CO2 Summit II: Technologies and Opportunities   Proceedings

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Kinetic enhancement of adsorbent for CO2 capture from atmosphere by porous material

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Outline

R&D — Capture Material

Wild absorbent

Na- or Ca-based sorbents with high heats of adsorption and high regeneration temperatures, e.g. 800 to 1200 K

Mild absorbent

Amine-functionalized porous solids, slow kinetics

Institute	Absorbent	Reaction atmosphere	Capacity mmol/g	Application
Georgia Tech.	PEI/silica	air	2.36	CO_2 air capture
Columbia Uni.	Ion exchange resin	air	1.73	CO_2 air capture
Hamburg Uni. of Tech.	Amino - silica	2500ppm	1.55	CO_2 removal submarines, space crafts or aircraft
United Tech. Res. Center	HSC+	2%	1.82	CO_2 removal in space shuttle applications
Korea Uni.	MOFs	Air	2.82	CO_2 air capture

Refs： J. Am. Chem. Soc. 2012, 134,7056−7065; Environ. Sci. Technol. 2011, 45, 9101–9108; Environ. Sci. Technol. 2011, 45, 6670-6675; Environ. Sci. Technol. 2011, 45, 2420–2427.

R&D — Capture Material

Research on CO_2 removal under ultra-dilute atmosphere in China

Institute	Absorbent	Reaction atmosphere	Capacity	Application
Zhejiang university	CNTs/TEPA、TETA	2% CO_2	2.52-3.56 mmol/g	CO_2 removal in confined space
PLA University of Science and Technology	LiOH	1% CO_2	1.89 mmol/g	CO_2 removal in submarine .etc
Tianjin university	5A molecular sieve	0.3%		CO_2 removal in spacecraft
Zhejiang university	Ion-exchange resin	air	1.72 mmol/g	Air capture
The 718 research institute of CSIC	Hollow fiber membrane contactor	0.1%-0.5% CO_2		CO_2 removal in confined space

R&D —Air Capture Kinetics

- Could be much lower compared to flue gas capture due to the lower CO_2 partial pressure;

  Inlet Concentration: 12 kPa : 40 Pa = 300:1

  Efficiency: ↓**90%** ↓**1%**

  Outlet Concentration : 1.2 kPa : 40 Pa = 30:1

Adsorption kinetics is crucial to **reactor design** and the **optimization of adsorption material**, but reports related are limited.

R&D —Air Capture Kinetics

The kinetics is expected to be improved by immobilizing functional group onto solid supports with large surface area, such as mesoporous silica, alumina and carbon black.

Material	Pore size (*nm*)	Surface area m^2/g (Before)	Surface area m^2/g (After)	Adsorption half time, (*mins*)
FS-PEI	1.057	--	79.9	300
T-PEI/silica	--	--	--	210
HAS6	5-6	200-500	71	100-150
AEAPDMS-NFC-FD	--	26.8	7.1	100
MOFS	--	3270	70	30
RFAS	7	--	150-300	10-20
Carbon Black	--	223	21	10
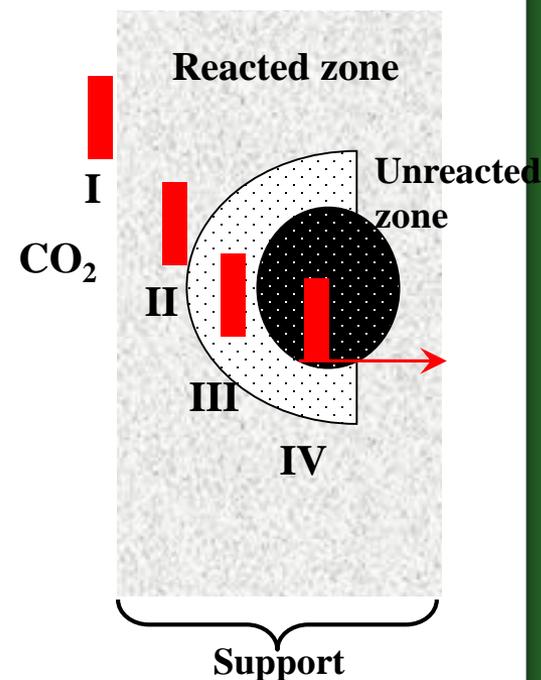
I: Boundary diffusion, II: Support diffusion
III: Product diffusion,   IV: Reaction

However, the inappropriate material selection or treatment process for sorbent could result in unexpected diffusion resistance.

Refs：J. Am. Chem. Soc. 2012, 134,7056−7065; Environ. Sci. Technol. 2011, 45, 9101–9108 Environ. Sci. Technol. 2011, 45, 2420–2427

