STUDY OF CO₂ ADSORPTIVITY OF ADSORBENTS UNDER HIGH TEMPERATURE AND PRESSURE FOR INORGANIC OXIDE-CO₂ CHEMICAL HEAT PUMP

TAKAYUKI SHIBATA, KYAW KYAW,
FUJIO WATANABE, HITOKI MATSUDA
AND MASANOBU HASATANI

*Department of Energy Engineering & Science, Faculty of Engineering,
Nagoya University, Nagoya, 464-01*

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It has been evaluated that decomposition of carbonates can be used for storing and temperature-upgrading of thermal energy, and that efficient CO₂ adsorbents will play an important role in storing the decomposed product CO₂. In this study, adsorptivity of CO₂ by zeolite 13X and super activated carbon at 100 – 1013 kPa and 287.5 – 573 K were studied. Both adsorbents exhibit an increase in adsorptivity with increase in pressures and with decrease in temperatures. It was found that the adsorptivity data of CO₂ by zeolite 13X and super activated carbon can be most accurately represented by Freundlich's equation. By using Freundlich's constants, heats of adsorption were estimated and adsorption isosteres were also established on a pressure-temperature diagram in order to evaluate the operating states of the corresponding heat pump system.

Introduction

Energy is extracted as heat energy in the form of high pressure steam or hot gas from primary energy sources by means of boilers, combustors and nuclear reactors. The heat energy can be used for various heating processes or for electrical power generation. Thus, energy is used by means of conversion and combination between chemical substances, heat energy, light, motion and electricity. In these processes, heat energy is not the only form of energy that has been firstly extracted from fuel sources—there is also the energy form that takes part in all types of conversion processes. This implies that the significant advancement in the field of heat energy storage will be a breakthrough technology for developing highly efficient energy conversion system. At present, storing large amounts of thermal energy seems more practical compared to that of storing electrical energy. Thermal energy can be stored by means of sensible heat, latent heat and reversible thermochemical reaction methods. During decomposition reactions, thermochemical reactions absorb heat energy for breaking and rearranging the chemical bonds. The absorbed energy is stored as newly formed chemical bonds which possess the potential to revert back to their original formation and regenerate the absorbed energy. As the reaction enthalpy is much higher than the sensible heat, heat losses in a chemical energy storage system are minimum. This makes the chemical reaction system very attractive for

storing high temperature thermal energy. Among thermochemical reaction methods, it has been found that the dissociation reaction of calcium carbonate is appropriate for storing heat energy at temperatures 773 to 1273 K and adsorbents having higher adsorptivity of CO₂ can be used for storing the decomposed product CO₂ gas, and that the operating thermal efficiency of the CaO-CO₂-adsorbent system is strongly affected by the adsorptivity of the adsorbent (Kyaw Kyaw *et al.*, 1996). As the adsorptivity data under high temperatures are rather scant (Shimizu, 1993), it has been decided to study the CO₂ adsorption characteristics of some adsorbents under high temperatures and pressures. A brief survey of some adsorbents, such as activated carbon, silica gel, and zeolites was carried out. Two of the most promising adsorbents, zeolite 13X and super activated carbon, were selected and as the first step, a study of their adsorptivity characteristics was carried out under 303 – 573 K and 100 – 1013 kPa ranges. The adsorptivity of both adsorbents is found to be most fittingly expressed by Freundlich's equation. Accordingly, respective Freundlich's constants and isosteric heats of adsorption were calculated. Finally, CaO-CO₂-zeolite 13X and CaO-CO₂-super activated carbon heat energy storage systems were proposed, and the thermal operating efficiencies COPs were evaluated.

1. Determination of CO₂ Adsorption Equilibrium for Zeolite 13X and Super Activated Carbon by Means of Volumetric Method

1.1 Preliminary evaluation for appropriate adsorbents

* Received on April 1, 1996. Correspondence concerning this article should be addressed to M. Hasatani.

