Synthesis of Amino-Functionalized Mesoporous Silica and Application to CO_2 adsorption

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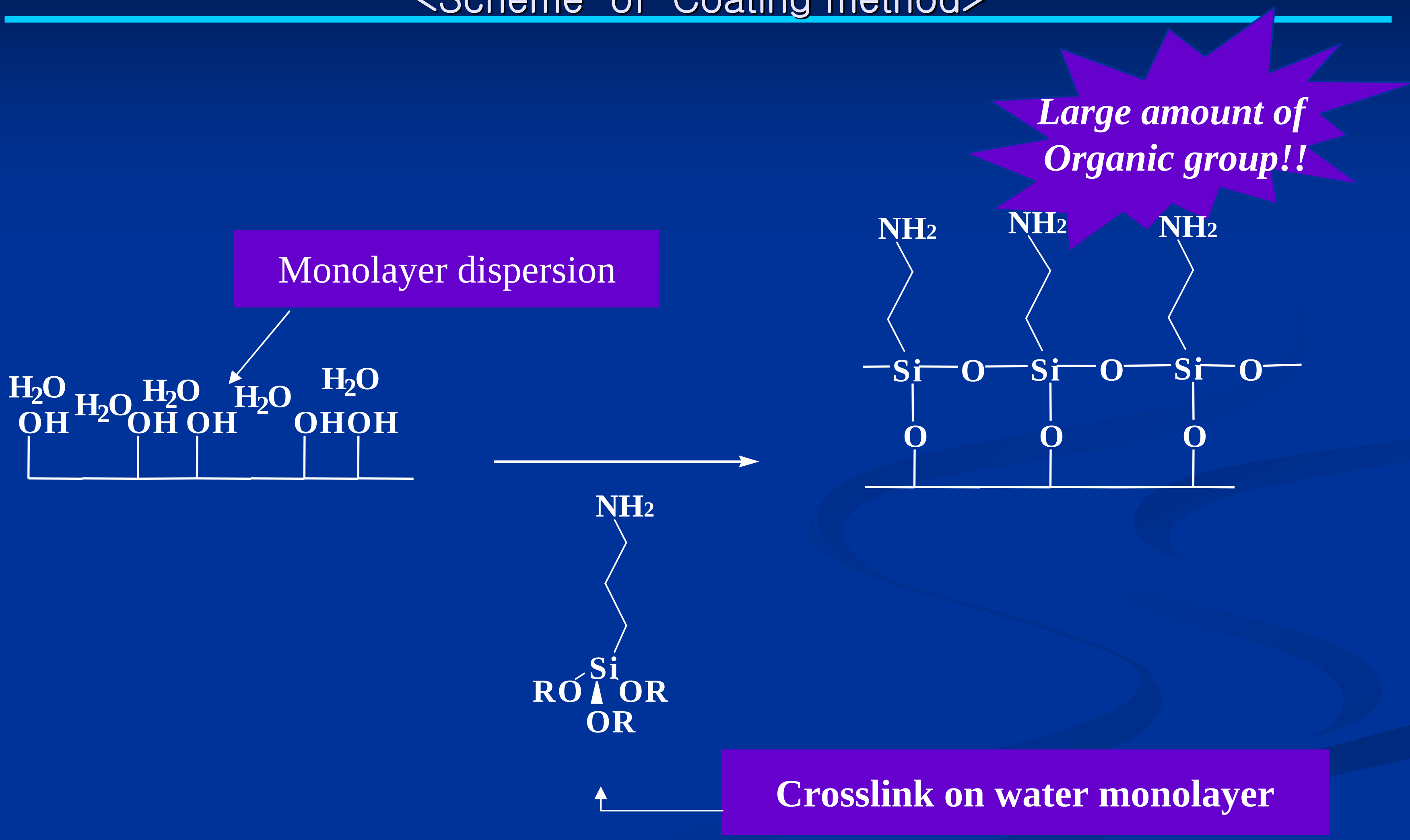
Introduction

Carbon dioxide의 선택적 제거 및 회수를 위하여 실리카 메조포어 분자체에 아민기를 도입하여 carbon dioxide(CO_2)를 선택적으로 흡착하는 방법이 연구되어왔으며, coating 및 grafting 방법 (메조 포어 분체를 합성한 다음 아민기를 나중에 도입시키는 방법) 이 적용 되어왔다. 음이온 계면활성제를 이용하여 아민기를 직접 합성과정에서 도입하는 방법은 경제적이고 상대적으로 많은 양의 아민기를 효율적으로 도입하는 방법이다. 본 연구에서는 AMS(Anionic-surfactant-templated Mesoporous Silica)를 문헌의 방법대로 합성하고, 국제적으로 처음 carbon dioxide(CO_2)의 흡착에 적용하였다.