Methodology of Kinetics Analysis

Int. J. Greenhouse Gas Control, 2013, 17, 332-340
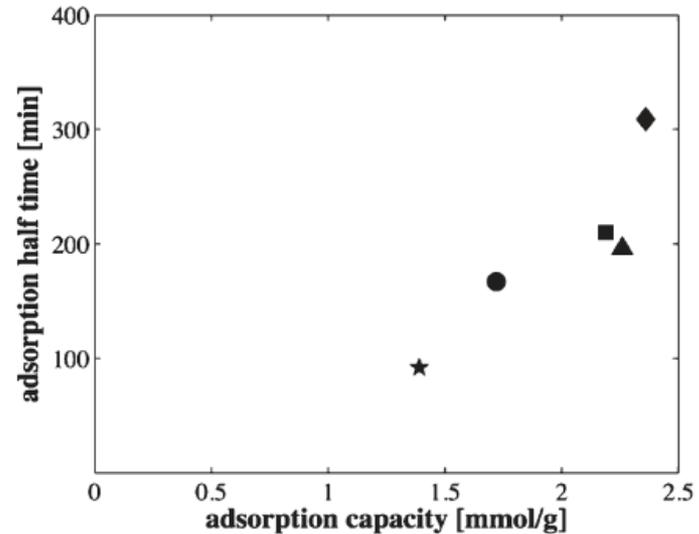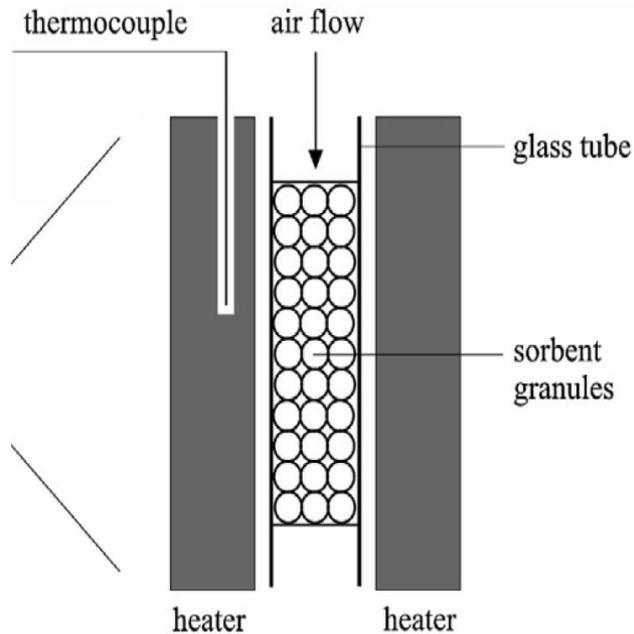
Figure 5. Comparison of adsorption capacity and adsorption half time of AEAPDMS-NFC-FD (star), HAS6 (sphere), PEI/silica (rhombus), A-PEI/silica (triangle), T-PEI/silica (square).[6,7].

Environ. Sci. Technol. 2011, 45, 9101-9108

Experiment- **The resistance from gas side diffusion is hard to be avoided on the fixed bed reactor.**

Model- **The existing indicator of half time is too simple to reflect the real reaction process under ultra low CO_2 concentration.**

Outline

1 **Background and motivation**

2 **Experiments and model**

3 **Results and discussion**

4 **Conclusion**

Experimental material

CO$_2$ (400 ppm)

CO$_2$ (5 kPa) + H$_2$O
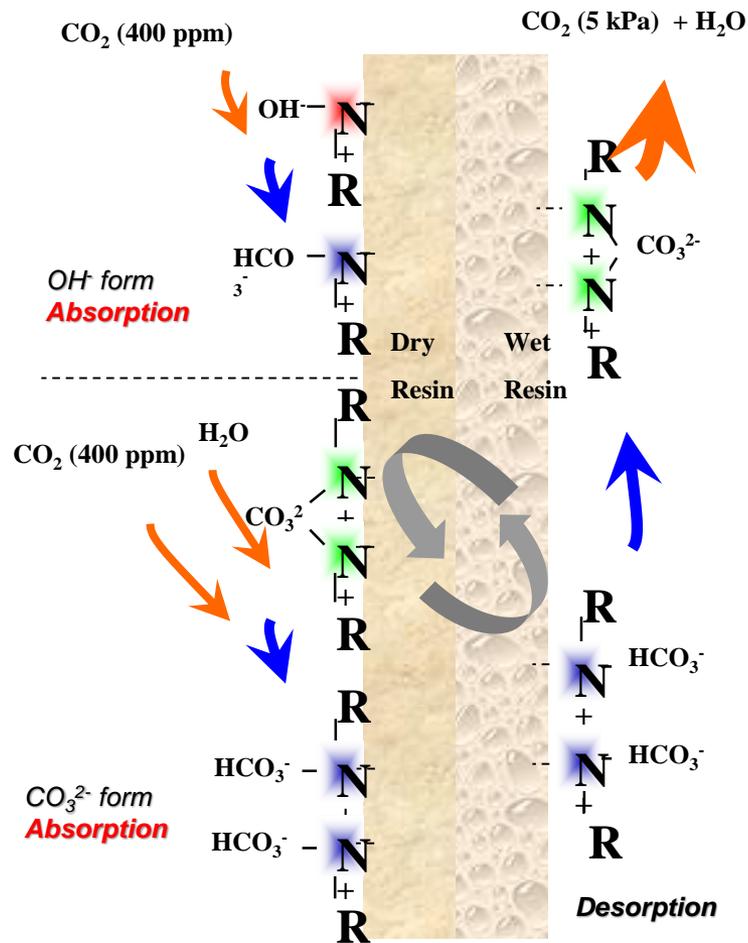
Ion Exchanged Resin Material

