Adsorption of Carbon Dioxide on Basic Alumina at High Temperatures

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Adsorption isotherms of carbon dioxide at temperatures ranging from 293 K to 573 K and pressures up to 1 bar on two types of commercial basic alumina are presented.

1. Introduction

Adsorption of gases on adsorbent materials is receiving increased attention in view of the importance of both the removal and the recovery of pollutant gases from air, especially those gases produced by various combustion processes. The discharge of carbon dioxide into the atmosphere due to the consumption of large amounts of fossil fuels has become one of the most serious global environment problems, which is now being more seriously addressed worldwide.[1−4] The topic is also very important in other areas, such as natural gas treatment,[5] purification of hydrocarbons,[6] production of hydrogen gas,[7] and the aerospace industry.[8]

Pressure swing adsorption (PSA) is well suited for the removal of carbon dioxide from any hot fuel gas and subsequent recovery. The PSA process can be operated at elevated temperatures, typically the temperature of the fuel gas source, to remove most of the carbon dioxide, and overcomes the need to cool the fuel gas to ambient temperature prior to the removal of carbon dioxide.[9] Therefore, in the last two decades, active research efforts have been made on the separation of carbon dioxide by the PSA process, and this technique has been industrialized. However, to use the PSA process for the removal and recovery of carbon dioxide from hot fuel gas streams at elevated temperatures, the first and most important issue is to find the appropriate adsorbent. Although all adsorbent materials, such as carbon-based adsorbents, molecular sieves, alumina, silica gel, plus other mixed oxides, either alone or in combination with each other, can be used in the PSA process, more recently, an all alumina PSA system has been proposed, as described in the literature.[10] The advantages of an all alumina system include lower adsorbent cost, vessel design which does not need screens to separate the two different adsorbents, and the fact that alumina adsorbents have a high adsorption capacity and resistance to steam and good mechanical and thermal stability properties.[9−13] It would be desirable however to develop adsorbents having an improved carbon dioxide capacity at high temperature and in the presence of water, to be used in a pressure swing adsorptive reactor (PSAR) for methane steam reforming, and smaller bed sizes with lower capital costs and less void gas being lost during depressurization. Meanwhile, the efficient design of PSA and PSAR devices requires the knowledge of adsorption isotherms at various temperatures. Therefore, experimental results of adsorption of carbon dioxide on alumina are particularly interesting for both fundamental and applied research. Unfortunately, the data of adsorption of carbon dioxide on alumina in the literature are very scarce.[9−11]

Table 1. Main Chemical and Physical Properties of Two Commercial Basic Aluminas from LaRoche Industries Inc.

property	98AA1149	98AX316
chemical description	basic alumina	basic alumina
form	sphere	sphere
particle diameter (mm)	2.1	3.1
LOI[a] (%)	3.17	3.80
bulk density ($g \cdot cm^{-3}$)	0.486	0.488
macroporosity ($cm^3 \cdot g^{-1}$)	0.096	0.091
BET surface area ($m^2 \cdot g^{-1}$)	285	249
abrasion loss (%)	0.13	0.24

[a] LOI: loss on ignition.

The aim of this work is to present experimental isotherms of carbon dioxide on two types of commercial basic alumina at high temperatures, in order to provide the experimental basis for developing basic alumina as adsorbents for carbon dioxide. This study is part of a research program on coupled reaction/separation processes in which it is intended to remove carbon dioxide in a steam reforming process and so increase the equilibrium conversion and work at temperatures lower than the conventional one.

2. Experimental Section

2.1. Materials and Reagents. In this study, two types of basic alumina from LaRoche Industries Inc. were used. Representative characteristics of the two basic alumina samples are reported in Table 1. The carbon dioxide (N48, 99.998% purity) was from Air Liquide (France).

2.2. Apparatus and Procedure. 2.2.1. Apparatus. A schematic diagram of the experimental apparatus for the measurement of single adsorption isotherms is shown in Figure 1. It has three major sections: mass measurement, gas providing system, and data acquisition. Mass measurements with 0.01 mg accuracy were performed with a microbalance (A) (CI−Robal, Wilshire, U.K.) in which a cage with samples inside is suspended in one of the arms (B). Pressure measurements were made with a Schaevitz P-3000 sensor (Lucas, Pennsauken) with a 0.3 mbar accuracy.