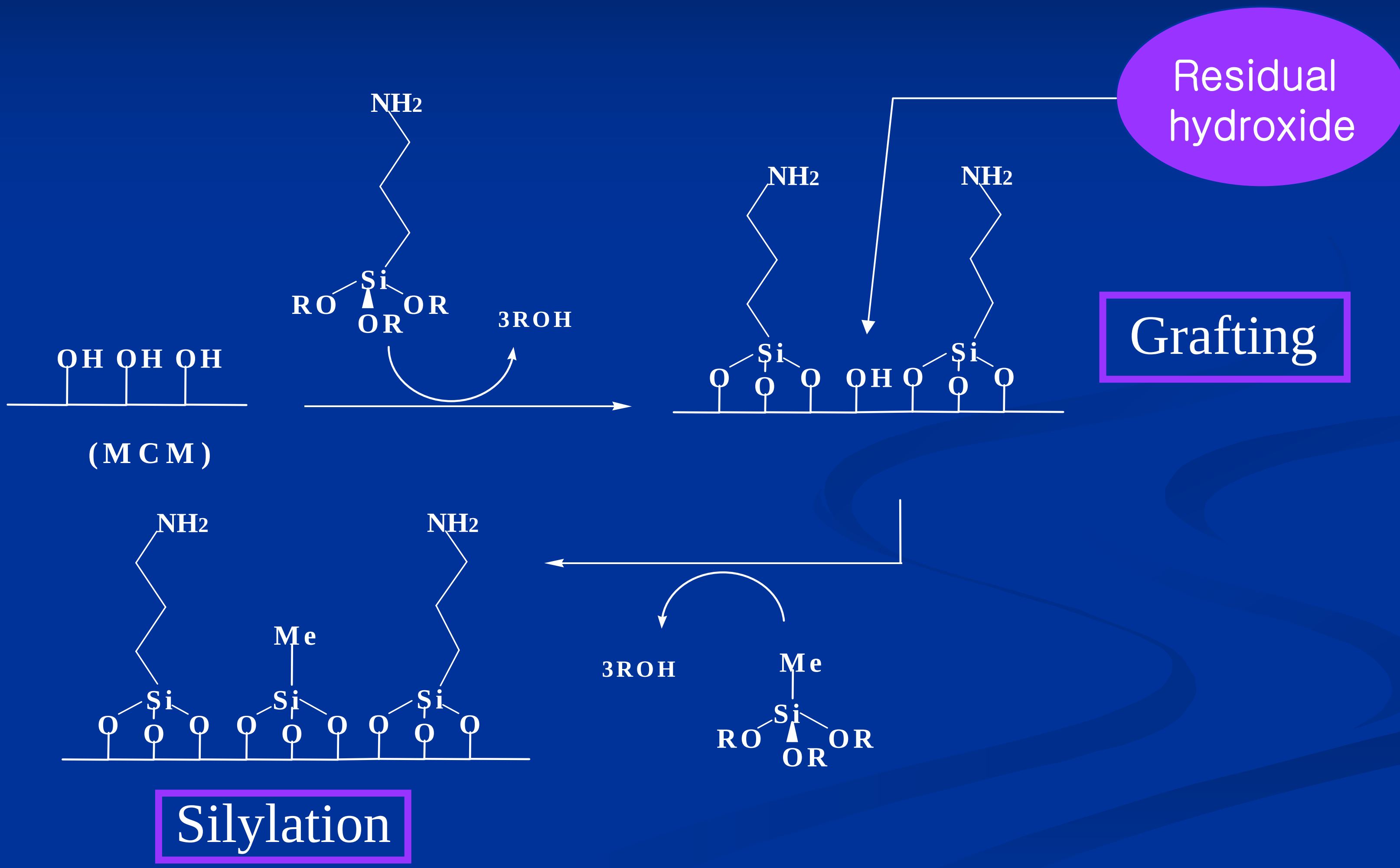
Synthesis of Amino-Functionalized Mesoporous Silica