OH$^-$ — N

R

OH$^-$ form
Absorption

HCO$_3^-$ — N

R

Dry Resin   Wet Resin

CO$_2$ (400 ppm)   H$_2$O

CO$_3^{2-}$

R

CO$_3^{2-}$ form
Absorption

HCO$_3^-$ — N

HCO$_3^-$ — N

R

R — N CO$_3^{2-}$ — N

R

R — N HCO$_3^-$

R — N HCO$_3^-$

R

Desorption

OH$^-$
CO$_3^{2-}$
F$^-$
SO$_4^{2-}$, …

$CH_3 - N^+ - CH_3$
CH_3
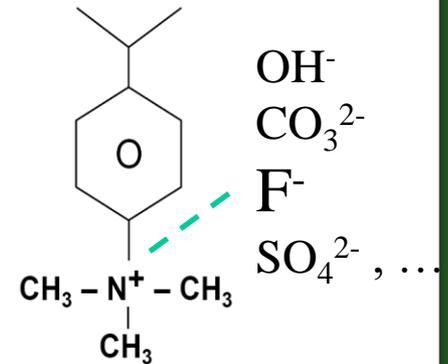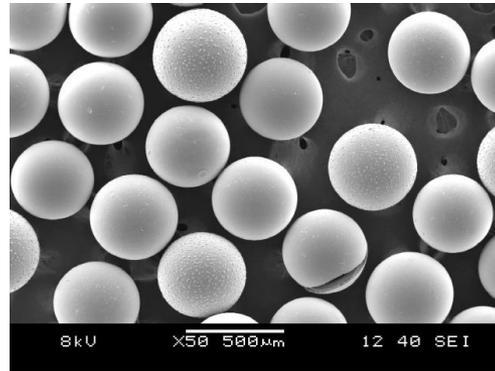
Developed and tested by Columbia University
Eur. Phys. J., 2009, 176, 93-106;
Environ. Sci. Technol., 2011, 45, 6670-6675.

An economically viable air capture method by avoiding expensive heating/cooling cycles or significant pressure changes.

9

Preparation of adsorption material

Ion exchange resin / NMP+ PEG-400 —**Mixed / Stirred**→ **PES** → solution —**Stirred**→ Uniform suspension —**Tape-casting method**→ Original membrane —**Heat treatment / Alkaline wash**→ Final membrane
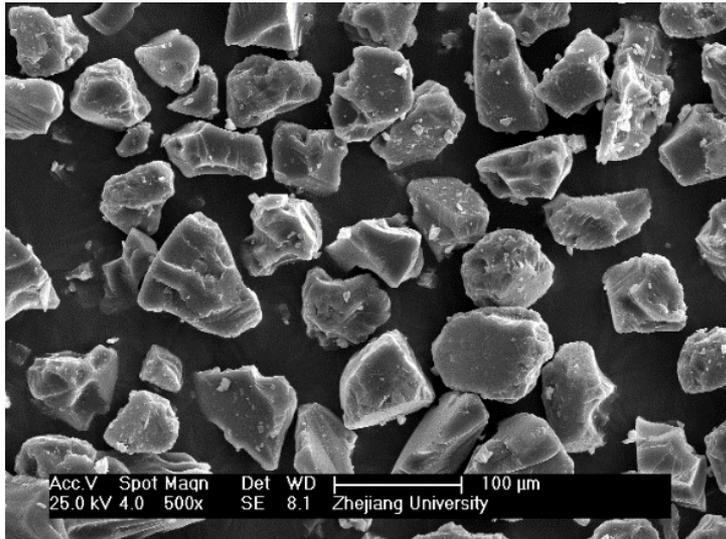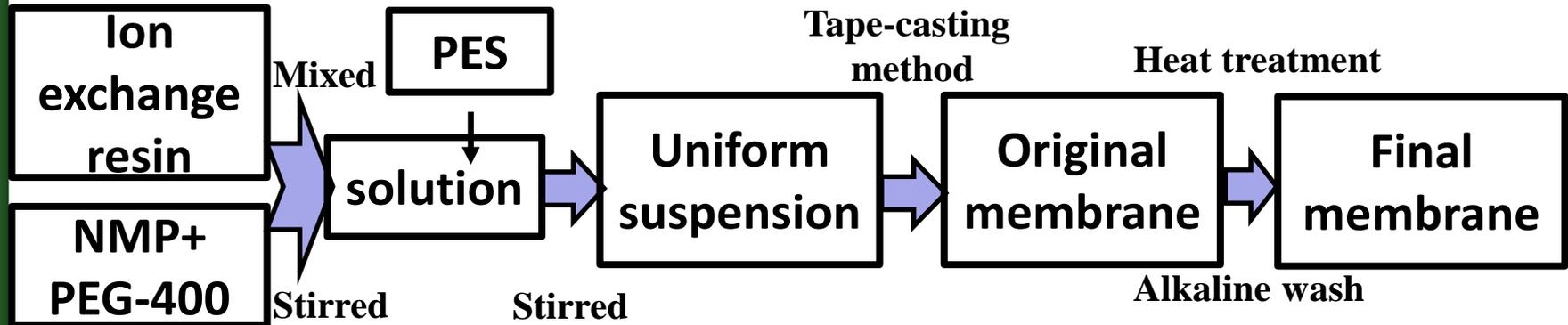
Resin with uniform size
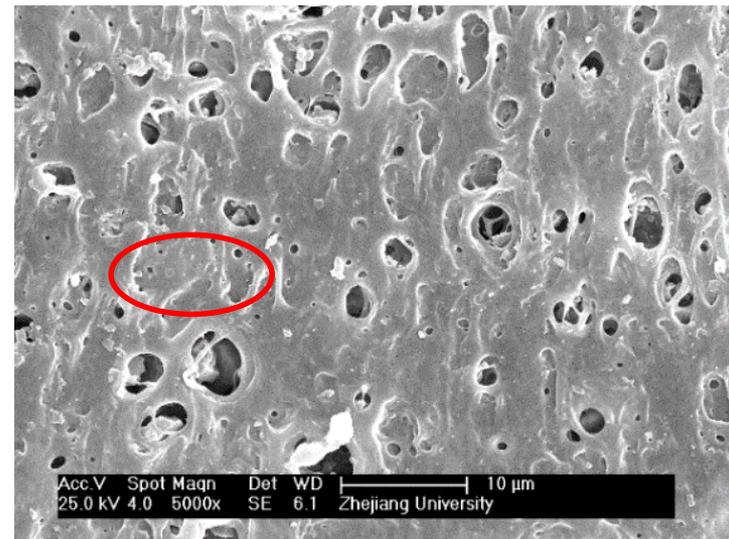
Membrane with Porous structure

