B-T-022en

Breakthrough curve measurement for binary gas mixtures (CO_2 and water vapor) by MS-5A packed bed in BELCAT II

1. Introduction

Water vapor is present as a raw material or byproduct in many physical and chemical processes, and when using adsorption process, it is well-known that the adsorption performance of the material changes depending on the presence or absence of water vapor. This is due to the competitive adsorption of each component into the adsorbent, and by evaluating adsorbents under the coexistence of multiple components, it is possible to evaluate their performance closer to practical conditions. This application note introduces an example of evaluation using the BELCAT II (MICROTRAC) to measure the adsorption breakthrough curve of CO_2 in the presence of low and high concentrations of water vapor and using CO_2 and humidity probes as detectors.

2. Experiment

After pretreatment of the adsorbent (Zeolite MS-5A), the adsorption/desorption curve measurement of CO_2 was performed, and the physisorbed amount was desorbed by N_2 purging at room temperature (desorption), and the chemisorbed amount was desorbed by TPD measurement (Temperature Programmed Desorption). The same measurements were also performed in a blank sample tube, and the differences in the waveforms output were used to confirm the amount adsorbed and desorbed in each process and the material balance in the entire measurement. To quantify both CO_2 and H_2O components simultaneously, the CO_2 and humidity sensor output values were used. Fig.1 shows flow path diagram and image of BELCAT II.

【Test measurement 1: Low concentration CO_2】

Zeolite molecular sieve 5A (MS-5A, weight: 0.1 g, particle size: 250 to 500 μm) was packed in a triple sample tube and adsorption/desorption measurements were performed under the following conditions.

(1). Pre-treatment:
Under 100%-N_2 (50 SCCM) flow, temperature was raised to 400 °C at 20 °C/min, held for 60 min, and then cooled to 25 °C.

(2). Adsorption breakthrough curve:
Adsorption gas with the following composition (total flow rate of 50 SCCM) was introduced at 25 °C for 100 min (6000 s).

- Single component measurement: 1000 ppm- CO_2 and N_2 balance
- Two-component measurement: 1000 ppm-CO_2, 8000 ppm-H_2O and N_2 balance

(3). Desorption by N_2 purge:
100% N_2 (50 SCCM) at 25 °C for 50 minutes

(4). Desorption by TPD:
Temperature was increased from 25 °C to 400 °C at 10 °C/minute and held there for 20 minutes under 100%- N_2 (50 SCCM) flow

【Test measurement 2: High concentration CO_2】

Zeolite molecular sieves 5A (MS-5A, weight: 3 g, particle size: 250 to 500 μm) were packed in a triple sample tube and adsorption/desorption measurements were performed under the following conditions.

(1). Pre-treatment:

Under 100%-N_2 (50 SCCM) flow, temperature is raised to 400 °C at 20 °C/min, held for 60 min, and then cooled to 25 °C.

(2). Adsorption breakthrough curve:

Adsorption gas of the following composition (total flow rate of 50 SCCM) was introduced at 50 °C for 300 min (18,000 s).

- Two-component measurement: 14%-CO_2, 7%-H_2O and N_2 balance

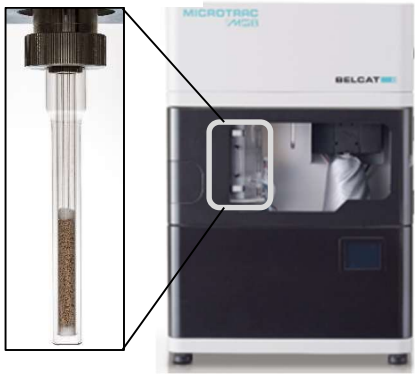
(3). Desorption by N_2 purge:

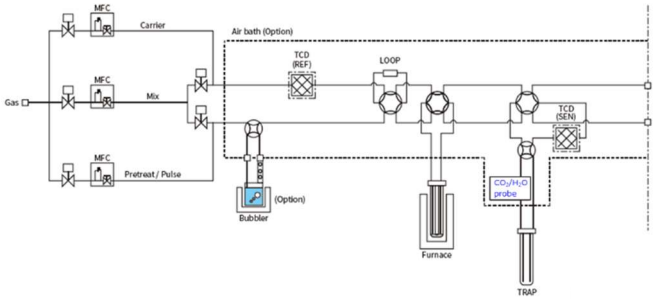
100% N_2 (50 SCCM) at 50 °C for 300 minutes

(4). Desorption by TPD:

Temperature was increased from 50 °C to 400 °C at 1 °C/minute and held for 60 minutes under 100%- N_2 (50 SCCM) flow

Image shows a triple tube sample cell for BELCAT II filled with 1 g of adsorbent





This is a partially simplified flow path diagram.