<Scheme of Coating method>



Synthesis of Amino-Functionalized Mesoporous Silica

<Scheme of Grafting and Silylation method>

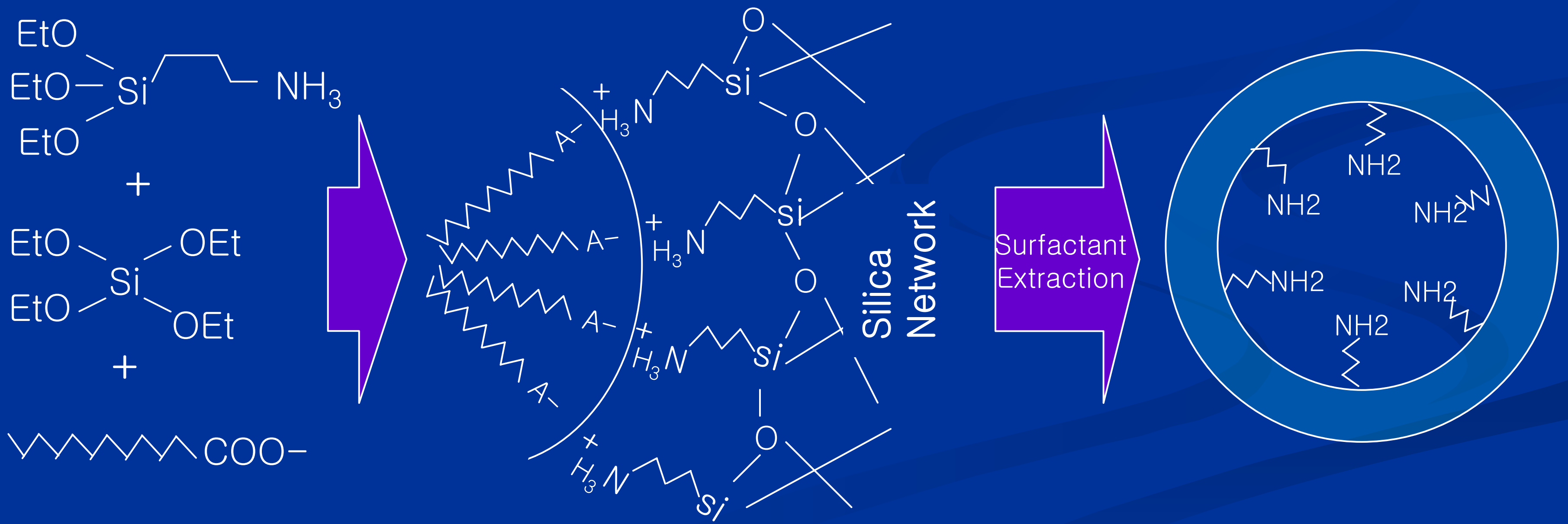


Synthesis of Amino-Functionalized Mesoporous Silica

< Anionic surfactant templating route >

Synthesis of AMS(Anionic-surfactant-templated Mesoporous Silica)
by "$S^-N^+\sim I^-$ pathway"
(S^- :anionic surfactant, N^+ :cationic amino group and I^- :inorganic species)

surfactant	co-structure directingagent (CSDA)
Lauric acid sodium salt (LAS)	3-aminopropyltriethoxysilane (APS)



Experimental

- Synthesis of AMS(anionic-surfactant-templated mesoporous silica)

WATER + ETOH
↓
Addition of LAS at 60 °C
For 30 min with vigorous stirring
↓
Cooling r.t
↓
APS + TEOS dropwise
↓
pH adjust to 10 and 1h stirring
↓
48h, 100 °C oven, static
↓
Filtering, Drying
↓
As-synthesized AMS

Extraction

As-synthesized AMS 1g
↓
Acetonitrile 100ml +
37wt% HCl (aq) 9.85
↓
25°C ,2h stirring
↓
Filtering (acetonitrile)
↓
Drying
↓
EX-AMS

Results

- Amine grafting results of MCM-41, pore-expanded-MCM-41

- Conventional MCM-41 and pore-expanded MCM-41(PE-MCM-41) silicas have been used as surpports for grafting 3-[2-(2-aminoethylamino)ethylamino]proryl trimethoxysilane(TRI) and tested for CO_2 adsorption.