10

Experimental system

Tachometer
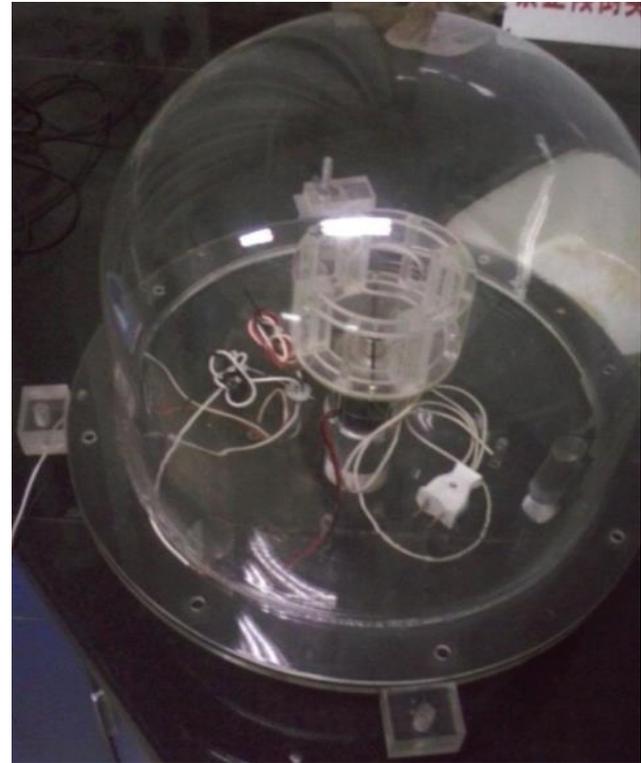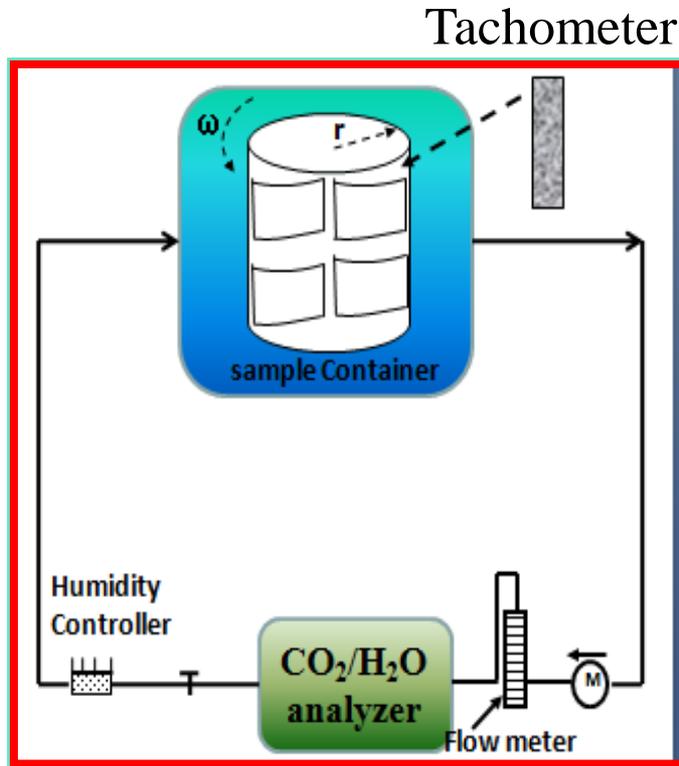
Experiment- *A revolving bed reactor is built to characterize the mass transfer limitations of CO_2 adsorption with relatively low kinetics.*

Kinetics model

Model-_the shrinking core model is modified to analyze the resistance during CO_2 absorption_

