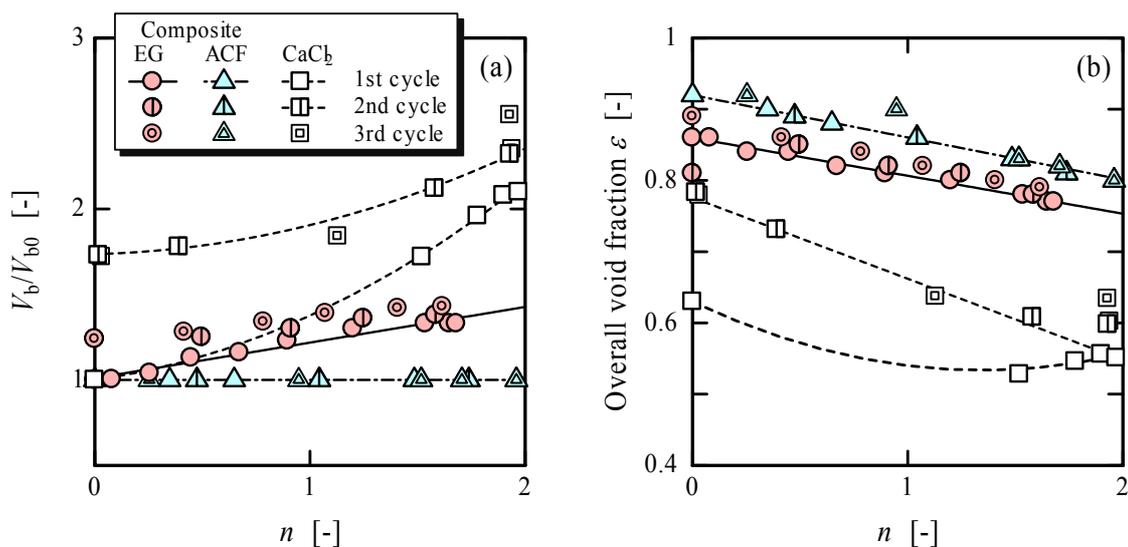


Fig.7. Variations of (a) bed volume and (b) overall void fraction with the mole ratio of methanol to CaCl_2 , n

The effective thermal diffusivity α_{eff} was obtained from the slope of the straight line in the plot of left hand side against right hand side of Eq.(5) as shown in Fig.6. Then the effective thermal conductivity λ_{eff} , was obtained from α_{eff} by using the relation of Eq. (6). The effective thermal diffusivities thus obtained are plotted against n , which represents the reactive gas substance reacted with CaCl_2 , in Fig. 8. The effective thermal diffusivity as well as the effective thermal conductivity depends on void fraction that varies with n . Then λ_{eff} is plotted against the overall void fraction ε in Fig. 9.

In the experiment, both the ACF and EG composite beds were allowed to expand or contract freely in the first three reaction cycles as shown in Fig. 7. After the third reaction cycle was completed, the bed was compressed mildly to reduce its volume. α_{eff} and λ_{eff} before compression are shown by open keys and those after compression are shown by closed keys in Figs. 8 and 9. In Fig. 8 α_{eff} decreased with increasing n for all samples because of the increase in heat capacity of the reactive solid with n . The effective thermal conductivity of EG composite increased up to 10 times larger than untreated CaCl_2 , indicating that the heat transfer property of the bed has been improved.

In Fig. 9 the effective thermal conductivity of EG composite bed before compression is about 60% as large as that of untreated CaCl_2 . After the compression was applied, the effective thermal conductivity increased steeply with the decrease in ε ; when the overall void fraction was reduced to 0.7 from 0.8, λ_{eff} increased by three times and when the overall void fraction was reduced to 0.64 λ_{eff} was nearly five times larger than that at $\varepsilon = 0.8$. On the contrary, the effective thermal conductivity of ACF composite