Fig.1 Flow path diagram and image of BELCAT II

3. Results & Discussion

Fig. 2 shows the comparative results of adsorption breakthrough measurement and desorption measurement (purging and increasing temperature) of 1,000 ppm single component CO_2 and two-component CO_2 in the presence of water vapor as an example of low-concentration CO_2 evaluation.

In the two-component measurement, CO_2 reaches the breakthrough and endpoints earlier than H_2O. This indicates that MS-5A can adsorb more H_2O than CO_2 under these conditions. As shown in Table 1, the amount of CO_2 adsorbed in the two-component measurement is lower than the amount of CO_2 adsorbed in the single component, so it can be said that the adsorption capacity of CO_2 decreases in the presence of H_2O. Furthermore, the CO_2 concentration ratio is also higher than single component run between 5,000 and 8,000 s, which suggests that the CO_2 adsorbed on the sample was desorbed by substitution of H_2O in the breakthrough curve measurement of the two-component measurement. It can also be confirmed that during desorption, H_2O is not easily desorbed by N_2 purging, and it is desorbed completely during TPD process. The fact that the mass balance was almost completely obtained in the adsorption and desorption processes indicates the authenticity of this measurement. Thus, by combining BELCAT II with the CO_2 and H_2O sensors to measure adsorption-breakthrough curves and desorption, it is possible to study the

adsorption behavior of not only a single component but also selectively study the adsorption behavior of individual components in multi-component mixtures.

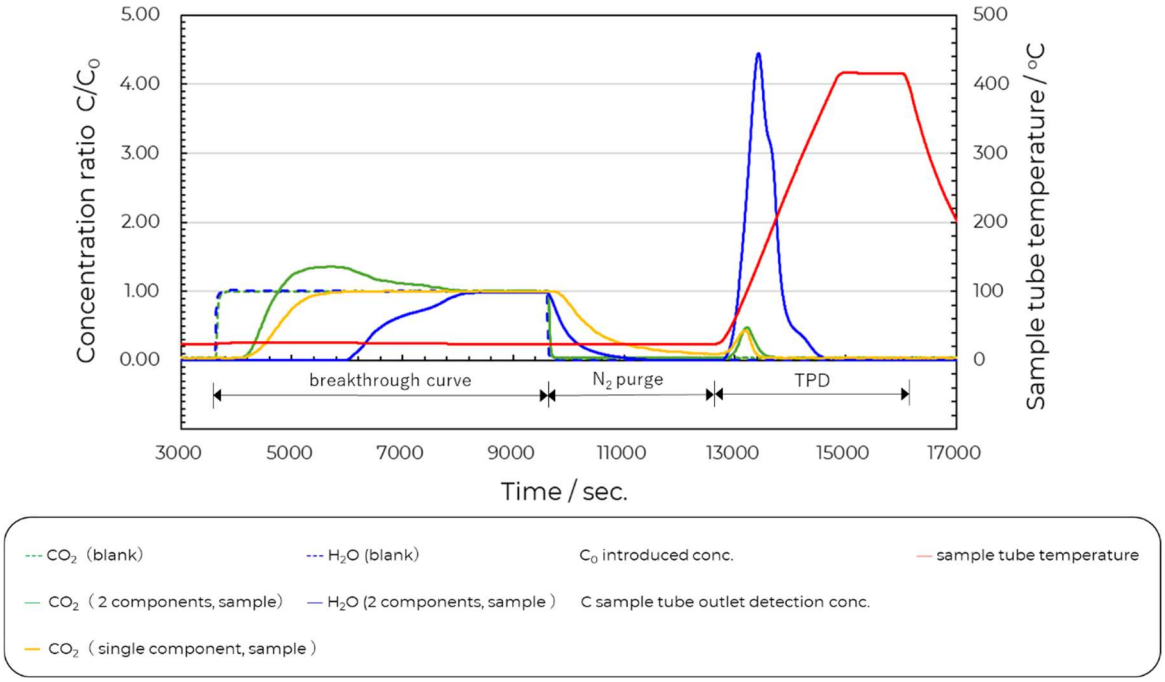


Fig. 2 Comparison of the adsorption and desorption behavior of CO_2 (1000 ppm) with and without water vapor through the processes of adsorption breakthrough curve, N_2 purging and TPD

Table 1 Adsorption and desorption amount of CO_2 single component and CO_2/H_2O binary component gas mixtures (mmol/g)