Support layer diffusion

Fick' Law:

$$-\frac{dN'_{CO_2}(t)}{dt} = SQ_A = SD_{e1}\frac{2(C_1 - C_2)}{L}$$

Support layer diffusion rate：

$$V_{film} = D_{e1}\frac{C_0}{2\rho L^2}$$

Support layer

Unreacted surface

Product layer

Surface of resin particle

$C_{AS} = C_A$

Gaseous CO_2 Concentration

C_A

$C_{AC} = 0$

$R \quad r \quad r_c \quad 0 \quad r_c \quad r \quad R$

Radial position
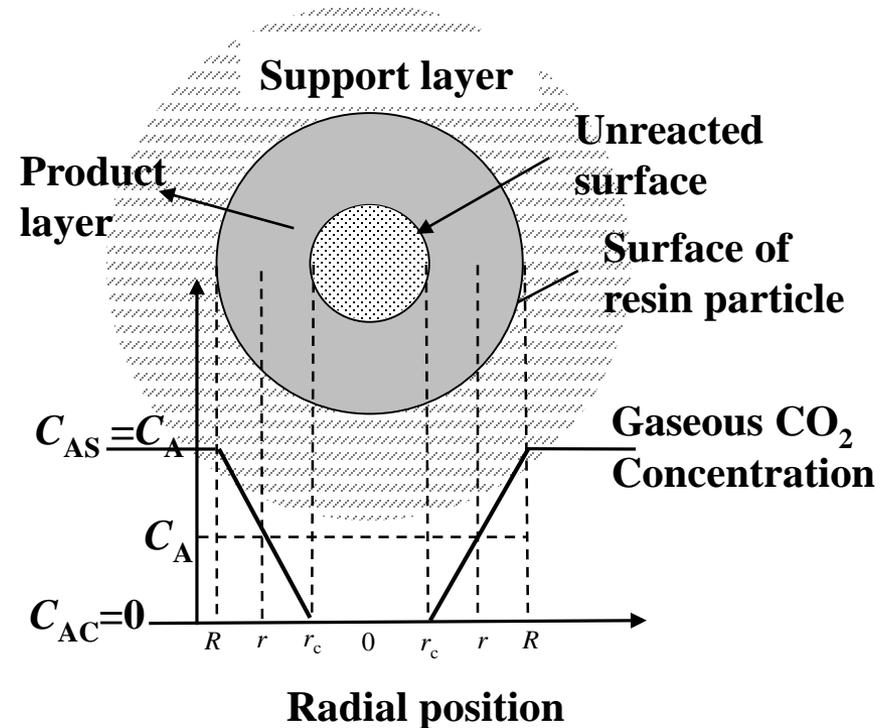
Kinetics model

Product layer diffusion rate：

$$V_{\text{diff}} = \frac{3D_{e2}C_0}{R^2 \rho_2[(1-\theta/\theta_{\max})^{-1/3}-1]}$$

The unknown parameter:
product layer diffusion coefficient

Chemical reaction rate:

$$V_{\text{diff}} = \frac{3kC_0(1-\theta/\theta_{\max})^{2/3}}{\rho_2 R}$$

The unknown parameter:
Chemical reaction rate coefficient

The total resistance during CO2 adsorption:

$$\lambda = \frac{L^2 \rho_1}{2D_{e1}C_0} + \frac{\rho_2 R^2[(1-\theta/\theta_{\max})^{-1/3}-1]}{3D_{e2}C_0} + \frac{\rho_2 R}{3kC_0(1-\theta/\theta_{\max})^{2/3}}$$

13

The effect of particle size

Kinetics at different sorbent size (dots are experimental data, square: diameter of 80 μm; triangle: diameter of 40 μm; circle: diameter of 30 μm; solid lines are the fitting date)
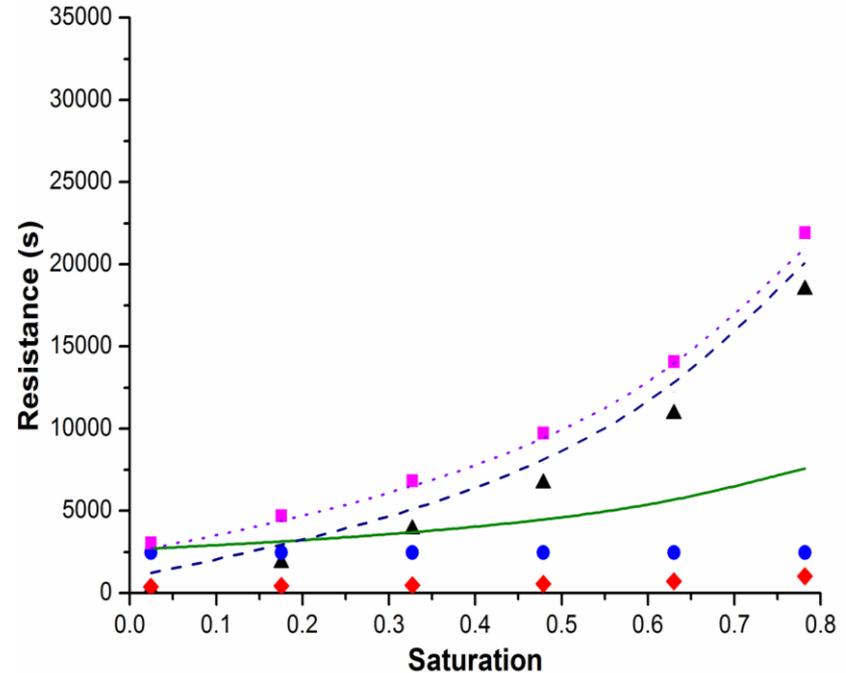
Resistance contributions from different steps at 0.5% vapor concentration. (square: total resistance; diamond: reaction resistance; triangle: production resistance; circle: support resistance; dashed line: total resistance (L/2); solid line: total resistance (R/2); dot line: total resistance (10k))