Fig. 1 Adsorption equilibria of CO₂ on various adsorbents at 298 K

A brief evaluation of the CO₂ adsorptivity of zeolite 13X, zeolite 4A (from Fuji-Davison Co. Ltd.), silica gels (amine and calcium doped) and barium titanate were made by means of a BET pore surface area and volume measurement apparatus (Watanabe, 1982). It can be seen from Fig. 1 that although the adsorptivity of zeolite 4A at 298 K increases very fast at low pressures, it almost levels off after 30 kPa. On the contrary, the adsorptivity of zeolite 13X at 273 K increases steadily at a slower rate with the increase in pressure until its adsorptivity value is about 30% higher than that of zeolite 4A at 101 kPa. The adsorptivity of silica gels and barium titanate are very poor—they can achieve only about one tenth of that of zeolite 13X. Shimizu (1993) has indicated that the adsorptivity of CO₂ by Colombia activated carbon at 298 K is appreciable and can attain about half the value of zeolite 13X at 101 kPa. As one type of

Fig. 2 Schematic diagram of adsorption experimental apparatus

activated carbon named super activated carbon from Osaka Gas Co., Ltd. offers active area about 5 – 15 times more than normally available activated carbon (refer to Table 1), it was decided to further evaluate the equilibrium adsorptivity values of zeolite 13X and super activated carbon under higher temperatures and pressures.

1.2 Apparatus

The experimental apparatus consists of a CO₂ gas cylinder, a gas chamber, an adsorber and a vacuum pump. The equipments are arranged in the order mentioned with a valve connecting each consecutive apparatus. A schematic diagram of the whole set up is shown in Fig. 2. The adsorber and the gas chamber (two stainless steel vessels of 29 mmφ×148 mmH) are provided with heating coils wrapped around the vessels. A thermocouple is placed inside at the middle of the axis of each vessel for measuring and controlling the temperature. Pressures inside the vessels are measured with pressure gauges which can measure with an accuracy of 5 kPa. Both vessels and the three interconnecting valves are housed in an insulated chamber.

Table 1 Physical properties of some adsorbents reviewed in this study

Sample	Zeolite 13X	Super activated carbon	Activated carbon	Silica gel (calcium doped)	Silica gel (amine doped)	Barium titanate (Ba TiO ₃)
Particle $d_p \times 10^3$ [m]	1.68 ~ 2.38	0.02	0.02 ~ 4.0	0.074 ~ 0.149	0.074 ~ 0.149	Powder
Surface area $S_A \times 10^{-3}$ [m ² ·kg ⁻¹]	440	3700	211 ~ 1000	249	238	2.36
Pore volume $V_p \times 10^3$ [m ³ ·kg ⁻¹]	0.272	2.2	0.8 ~ 0.9	0.98	0.86	0.0045
Avg. pore $d \times 10^{10}$ [m]	10	15 ~ 18	15 ~ 18	145	131	37.9

Note: Data for Zeolite 13X is obtained from Fuji Silysia, Super activated carbon from Osaka Gas Co. Ltd., Activated carbon from Shimizu

1.3 Procedure

After the whole set-up was flushed with CO₂, valve V-2 was closed and the CO₂ gas allowed to accumulate in the gas chamber. When the pressure reached a certain value, the gas chamber was isolated from the CO₂ bottle by closing valve V-3. About 1 g of adsorbent was placed in the adsorber. The adsorber was heated to 573 K and evacuated for 6 hr. After evacuation, the adsorber was isolated from the vacuum pump by closing valve V-1. When preliminary preparation for both vessels was finished, the temperatures of the vessels were adjusted by means of the controlled heating system. After reaching a certain predetermined temperature, valve V-2, which connects the gas chamber and the adsorber, was opened and the adsorption process was started. The amount of CO₂ adsorbed was calculated in relation to the changes in pressures in the vessels. In the desorption experiment, the pressure in the gas chamber was reduced to a value lower than that of the pressure in the adsorber. By opening valve V-2, the pressure in the two vessels equalizes, which will eventually cause the adsorbent to release some amount of CO₂ that had been adsorbed.

2. Results and Discussions

2.1 Adsorption and desorption isotherms

The adsorption and desorption isotherms for zeolite 13X and super activated carbon are shown in Figs. 3 and 4 respectively. It can be seen that the higher the pressure, the more gas adsorbed, and that lowering the temperature favors adsorptivity of the adsorbents. However, for zeolite 13X, the rate of adsorptivity increment with respect to pressure is strongly affected by the temperature; the higher the temperature, the steeper the adsorptivity isotherm. As the adsorptivity isotherms for lower temperatures, e.g. at 303 K, are almost horizontal with respect to pressure, it can be concluded that, in an isothermal adsorption, zeolite 13X can attain maximum adsorptivity even at relatively low pressures, e.g. around 300 kPa. On the other hand, super activated carbon exhibits a constant increment in adsorptivity with the increase in pressure for all the experimental temperature conditions. Both adsorbents exhibit no hysteresis at all in the experimental states and they show some degree of adsorptivity q (kg of CO₂/kg adsorbent) at 573 K when the pressure is 1 MPa (with 0.02 kg of CO₂/kg of zeolite 13X and 0.03 kg of CO₂/kg of super activated carbon).

