Enhancement of the effective thermal conductivity in packed beds by direct synthesis of carbon nanotubes

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Received 28 January 2015

Abstract
The low heat conductivity of the packed bed is a key issue in thermal engineering fields. It is also one of the dominant factors behind realizing a fuel cell vehicle society because it prevents quick recharging of hydrogen due to its exothermic reaction. In this study, we examined the enhancement in the effective thermal conductivity of the packed bed with the use of single-walled carbon nanotubes, which were directly synthesized on the particles of the packed bed. We employed two kinds of particles for the packed bed; one was alumina of 10 μm in diameter, which is comparable to usually used in actual system and the other was zeolite, which was used for synthesizing high quality carbon nanotube. Consequently, 10 vol. % of carbon nanotube enhanced three times of effective thermal conductivity.

Key words: Packed bed, Heat transfer, Effective thermal conductivity, Carbon nanotube, Direct synthesis

1. Introduction
Packed beds generally possess large specific surface areas, which makes them suitable for use in the chemical reactions; further, their basic properties such as heat conduction (Meyer and Work, 1937, Morales et al., 1951), flow models (Bernard and Wilhelm, 1950, Kunii and Smith, 1960), and mass transfer (Ergun and Orning, 1949, Plautz, and Johnstone, 1955) have been studied for 80 years, particularly among researchers in the chemical engineering field. Of these properties, the low heat conduction in a packed bed is a topic of significant concern in the thermal engineering field. The low heat conduction in packed beds results from the void space among particles because the effective thermal conductivity (ETC) of void space is usually 1000 times smaller than that of the solid materials present in the packed bed. To resolve this issue, the use of forced convection by reducing the pressure loss (Bartlett and Viskanta, 1996, Hsiao, 1998) and inserting a fin system (Fukai et al., 2000) was examined. The former technique is only available for specific purposes and the latter only improves the ETC locally where the fin exists although it does not enhance the ETC of the entire system. Recently, the techniques of adding carbon or aluminum powder for making complex materials with the particle (Groll, 1993) and use of thin carbon brush as a heat conduction lane (Nakaso et al., 2007) were reported. In these techniques, the employed materials are smaller than the conventional fin system, so that the improvement of ETC is achieved uniformly. However, the contact thermal resistance between particles and conductive materials still remains and is a dominant factor for the ETC. This is a key issue for the realization of a fuel cell car system. With respect to global energy and environmental concerns, the use of hydrogen is effective in saving fossil fuels and protecting the environment. In addition, due to the increased regulations pertaining to the control of vehicle
exhaust in urban areas, the adoption of a fuel cell car is desirable. There has been focus on the equipment of the infrastructure and the development of the hydrogen storage systems. These efforts have resulted in the development of some promising materials for energy storage that satisfy the minimum requirements enacted by the U.S. Department of Energy (DOE), New Energy and Industrial Technology Development Organization (NEDO), and International Energy Agency (IEA). However, the problem of heat conduction remains to be solved. The present ETC of packed beds does not satisfy the necessary absorption rate hydrogen.

Recently, Inoue et al. estimated the ETC of packed beds using single-walled carbon nanotubes (SWCNT) (Iijima, 1991, Iijima and Ichihashi, 1993), and showed the possibility of drastic enhancement (Inoue et al., 2012). We succeeded in synthesizing SWCNT directly on metal hydride and estimated the ETC by assuming negligible thermal resistance between SWCNT and particles due to direct synthesis. Consequently, a tenfold increase in the ETC was achieved. This value is considered to satisfy the practically demanded absorption rate. At present there are reports (Khoshnevisan et al., 2007, Suttisawat et al., 2009, Ranjbar et al., 2010) using SWCNT for fuel cell as a part of electrode or mixing into conventional metal hydride to enhance the absorption property; on the other hand, there is no report with respect to the effective thermal conductivity of the packed bed using SWCNT. In this study, we developed an apparatus for measuring the ETC of packed beds with SWCNT by realizing steady states. For simplicity, we employed two kinds of particles; one is alumina powders of 10–15 μm in diameter and the other is zeolite. The former one has a comparable diameter with ordinary hydrogen storage alloy and the latter is typical catalyst supporter for synthesizing SWCNT.