15

The effect of particle size
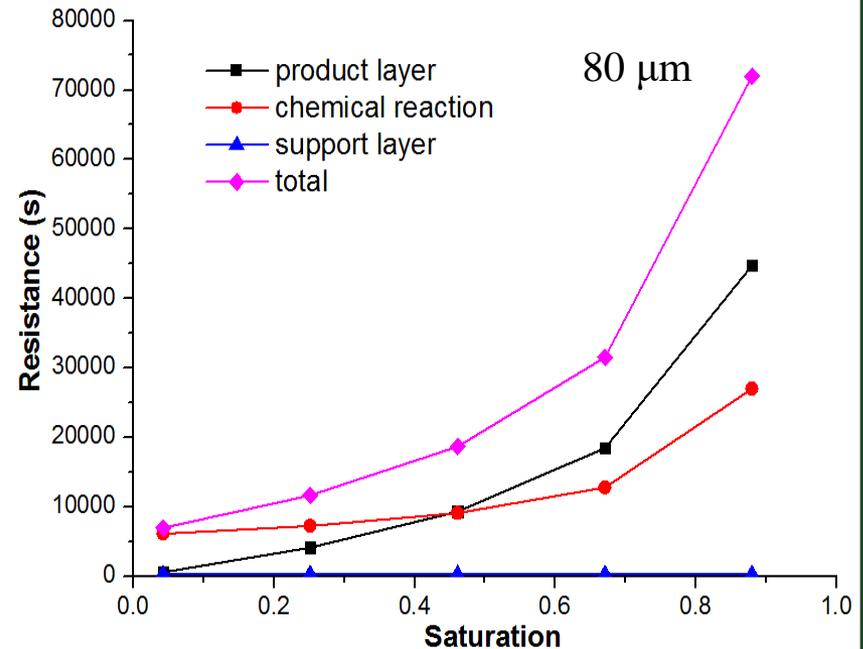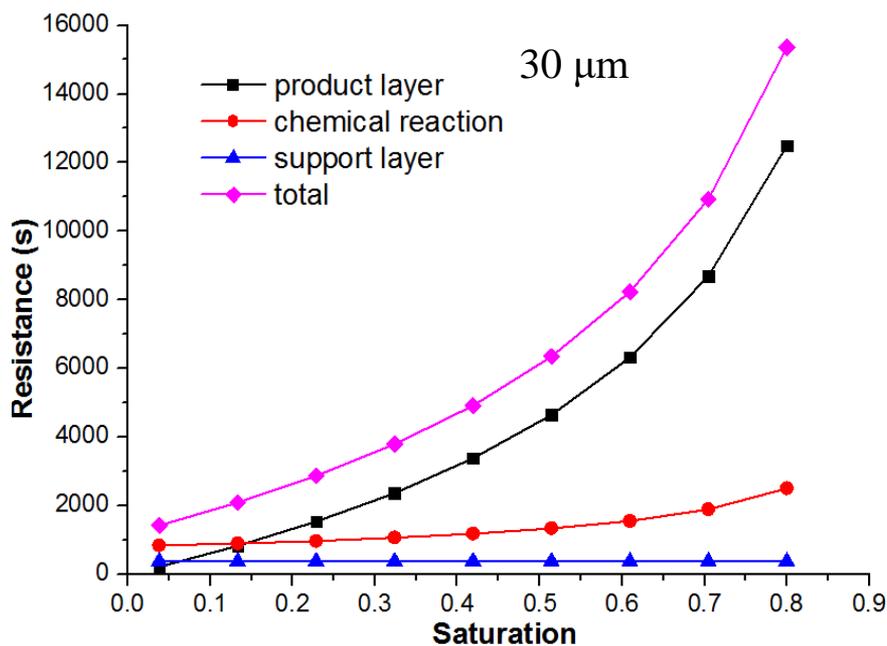
Decomposition of mass transfer resistance under different particle size. (20 °C and 21.2% relative humidity)

The adsorption rate increases significantly with decreasing sorbent size, indicating a resin particle dominated kinetics, rather than support layer dominated kinetics.