Table1. Summary of support material characteristics

support	BET surface area (m^2/g)	pore diameter (nm)	volume (cm^3/g)
MCM-41	1140	3.7	1.03
PE-MCM-41	950	10	2.2

- When both supports were grafted under the same conditions, PE-MCM-41 was grafted with slightly larger quantities of amine than MCM-41 for all controlled silane additions.

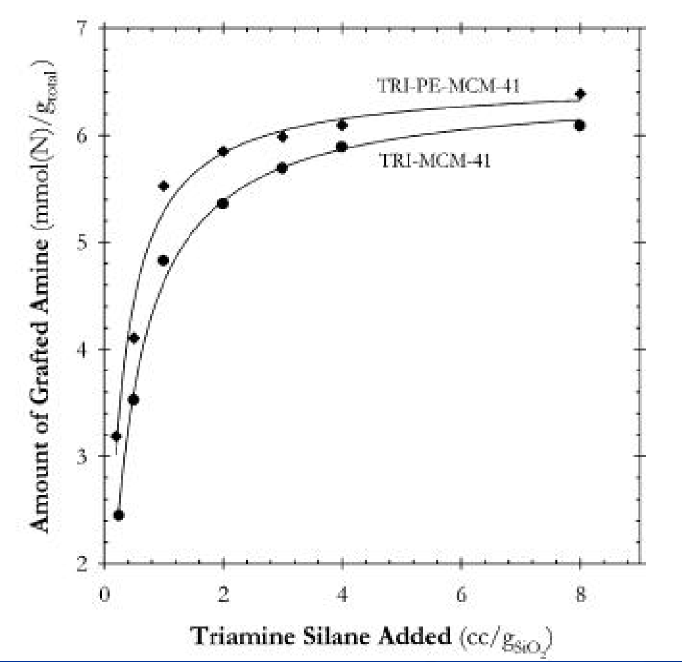


Figure 1. Effect of the amount of TRI added to the grafting Mixture on the amount of TRI grafted MCM-41 and PE-MCM-41 at 110℃

- Reference - Peter J.E. Harlick ;Abdelhamid Sayari. Ind.Eng.Chem.Res. 2006,45,3248.

Results

●Characterization of AMS(Anionic surfactant-templated Mesoporous Silica)

❖ XRD

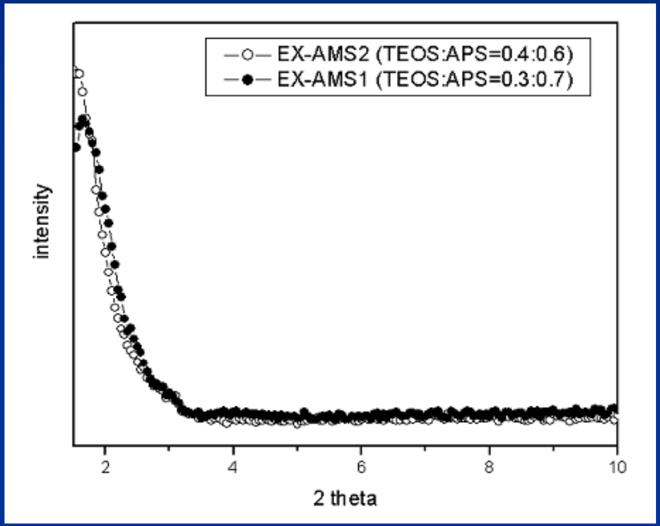


Figure 2. XRD of EX-AMS1 (APS:TEOS=0.3:0.7) and EX-AMS2 (APS:TEOS=0.4:0.6)