	B.T(Ads.)	B.T(Des.)	N_2 purge (Des.)	TPD(Des.)
single-CO_2	0.42	—	0.35	0.06
binary-CO_2	0.31	0.24	0.00	0.06
binary-H_2O	9.8	—	1.2	7.9

Fig. 3 shows the results of adsorption breakthrough measurement of relatively high concentrations of 14% CO_2 and 7% H_2O, assuming gas mixtures from factory exhausts. Under these conditions, the concentrations of CO_2 and H_2O are approximately 140 times and 9 times higher, respectively, than in Fig. 2, indicating that CO_2 is more concentrated than H_2O. Table 2 shows that MS-5A can adsorb more H_2O than CO_2 even under these conditions. Furthermore, the CO_2 concentration ratio is higher than 1 between about 3,000 and 15,000 s. In the breakthrough curve measurement of the two components of CO_2 and H_2O, the amount of CO_2 adsorbed on the sample and then desorbed by its replacement with H_2O can be confirmed to be the same as the results in Fig. 2.

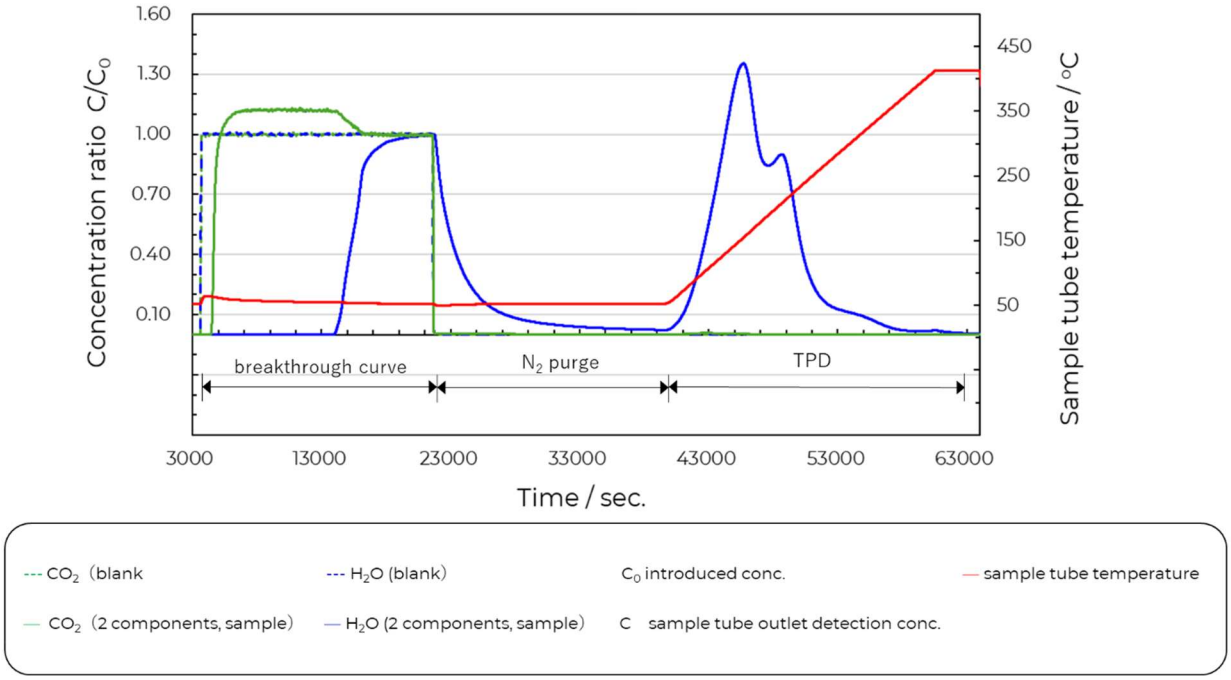


Fig. 3 Adsorption and desorption behavior of CO_2 (14%) and H_2O (7%) gas mixture through the processes of adsorption breakthrough curve, N_2 purging and TPD

Table 2 Adsorption and desorption amount of CO_2 and H_2O binary gas mixtures (mmol/g)

	B.T(Ads.)	B.T(Des.)	N_2 purge (Des.)	TPD(Des.)
binary-CO_2	1.8	1.9	0.1	0.1
binary-H_2O	10.4	—	2.2	7.4

4. Summary

These results indicate that the BELCAT II can be used in combination with CO_2 and H_2O sensors to evaluate and study the adsorption and desorption behavior of carbon dioxide, including the adsorption/breakthrough curve evaluation, for single-component CO_2, two-component CO_2, and H_2O, with the aim of finding solutions for a carbon neutral future.

References

For further information please contact us at:
www.microtrac.com