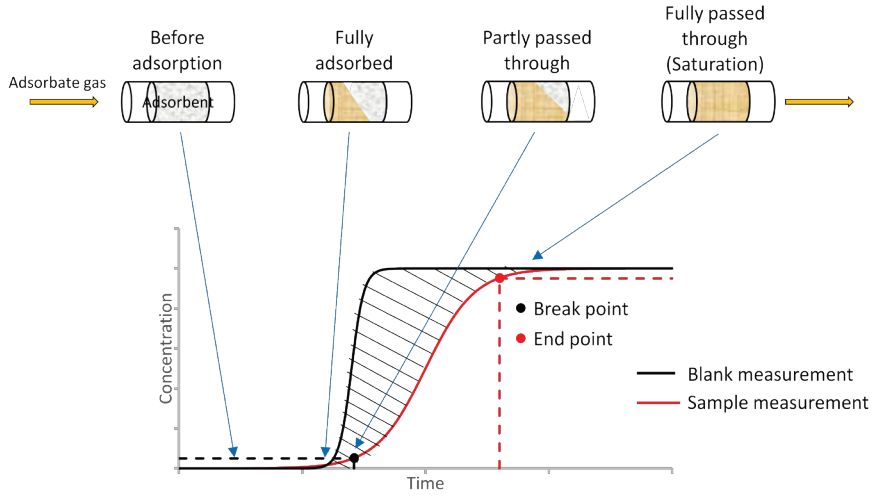
Application note (AN-2015-02EN)

Breakthrough curve measurement using BELCAT II

Introduction

Breakthrough curve measurement is very important for gas separation and purification technology. Adsorption capacity can be evaluated from gas adsorption isotherm but gas separation technology requires adsorption kinetics as well. A breakthrough curve provides the kinetic information. When a carrier gas which contains an adsorbate gas flows in a fixed bed column packed with adsorbent particles, the adsorbate will be removed from the fluid, and only the carrier gas will come out from the column for a certain time. The adsorbent starts to be saturated with the adsorbate from the inlet of the column, and, at some point, the adsorbate will emerge from the outlet of the column. This status is called breakthrough, and the point when the breakthrough occurs is called as the breakpoint. In general, the point when concentration of adsorbate at the outlet for initial concentration exceeds 5-10% is defined as breakpoint, and it is regarded that the adsorption column is saturated at the point. The saturation further proceeds and the point when adsorbate concentration exceeds 90-95% is called the end point. Duration time between the breakpoint and the end point is related to the adsorption kinetics. The ratio of outlet adsorbate concentration to inlet concentration in the fluid as a function of time from the start of flow is breakthrough curve.



The adsorption amount can be calculated from the difference between the blank measurement and the sample measurement (a shaded area).

Experimental

The sample was placed in the sample cell. As shown in Fig. 1, the carrier gas flew through the sample cell and then, the gas flow was switched to the adsorbate gas by the 6-way valve.

First, the breakthrough curve measurement was conducted for the sample cell with the sample. Then, the blank measurement was done for the empty sample cell.

The adsorption amount is calculated from the difference between the detected value at fully adsorbed status and saturated status, the concentration of the adsorbate gas and the gas flow rate.

The breakthrough curve for the single component gas was measured by using a standard TCD, and for the multicomponent gas, a QMS (BELMass) was used for a detector.

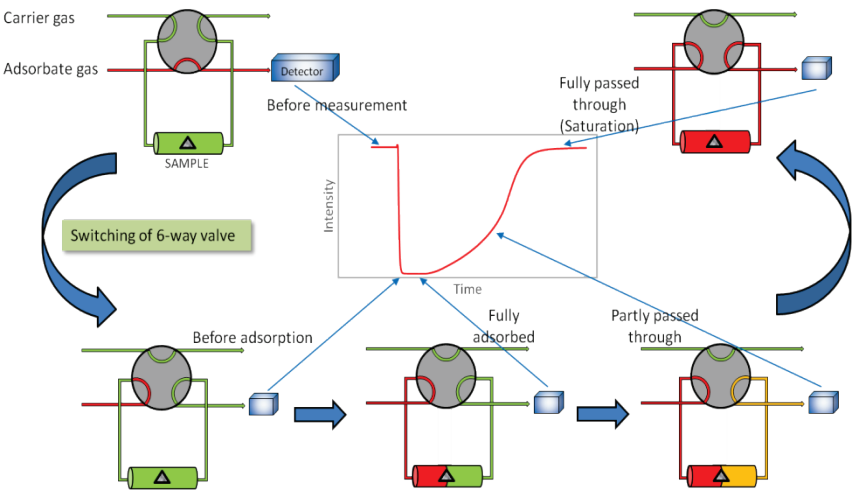


Fig 1. Measurement process

Results and Discussion

Fig 2. shows the breakthrough curve of MFI zeolite for NH_3 gas.