❖ BET

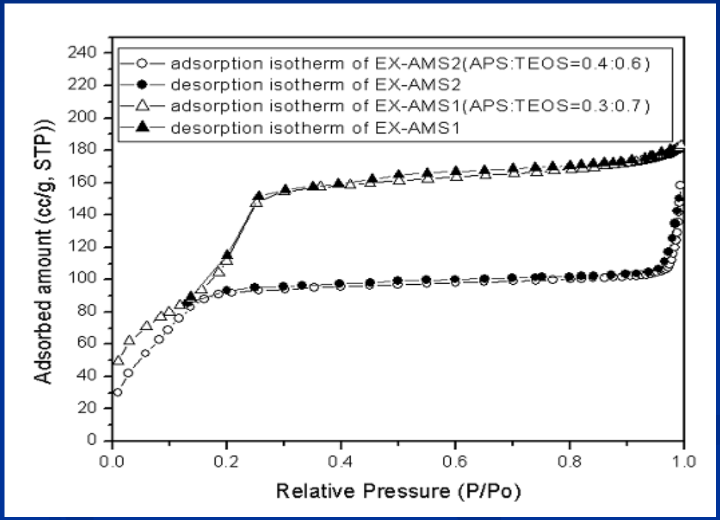


Figure 3. Adsorption /Desorption isotherm of EX-AMS1 and EX-AMS2

	surface area(m^2g^{-1})	pore volume($cm^3\ g^{-1}$)	pore radius(nm)
EX-AMS1(APS:TEOS=0.3:0.7)	430	0.32	4.6
EX-AMS2(APS:TEOS=0.4:0.6)	372	0.19	4.7