2.2 Evaluation of adsorption isosteres and isosteric heat of adsorption

Among adsorption expressions proposed by various workers, it was found that the experimental adsorptivity data of CO₂ by zeolite 13X and super activated carbon can be most accurately represented

Fig. 3 Comparison of adsorption isotherms of zeolite 13X against values obtained by using Freundlich expression $q = kP^{1/n}$

Fig. 4 Comparison of adsorption isotherms of super activated carbon against values obtained by using Freundlich expression $q = kP^{1/n}$

by the Freundlich's equation

$$q = kP^{1/n} \quad (1)$$

where q is the amount of CO₂ adsorbed (kg of CO₂/kg adsorbent), P the pressure of CO₂ (kPa) and k and n are Freundlich's constants. The corresponding

Table 2 Calculated isosteric heat of adsorption in 473–573 K

Adsorptivity [kg·kg ⁻¹ -ads]	Zeolite 13X [kJ·kg ⁻¹ -CO ₂]	Super activated carbon [kJ·kg ⁻¹ -CO ₂]
0.01	1495.5	554.5
0.02	1238.6	518.2
0.04	981.8	481.8
0.06	831.8	459.1
0.08	725.0	445.5
0.1	640.9	434.1

Freundlich's constants are shown in Figs. 3 and 4.

Based on the adsorption isotherms, isosteric heats of adsorption are approximated by using the Clausius-Clapeyron's equation

$$\log\left(\frac{p_1}{p_2}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (2)$$

where H is the enthalpy (kJ·mol⁻¹), R the gas constant and T the temperature (K). The obtained isosteric heats of adsorption are listed in **Table 2**. It can be seen that both adsorbents exhibit higher values of isosteric heat of adsorption at their initial stages of adsorption and gradually drop to much lower values with the progress in adsorption. However, the rate of drop occurs in a very steep manner with zeolite 13X, in that the heat of adsorption developed at the saturation stage is less than half of the heat developed at the initial stage. On the contrary, the drop occurring with super activated carbon is so slight that compared to zeolite 13X, its heat of adsorption is relatively constant throughout the adsorption process. Moreover, the heat of adsorption developed by zeolite 13X is two to three times higher than that of super activated carbon. Accordingly, the adsorption isostere diagrams (Figs. 5 and 6) are established.

2.3 Comparison of the adsorptivities of zeolite 13X and super activated carbon

As mentioned earlier, zeolite 13X exhibits a stronger tendency to attain maximum adsorptivity even at relatively low pressures (Fig. 3). This special characteristic is quite noticeable in Figs. 5 and 6; e.g. at 10 kPa and 373 K, although super activated carbon can attain 0.02 kg of CO₂/kg super activated carbon, zeolite 13X can achieve 0.10 kg of CO₂/kg zeolite 13X of adsorptivity. Moreover, according to the isosteres lines, zeolite 13X can more readily raise the CO₂ gas pressure even at relatively low desorption temperatures; e.g. when 0.02 kg of CO₂/kg super activated carbon is heated to 666 K, the partial pressure of CO₂ gas developed will be only 700 kPa, whereas, 0.02 kg of CO₂/kg zeolite 13X will raise the pressure of desorbed CO₂ gas over 20,000 kPa at 666 K. For a chemical reaction heat energy storage system oper-

Fig. 5 Schematic pressure-temperature operation diagram of CaO–CO₂–zeolite 13X energy storage system. Note loci of CO₂ gas of volume equal to that of specific volume of adsorbent

Fig. 6 Schematic pressure-temperature operation diagram of CaO–CO₂–super activated carbon energy storage system. Note loci of CO₂ gas of volume equal to that of specific volume of adsorbent

ating in a temperature upgrading configuration, it is required that the working fluid (steam, CO₂, H₂, etc.)

be removed at relatively low pressures and temperatures and has to be delivered readily back again at preferably higher pressures (Garg, 1985; Kyaw Kyaw *et al.*, 1996; Raldow and Wayne, 1979; Raldow, 1981). As evaluated earlier, zeolite 13X, which can adsorb CO₂ gas at relatively low pressures and can deliver CO₂ gas at higher pressures when desorbed, seems very attractive as an adsorbent for CO₂ gas storage in an inorganic oxide-CO₂ energy storage system.