The effect of humidity
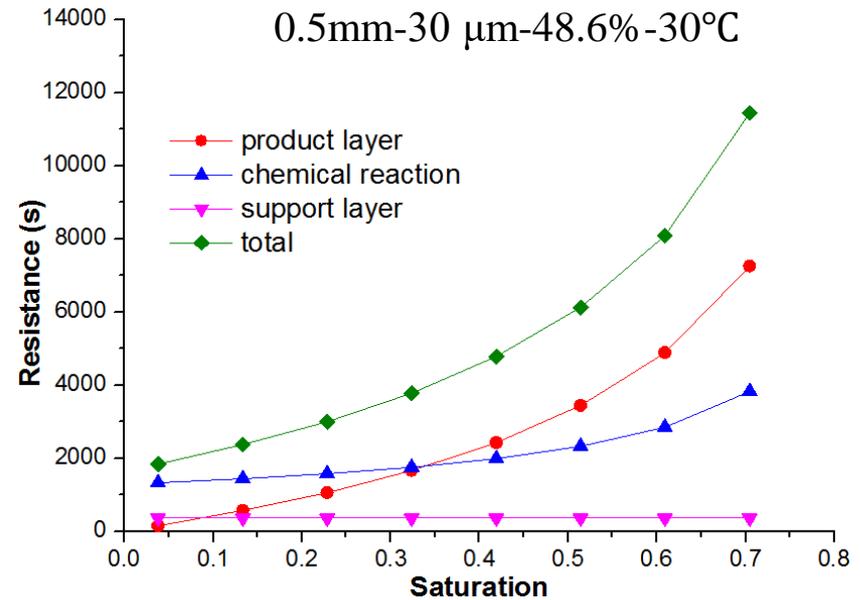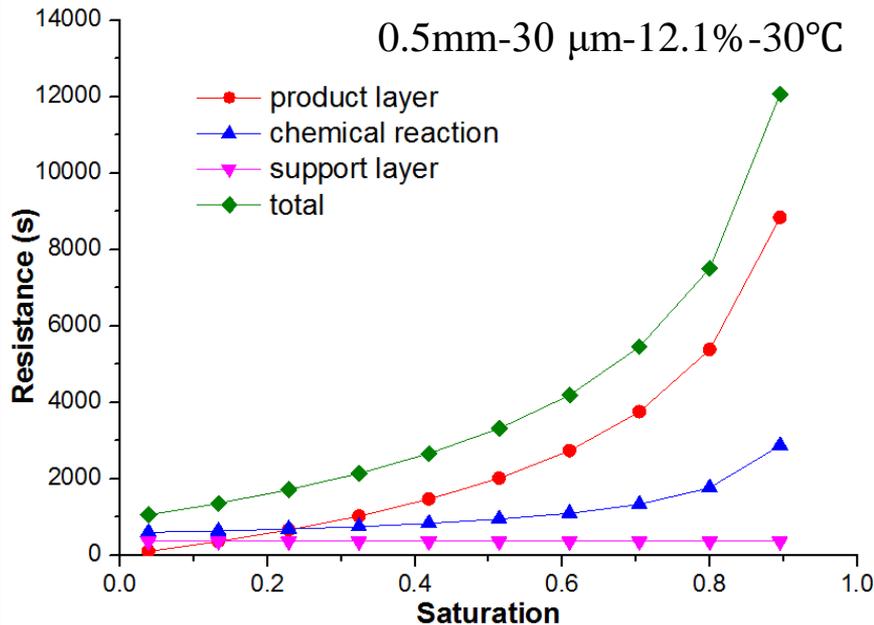
Decomposition of mass transfer resistance under different humidity.

The relative humidity affects the rates of physical diffusion and chemical reaction simultaneously, and it impacts the chemical reaction more significantly than physical diffusion in the moisture swing adsorption.

The effect of temperature
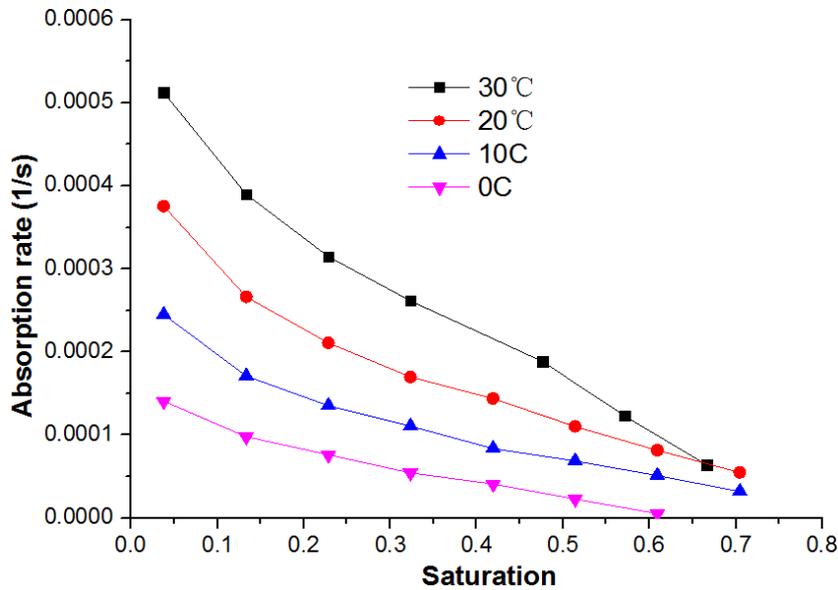
Absorption rate under different temperature.
(particle size: 30μm, 50% relative humidity)
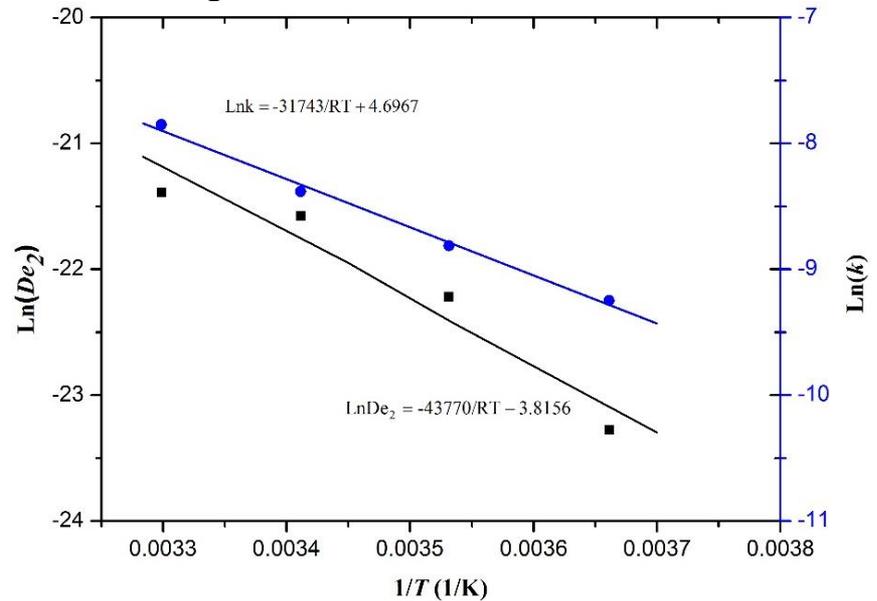
Temperature dependence of chemical reaction rate, k (m/s)
and effective product layer diffusion coefficient, D_{e2} (m²/s).