Table 2. BET of EX-AMS1 and EX-AMS2

Results

❖ TG-DTA

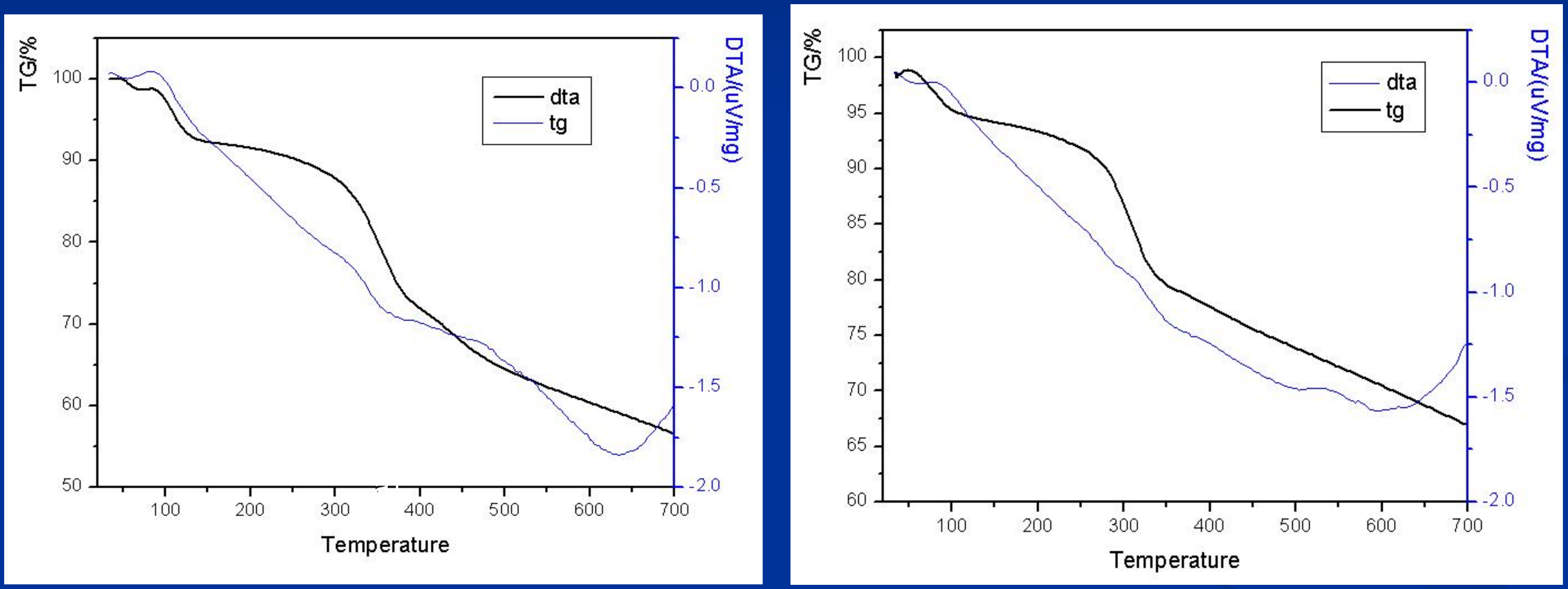
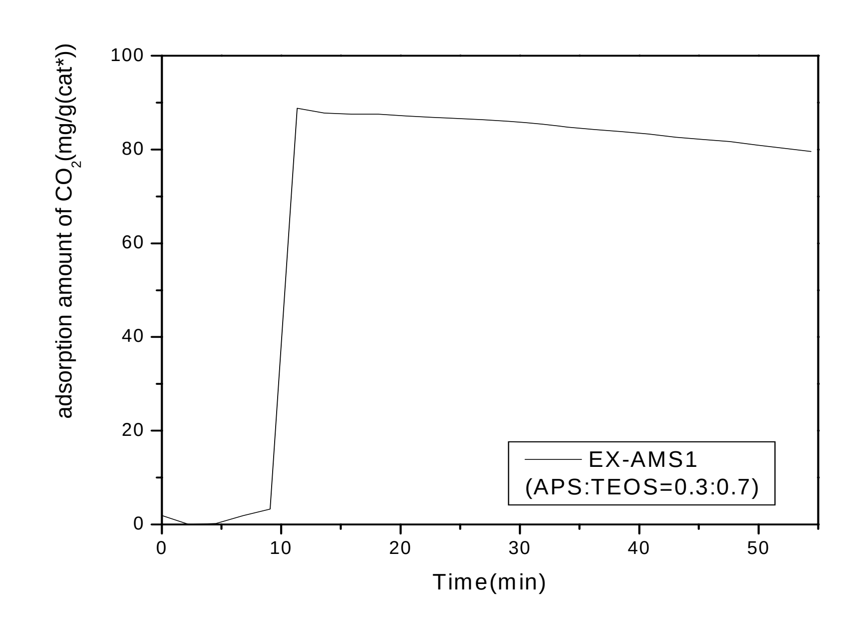
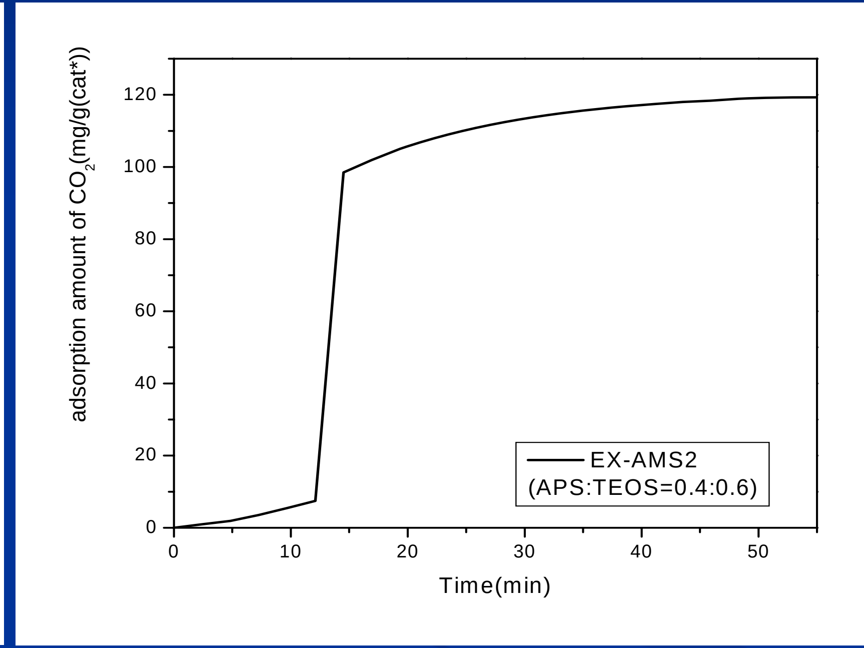


Figure 6. TG-DTA EX-AMS1 and EX-AMS
a) EX-AMS1 (APS:TEOS=0.3:0.7) ,b) EX-AMS2 (APS:TEOS=0.4:0.6)