2. Experimental

For comparison, alumina particles were employed as packed bed particles as they have a diameter of 10–15 μm, which is comparable to that of metal hydrides and we also prepared USY type zeolite (Topsoe, 390HUA, 0.3 μm in diameter), which is typical catalyst supporter for SWCNT. To synthesize SWCNT, catalysts were prepared on the alumina and zeolite powder using an impregnation method (Mukhopadhyay et al., 1998). The size of catalysts prepared by this method is much smaller than aluminum oxide so that the particle size is considered to be same. Cobalt acetate and iron acetate were used for preparing catalysts and were dispersed in ethanol with aluminum oxide. The solution was then dried for 1 day at 80 °C. The amount of cobalt and iron were controlled to be 0.05 wt. % each. Figure 1 shows the chemical vapor deposition apparatus for synthesizing SWCNT. The catalyst powder was placed in the center of electric furnaces and the ethanol was supplied through the inner tube. Before the synthesis, the catalysts were reduced by Ar/H₂ gas (95 vol. %, 5 vol. %, respectively) while the reactor was heated up to the target temperature of 800 °C with a flow rate of 400 sccm. In case of zeolite, we changed reaction time and controlled the concentration of SWCNT. The ethanol was supplied for 30 s to 20 min at 1 kPa after the evacuation of Ar/H₂ gas. The derived samples were characterized using Raman spectroscopy and the amount of SWCNT was measured using thermo-gravimetric analyzer (TGA). We synthesized many times and mixed them to homogenize the experimental condition for each experimental condition. Figure 2 is the measurement system of effective thermal conductivity and it was measured by steady state method. A few millimeter thickness of packed bed is formed in the center of the acrylic pipe, where both sides consist of stainless steel (SS304). The temperature of SS304 was measured by thermocouples of 0.5 mm in diameter at 10 mm increments as shown in Fig. 2. Two copper blocks were attached to each end of the stainless steel. Two Peltier elements, serving as a heater and cooler, were each attached to the copper blocks. The circumference of the cylinder was insulated by Aeroflex®. Because the thermal conductivity of copper is more than ten times larger than that of stainless steel, the temperature of the boundaries are assumed to be uniform; thus, this system is assumed to be one-dimensional after it becomes steady state. Because the contact resistance depends on the pressure, we control the...
pressure by placing the constant weight. When the pressure of the cross section is constant, the contact thermal resistance between the packed bed and stainless steel is considered to be constant. Thus, the total thermal resistance of the packed bed including the contact thermal resistance is expressed as Eq. (1).

\[ R = \frac{L}{\lambda_e} + 2R_c = \frac{\Delta T}{q} \tag{1} \]

where \( R \) is total thermal resistance, \( L \) is the thickness of the packed bed, \( \lambda_e \) is the effective thermal conductivity of the packed bed, \( R_c \) is the contact thermal resistance between the packed bed and stainless steel, \( \Delta T \) is temperature difference (typically 1.0 – 1.2 K) in SUS304 rod, and \( q \) is the heat flux. Because the system achieves a steady state, the heat flux along the axis direction must be constant. The heat flux can be calculated using the Fourier’s law shown Eq. (2).

\[ q = -\lambda_s \frac{\Delta T}{\Delta z} \tag{2} \]

Here, \( \lambda_s \) is the thermal conductivity of SS304. In this experiment, because \( \lambda_s \) is known, measuring the temperature difference between certain thicknesses of \( \Delta z \), the ETC can be obtained. Through our experiment the average packed ratio was 55 vol. %.

3. Results and Discussion

Figure 3 shows the result of Raman spectroscopy using the excitation wavelength of 514.5 nm. The sharp peak found around 1580 cm\(^{-1}\) indicates SWCNT. Generally, the purity of SWCNT is roughly estimated by the ratio of the D mode (1350 cm\(^{-1}\)) originated from defect in SWCNT or the amount of amorphous carbon, to the G mode (1580 cm\(^{-1}\)) originated from \( sp^2 \) graphite structure. Compared Fig. 3(a) with Fig. 3(b) and our past results (Inoue et al., 2005a), the G/D ratio is very low. This indicates that quality of SWCNTs synthesized on alumina is poor. This is also found in radial breathing mode shown in small window in Fig. 3. Generally, for the synthesis of pure SWCNT, it is necessary to keep the catalyst’s size comparable to the diameter of SWCNT (Inoue and Kikuchi, 2005b, Kohno et al., 2011) and to prevent the migration of catalysts during thermal process. Nano-porous Zeolite, Nano scale aluminum are used as a supporting material for catalysts. However, in this experiment, large particles are used for comparison with the metal.
hydride packed bed. Thus, the synthesis condition is not optimized in case of alumina; however, we can compare the effect of SWCNT quality on improving ETC.