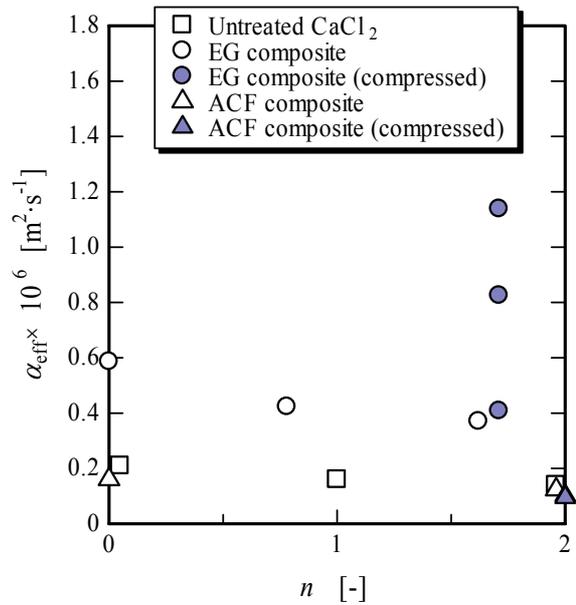


Fig. 8. Variations of effective thermal diffusivity with mole ratio of methanol to CaCl_2 , n

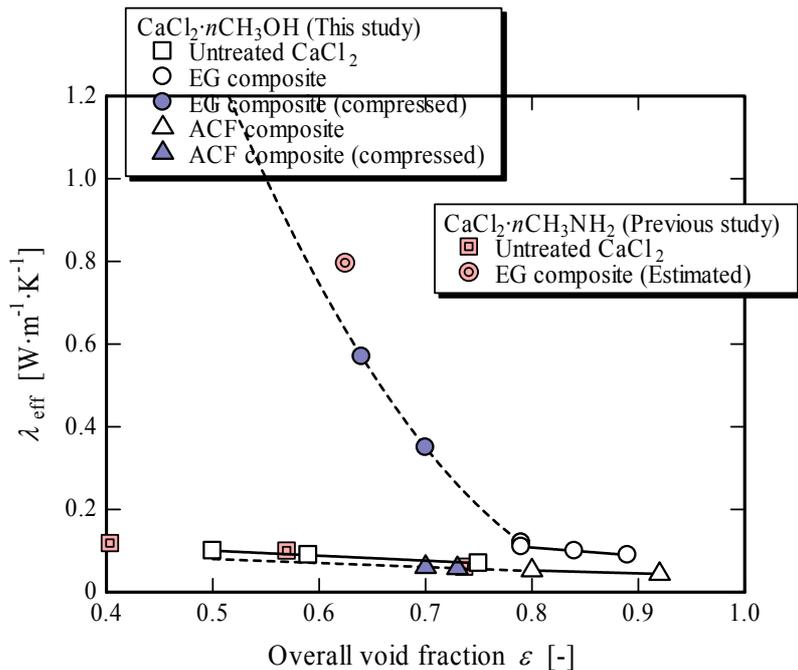


Fig.9. Relation between effective thermal conductivity and the overall void fraction

was lower than that of untreated CaCl_2 and no difference was observed in the dependency of λ_{eff} on ε before and after compression.

It is obvious from Fig. 9 that the steep increase in the effective thermal conductivity is not solely due to the decrease in the void fraction, since the dependency of λ_{eff} on ε changed after compression. The following reasoning will be possible: the particles of EG composite are linked to each other forming the continuous path of heat flow by the compression. Reduction of the contact resistance between particles as well as that between CaCl_2 grain and graphite wall may contribute the increase in λ_{eff} . On the other hand, the compression seems to cause only the decrease in void space between particles in the ACF composite. Such a difference from EG composite would be due to the structure of ACF composite where CaCl_2 and carbon fibers are not mixed microscopically.

In Fig. 9 the effective thermal conductivity of $\text{CaCl}_2/\text{CH}_3\text{NH}_2$ obtained in our previous study [3] has also been shown. It was obtained so that the simulated time variations of conversion and temperature fit the experimental results measured in a thin packed bed reactor. The estimated λ_{eff} of EG composite/ CH_3NH_2 is a little higher but close to that of the EG composite/ CH_3OH in this study. It indicates that the volume expansion of CaCl_2 due to the absorption of reactive gas brought about the similar effect on the contact state of particles by compression.

CONCLUSIONS

Two composite reactants have been developed combining calcium chloride with expanded graphite (EG) and activated carbon fiber (ACF) to enhance the heat transfer in a packed bed reactor. The bed volume and the overall void fraction of composite particle bed varied only slightly with the amount of methanol reacted, while those of noncomposite or untreated calcium chloride bed were largely influenced by reaction. The effective thermal conductivity of EG composite bed was larger than about 60 % that of the untreated calcium chloride bed under free expansion condition. When the overall void fraction was reduced to below 0.78 by compression, the effective thermal conductivity of EG composite particle bed was sharply increased. The effective thermal conductivity of ACF composite bed was lower than the untreated calcium chloride bed and no effect of compression was observed.

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