Results

- CO_2 Adsorption

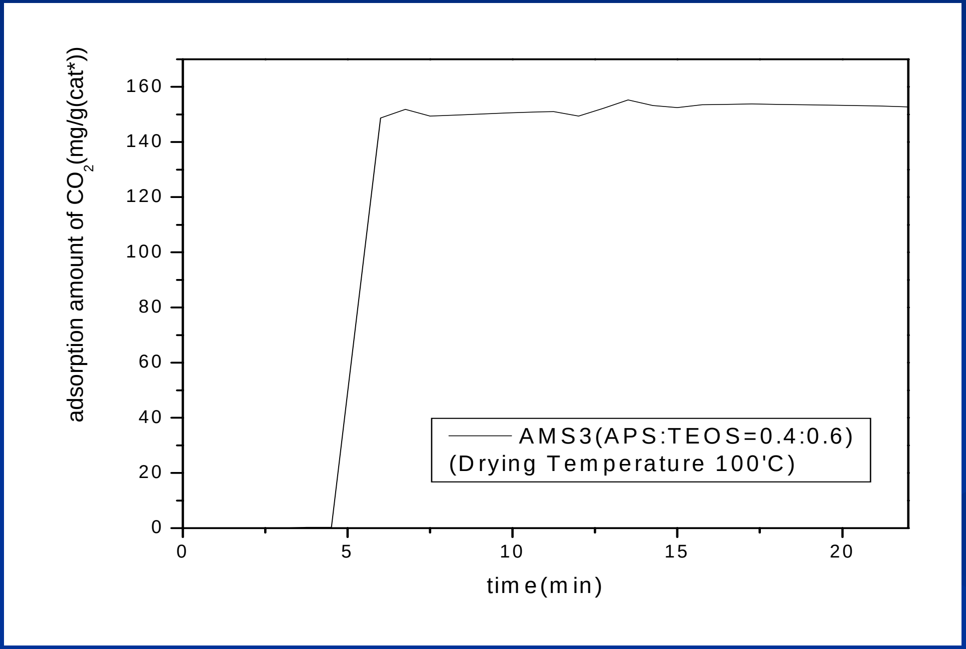




- 25℃ adsorption-150℃ desorption (5%CO_2/95%He)
- Drying Temperature 50 ℃

Results

- CO_2 Adsorption



- 25℃ adsorption–110℃ desorption (5%CO_2/95%He)
- Drying Temperature 100 ℃

Results

- Result of CO_2 Adsorption Capacity of EX-AMS

Material	Drying Temperature	Amount grafted (mmol(N)/g(cat*))	Adsorption Capacity (mg(CO_2)/g(cat*)	Adsorption Capacity (mg(CO_2/mmol(N))
EX-AMS1 (APS:TEOS=0.3:0.7) [25℃ adsorption-150℃ desorption]	50	3.8	88.7	23.3
EX-AMS2 (APS:TEOS=0.4:0.6) [25℃ adsorption-150℃ desorption]	50	4.0	112.6	28.2
EX2-AMS2 (APS:TEOS=0.4:0.6) [25℃ adsorption-110℃ desorption]	100	4.0	151.4	37.8

Results & conclusions

Material	Amount grafted (mmol(N)/g(cat*))	Adsorption Capacity (mg(CO_2)/g(cat*))	Adsorption Capacity (mg(CO_2)/mmol(N))
TRI-grafted MCM-41 #1	5.6	42.6	7.6
TRI-grafted Pore expanded-MCM-41 #1	5.9	62.0	10.5
EX-AMS 1 (APS:TEOS=0.3:0.7)	-	88.7	23.3
EX-AMS 2 (APS:TEOS=0.4:0.6)	-	112.6	32.2
EX2-AMS 2 #2 (APS:TEOS=0.4:0.6)	-	151.4	37.8

#1 TRI-grafted MCM-41 , TRI-graftedpore expanded MCM-41 : ● Reference - Peter J.E. Harlick ;Abdelhamid Sayari. Ind.Eng.Chem.Res. 2006,45,3248.
#2 Drying temperature 100℃

❖The CO_2 adsorption capacity of EX-AMS was significantly higher than that of TRI-grafited-MCM-41 and TRI-grafited-PE-MCM-41.