Measurement condition
- Sample amount : 50 mg
- Pretreatment : At 500˚C for 1H in He flow.
- Measurement temp. : RT
- Adsorbate gas : 5%NH_3/He, 30sccm
- Detector : TCD

Result
- Adsorption amount : 2.6 mmol/g
- 5% Break point : 75 sec*
- 95% End point : 210 sec*

*From the point when 6-way valve was switched.

Fig 2. NH_3 breakthrough curve measurement on zeolite

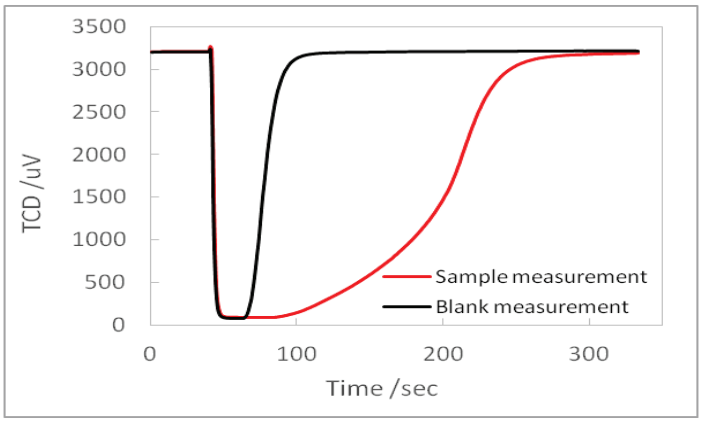
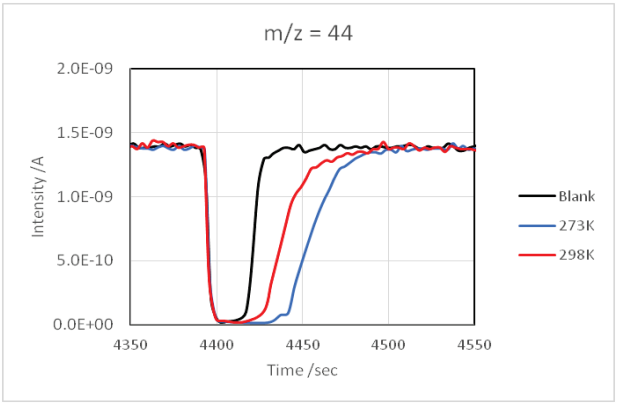
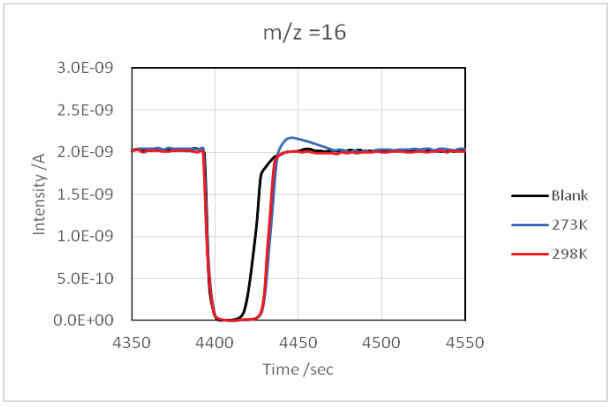


Fig. 3 is the measurement result of multicomponent gas(CO_2/CH_4) for MOF sample.

Fig 3. CO_2/CH_4 breakthrough curve measurement on MOF





Measurement condition
- Sample amount : 100 mg
- Pretreatment : At 150˚C for 500min in He flow.
- Measurement temp. : 273K, 298K (CATCryo II)
- Adsorbate gas : 10%CO_2/10%CH_4/He, 50sccm
- Detector : BELMass

Result

	CO_2 (m/z:44)		CH_4 (m/z : 16)	
	273K	298K	273K	298K
5% Break point /sec	44	35	40	39
95% End point /sec	88	80	44	47
Duration time /sec	44	45	4	8

The result shows that there was a clear difference in CO_2 (m/z : 44) breakthrough curve results measured at 273K and 298K, but little in CH_4 (m/z : 16) results. The rate of CH_4 adsorption is faster than CO_2. A positive peak can be seen in the CH_4 breakthrough curve at 273K. It is because of the replacement of adsorbed CH_4 by CO_2 adsorption.

Conclusion

In addition to the function for the catalyst evaluation (TPD, Pulse chemisorption, TPR/TPO, BET single point measurement). the breakthrough curve measurement is possible with BELCAT II.
The evaluation of adsorption kinetics and amount can be conducted easily using BELCAT II.

Key words : Break through curve, Break point, End point, Adsorbent, PSA, Gas separation, Gas purification, Mixture gas adsorption