One superior aspect of the adsorbents over mechanical compression for storing CO₂ is quite evident by comparing these isosteres against the loci of the P-T states where 0.01, 0.05 and 0.1 kg of CO₂ gas occupy the space equal to the specific volume of the adsorbent in study (note: the packed bed densities for zeolite 13X and super activated carbon are 700 kg/m³ and 500 kg/m³, respectively). One kg of zeolite 13X will be able to adsorb 0.1 kg of CO₂ at 400 K and 500 kPa, whereas, if the CO₂ is compressed and stored in a container having a volume equal to that of 1 kg zeolite 13X, the amount of compressed CO₂ gas under the same pressure-temperature will come up to only 0.01 kg (Fig. 5). This is the same with super activated carbon as well, where 1 kg of super activated carbon will adsorb 0.1 kg of CO₂ at 500 K and 1000 kPa, whereas, the amount of CO₂ gas that has a volume equal to the specific volume of super activated carbon under this pressure-temperature condition will be only 0.05 kg (Fig. 6).

3. Case Studies of CaO-CO₂-Adsorbent Energy Storage Systems

3.1 CaO-CO₂-zeolite 13X system

By using the CaCO₃ equilibrium dissociation pressure and temperature relationship expression provided by Hill and Winter (1956), a pressure-temperature operation diagram for CaO-CO₂-zeolite 13X thermal energy storage system in a temperature upgrading mode can be constructed as in Fig. 5. In this system, heat at 1003 K is used for decomposing CaCO₃ and the product CO₂ gas at 7.2 kPa is removed by the zeolite 13X at 332 K. This is equivalent to storing thermal energy at 1003 K in the decomposed product CaO. The zeolite vessel is then sealed off and heated from 332 K to 574 K. This heating process brings about desorption in the zeolite 13X from 0.06 kg of CO₂/kg zeolite 13X to 0.01 kg of CO₂/kg zeolite 13X and raises the desorbed CO₂ gas pressure from 7.2 kPa to 500 kPa. The temperature of the high pressure CO₂ gas is raised furthermore to 1003 K before the gas is sent to react with the CaO. Since the CO₂ gas used for the carbonation reaction is at 500 kPa, the reaction heat generated will be able to raise the temperature of the products to the equilibrium temperature of 1250 K. The zeolite 13X will be ready for CO₂ removal again after the pressure and

temperature of the zeolite vessel is adjusted back to 7.2 kPa and 456 K. In this manner, heat at 1003 K can be stored and the temperature of this heat energy can be upgraded to 1250 K by a CaO-CO₂-zeolite 13X system.

3.2 CaO-CO₂-super activated carbon system

As the adsorptivity of super activated carbon is rather poor in low pressure regions compared to zeolite 13X, the CaO-CO₂-super activated carbon energy storage system is considered in the temperature regions where the partial pressure of CO₂ is significant. In such a system as in Fig. 6, for example, heat at 1113 K is used for decomposing CaCO₃ and the product CO₂ gas at 100 kPa is removed by super activated carbon at 333 K. The super activated carbon vessel is sealed off and heated to 694 K. The higher temperature causes the super activated carbon to desorb from 0.06 kg of CO₂/kg super activated carbon to 0.01 kg of CO₂/kg super activated carbon and subsequently raises the pressure of CO₂ from 100 kPa to 500 kPa. The high pressure CO₂ gas is heated to 1113 K before being allowed to react with the decomposed product CaO for generating reaction heat at 1250 K. The super activated carbon (0.01 kg/kg adsorbent) can be used for CO₂ removal again after the pressure and temperature of the adsorbent vessel is adjusted back to 100 kPa and 456 K. In this way, a CaO-CO₂-super activated carbon system can store and upgrade the temperature of heat energy at 1113 K.