2.2.2. Procedure. Experiments for the single adsorption isotherms were carried out as follows: a small amount of

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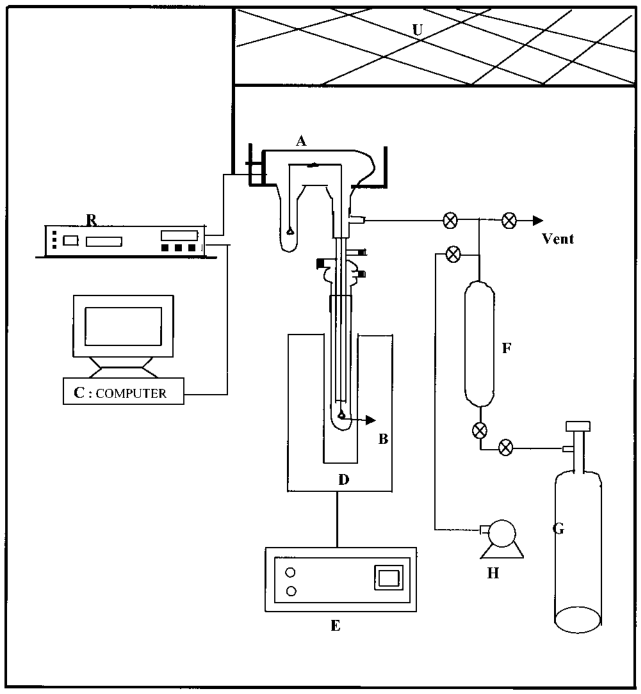

Figure 1. Schematic diagram of the experimental apparatus for measuring the adsorption equilibrium isotherm by the gravimetric technique: A, microbalance; B, cage with samples; C, computer; D, radiant oven; E, PID control of oven; F, buffer bottle; G, carbon dioxide gas bottle; H, vacuum pump; R, microbalance control unit; U, gas exhaust.

basic alumina sample (80−100 mg) was introduced into the microbalance basket, and the sample was submitted to a controlled temperature ramp of (4−5) K·min^{-1} under vacuum conditions (total pressure of ~0.2 kPa) until the required temperature was reached. The sample was kept at the required temperature and ~0.2 kPa for (3−4) h until no further variations in the mass were detected. The required temperature of the single adsorption isotherms is fixed in the oven, and the system is kept waiting until steady conditions are achieved. The experimental isotherm starts from the vacuum condition of nearly 0.2 kPa (adsorption path); then small amounts of carbon dioxide are introduced step by step until atmospheric pressure is reached. The typical equilibration time is 4−6 min in the low-pressure range (<0.1 bar) and 10 min above 0.1 bar. The total time to measure one isotherm was about 3 h.

3. Results and Discussion

The adsorption isotherm data for carbon dioxide on the two basic alumina samples at (293, 473, and 573) K were obtained at pressures up to 1 bar. The experimental data are presented in Table 2 and Figures 2 and 3. The results show that the adsorption capacities of 98AA1149 at (293 and 573) K are higher than the ones of 98AX316. Although the 98AA1149 sample has a larger BET surface area than the 98AX316 sample, this fact does not justify such a difference in capacity. In fact, the XPS spectra and the Na content (5.3%) for both samples are similar; however, the C content is 4.6% for sample 98AA1149 and 2.4% for sample 98AX316.

The adsorption capacities for sample 98AA1149 at three temperatures are in the order $Q_{(293K)} > Q_{(573K)} > Q_{(473K)}$, which deserves some comments. The reason is that experiments for the single adsorption isotherms were carried out in a vacuum and started when no variations in sample weight were observed. Actually, before the measurement

Table 2. Experimental Adsorption Equilibrium Isotherm Data for CO_2 on Basic Alumina