$$\omega_i = A_i \exp(-E_{a-i}/(R_c T))$$

Where ω_i is the rate constant, A_i is the frequency factor, E_{a-i} is the activation energy, and R_c is the universal gas constant. The A_i and E_{a-i} can be determined by linear fitting as shown in Fig. The activation energy of chemical reaction is 31.7 kJ/mol, which is at the same level as reported for amine based reaction with CO_2

18

$$t = \int \left(\frac{2\rho_1 L^2}{D_{e1} C_0} + \frac{R^2 \rho_2 [(1 - \theta / \theta_{max})^{-1/3} - 1]}{3 D_{e2} C_0} + \frac{\rho_2 R}{3 k C_0 (1 - \theta / \theta_{max})^{2/3}} \right) d\theta$$
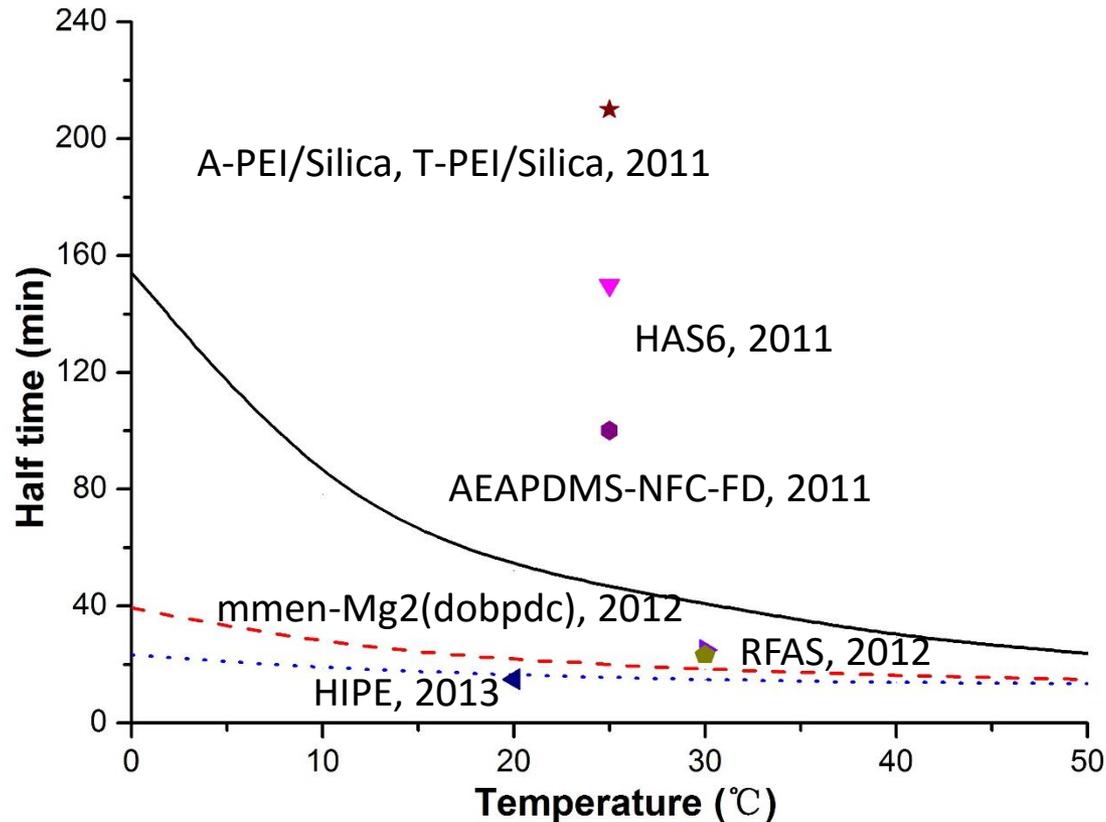
Comparison of CO_2 adsorption half time with different adsorbents. Solid line: 30 μm, dash line: 10 μm, dot line: 5 μm. Scattered dots are experimental data in literatures.

Refs: Energy Environ. Sci., 2013; 6, 488-493; J. Am. Chem. Soc., 2012; 134, 7056-7065; Environ. Sci. Technol. 2011, 45, 9101–9108; Chemical engineering journal, 2012; 189-190, 13-23.

Conclusion

➤ the adsorption kinetics could be enhanced by employing sorbent with smaller particles

➤ Both the diffusion coefficient and chemical reaction constant drop significantly with decreasing temperature or increasing relative humidity.

➤ The sorbent exhibits significant product layer diffusion controlled kinetics

➤ By preparing sorbent with μm sized particles, the half-time of sorbent in this study could reach the same level of recently developed air capture sorbent with much more expensive material, such as MOFs and nanomaterial.