3.3 COP evaluation of the CaO-CO₂-zeolite 13X, CaO-CO₂-super activated carbon and CaO-CO₂-compressor systems

The applicability of the adsorbents is further evaluated in terms of COP for a CaO-CO₂ energy storage and temperature upgrading system using zeolite 13X, super activated carbon and a compressor as CO₂ storage arrangements. The operational details, schematic operation diagrams, etc., are described elsewhere (Kyaw Kyaw *et al.*, 1996).

In the present paper, it is assumed that a heat source at 1003 K is available for the decomposition of CaCO₃ and the adsorbents operate in the adsorptivity range of (1 g of CO₂/100 g of adsorbent) to (6 g of CO₂/100 g of adsorbent) for storing the decomposed product CO₂ gas. These systems, CaO-CO₂-zeolite 13X and CaO-CO₂-super activated carbon systems, are denoted as Z:1-6 and SAC:1-6. However, in the CaO-CO₂-compressor storage system, denoted as COMP, it is assumed that the product CO₂ gas is isothermally compressed at 373 K and stored. The COPs of the three systems are shown in Fig. 7. Between the two adsorbents, the COP of the super activated carbon system SAC:1-6 is much higher than the zeolite 13X Z:1-6 system when used for energy storage only. This is evident from the lower values of heat of desorption. However, as the isosteres have indicated, super activated carbon needs a lot of

Fig. 7 COP of CaO-CO₂ energy storage system using zeolite 13X, super activated carbon and compressor for CO₂ gas storage

sensible heat energy to raise it to much higher temperatures for desorbing CO₂ at higher pressures (higher CO₂ pressures are required for developing higher exothermic carbonation reaction temperatures), which results in a drastic reduction of COP at higher temperature upgrading operations. For example, in upgrading the temperature of heat energy from 1003 K to 1250 K, super activated carbon has to be heated to 694 K, whereas, in case of zeolite 13X, the material should only be brought up to 570 K. Consequently, the COP of the SAC:1-6 energy storage system will be reduced from 0.7 to a mere 0.16, but, on the contrary, the COP of the Z:1-6 system will be reduced from 0.5 to 0.3.

The degree of adsorption also plays an important role on the thermal operating efficiency of the adsorbent system. It is quite evident by looking at the two COP curves of the two zeolite 13X systems, Z:1-6 and Z:1-10 (Z:1-10 is also a CaO-CO₂-zeolite 13X energy storage system in which the adsorptivity of zeolite 13X is assumed to operate in the range 1 g of CO₂/100 g of adsorbent to 10 g of CO₂/100 g of adsorbent). Moreover, it can be seen that the gap between the efficiency curves of zeolite 13X and compressor systems becomes narrower as the adsorptivity operation range of the adsorbent increases.

Conclusion

Adsorptivity of CO₂ at 287.5 – 573 K and 100 – 1000 kPa by zeolite 13X and super activated carbon were studied by using a volumetric method. Adsorption equilibrium values of zeolite 13X and super activated carbon indicate that 2 – 3 g of CO₂/100 g of adsorbent can be adsorbed at 573 K when the pressure

is 1000 kPa. No hysteresis is observed for both adsorbents. Both adsorbents exhibit an increase in adsorptivity with the increase in pressure. For zeolite 13X, the increment is slight at lower temperatures whereas the increment is almost constant with super activated carbon over all experimental temperatures.

Adsorption isosteres were constructed and the corresponding isosteric heat of adsorption were estimated by using Clausius-Clapeyron's equation. The heat developed for zeolite 13X at the initial stage of adsorption is two to three times higher than the heat developed at the later stages of adsorption. On the contrary, the heat developed for super activated carbon is relatively the same throughout the adsorption process.

From adsorption isosteres diagrams, it is obvious that zeolite 13X can more readily adsorb the CO₂ gas at relatively low pressures and temperatures and can be made to desorb the CO₂ gas at very high pressures by heating to a slightly higher temperature. These characteristics make the zeolite 13X more attractive than the super activated carbon for CO₂ storage in an inorganic oxide-CO₂ thermal energy storage and temperature upgrading system in which product CO₂ gas from the dissociation of a carbonate material has to be removed at very low pressure and has to be delivered back again at very high pressures. The COP of the CaO-CO₂ energy storage system using zeolite 13X, super activated carbon and compressor suggested that zeolite 13X and super activated carbon can be used as CO₂ storage in the CaO-CO₂ energy storage and temperature upgrading system.

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