P/bar	Q/mmol·g^{-1}	P/bar	Q/mmol·g^{-1}	P/bar	Q/mmol·g^{-1}
Sample 98AA1149					
T = 293 K					
0.009	0.107	0.191	0.519	0.678	0.842
0.016	0.203	0.251	0.570	0.751	0.877
0.030	0.270	0.317	0.621	0.825	0.917
0.044	0.321	0.389	0.671	0.894	0.952
0.065	0.364	0.459	0.717	0.941	0.976
0.092	0.404	0.533	0.760	0.997	1.005
0.136	0.460	0.605	0.800		
T = 473 K					
0.006	0.035	0.155	0.170	0.548	0.278
0.015	0.076	0.204	0.188	0.631	0.293
0.029	0.102	0.257	0.206	0.730	0.308
0.049	0.119	0.316	0.227	0.852	0.326
0.074	0.135	0.394	0.247	0.926	0.336
0.112	0.153	0.466	0.262	0.993	0.349
T = 573 K					
0.006	0.090	0.190	0.337	0.690	0.529
0.014	0.157	0.245	0.365	0.771	0.551
0.025	0.191	0.299	0.388	0.843	0.574
0.043	0.225	0.365	0.416	0.920	0.596
0.069	0.253	0.434	0.439	0.992	0.619
0.101	0.275	0.534	0.467		
0.140	0.304	0.609	0.501		
Sample 98AX316					
T = 293 K					
0.006	0.026	0.155	0.219	0.605	0.435
0.015	0.048	0.204	0.249	0.677	0.464
0.026	0.081	0.263	0.286	0.751	0.483
0.042	0.104	0.325	0.316	0.823	0.502
0.059	0.137	0.388	0.345	0.921	0.535
0.088	0.167	0.463	0.371	0.993	0.561
0.119	0.193	0.535	0.409		
T = 573 K					
0.007	0.044	0.184	0.222	0.592	0.331
0.017	0.089	0.238	0.241	0.660	0.337
0.029	0.120	0.288	0.261	0.727	0.343
0.044	0.133	0.339	0.276	0.808	0.356
0.063	0.165	0.402	0.289	0.923	0.369
0.094	0.184	0.465	0.305	0.998	0.385
0.137	0.203	0.532	0.321		

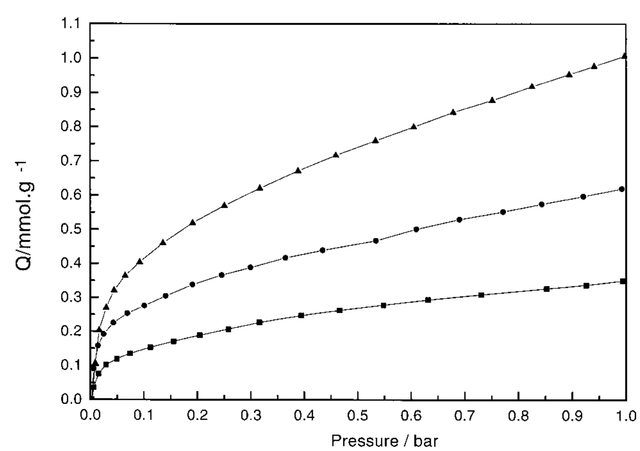

Figure 2. Adsorption equilibrium isotherms for carbon dioxide on basic alumina (98AA1149) at 293, 473, and 573 K and 1 bar: ▲, 293 K; ■, 473 K; ●, 573 K.

started, the sample was heated to the desired temperature. It was reported[14] that, upon activation at 573 K, an eta-alumina phase with higher surface area can be formed. However, the XRD analysis performed at room temperature indicated the presence of csi-alumina although some peaks are common to the spectra of csi- and eta-aluminas. Further study of the chemical composition of samples and

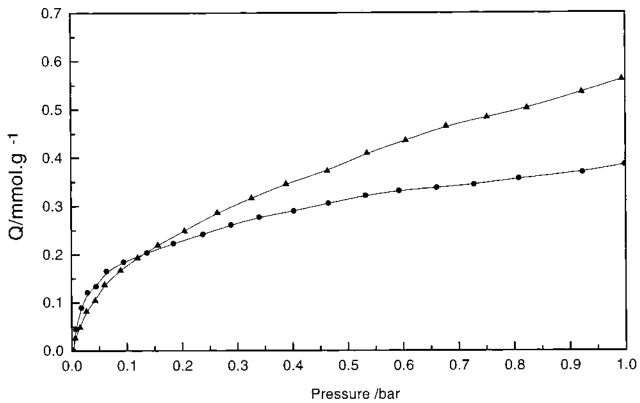

Figure 3. Adsorption equilibrium isotherms for carbon dioxide on basic alumina (98AX316) at 293 and 573 K and 1 bar: ▲, 293 K; ●, 573 K.

XRD analysis at the temperature of formation of eta-alumina will help us understand the effect of temperature on the adsorption capacity.

4. Conclusions

Two types of commercial basic alumina samples were studied as adsorbents for carbon dioxide at elevated temperatures. Both have an adsorption capacity for carbon dioxide higher than 0.30 mmol/g at 300 °C and 1 bar, which meets the requirement for the sorption-enhanced reaction process.[15] Basic alumina can be directly used as adsorbents for the removal and recovery of carbon dioxide from power plant fuel gases.

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