Figure 4 shows the TGA of the as-grown samples synthesized on alumina. This technique takes advantage of the different oxidation temperatures of various substances in the sample. First, the catalysts become oxidation products such as FeO\(_x\) and CoO\(_x\); therefore, the total weight (\(TG\)) increases with the temperature. The \(TG\) suddenly decreases around 400 °C, because carbon products are burned as CO\(_2\). The horizontal axis indicates not only the temperature but also time because the temperature increases at a constant rate. If temperature increasing rate is slow enough, we can distinguish some oxidation temperature by taking the derivative of weight (\(\frac{d}{dt} TG\)) with respect to time. In this experiment, we assume that all burned products are the SWCNT. This results in the underestimation of the effect of CNT on the thermal conductivity. Referring to Figure 4, because the lost weight is about 2.8 %, the amount of SWCNT is calculated to be 2.88 weight–percent for the particles. We also measured the concentration of SWCNT in zeolite and those were 0.40 wt. %, 2.81 wt. %, and 3.80 wt. % for zeolite.

The total thermal resistance, including the contact resistance between the packed bed and stainless steel (used for measuring heat flux), is shown in Figure 5. Referring to the previous equation, the slope of this line indicates the reciprocal number of the ETC and the intercept is the contact resistance. As for the contact resistance, the value shows a small difference in each case, but the relation between the thickness and thermal resistance exhibits strong linear relationship. Compared with pure alumina and pure zeolite, thermal resistance indicates same value; thus, in this study heat transfer characteristics is considered to be comparable. If we apply the Kunii-Smith equation to this system to estimate the ETC, the value for the pure aluminum oxide packed bed is about 0.3 W/(m·K). Here, the fluid is air, the thermal conductivity of aluminum oxide or zeolite is assumed to be 20 W/(m·K), and the porosity is 0.45, which is equivalent to our experimental condition. Focusing on the influence of SWCNT concentration on the thermal conductivity, we can see that the ETC increases with the SWCNT concentration.
resistance, thermal resistance decreases as the concentration becomes higher. Compared with inclines of cases of pure zeolite, low concentration, medium concentration, and high concentration, the incline also becomes smaller, so that ETC becomes higher. Here, if we consider the effect based on weight concentration, improvement in alumina packed bed seems to be effective, because the concentration of SWCNT in alumina packed bed is comparable with the case of medium concentration in zeolite packed bed. However, heat conduction takes place through the space, so that we should discuss in volumetric concentration. Figure 6 shows correlation between volumetric concentration and ETC. In this figure, we employed densities were 1 g/cm$^3$, 2 g/cm$^3$, and 4 g/cm$^3$ for SWCNT, zeolite, and alumina, respectively. As we mentioned above, quality of SWCNT was much different between alumina and zeolite, but in this experiment there was no particular difference. We consider that ETC behavior might exhibit logistic curve like sigmoid function. Because at lower concentration there is no connection of high thermal conductivity area formed by CNT, enhancement of ETC is limited. But then it suddenly increases as shown in Fig. 7 owing to inhomogeneous distribution of SWCNT and that works as a bypass for reducing thermal resistance.

4. Conclusion

In this experiment, we developed the measurement system of ETC using a steady state method. The ETC of the pure aluminum and zeolite packed bed was approximately 0.3 W/(m·K), which is close to the value estimated by the Kunii–Smith equation. SWCNT synthesized on the aluminum oxide surface were of lower quality compared to grown on zeolite. The existence of SWCNT was confirmed by Raman spectroscopy. At lower concentration enhancement of ETC does not show particular dependence on quality of SWCNT. ETC behavior is expected to exhibit logistic curve representing by sigmoid function owing to forming bypass area by inhomogeneous distribution of SWCNT in the packed bed. At lower concentration as conducted in this study ETC enhancement is considered to be in the range of initial stage, which is far before inflection point; therefore, SWCNT quality did not affect on the enhancement of ETC. Consequently, only 10% of SWCNT increases ETC by three times.

Acknowledgement

The measurement of Raman spectroscopy was made using HORIBA-JY T64000 at the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. Part of this research was supported by JSPS the Grant-in-Aid for Young Scientists (B) (No. 23760188) and Electric Technology Research Foundation of Chugoku.

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