6-21-2016

SOx trapping performances of cuo based silica mesoporous adsorbents for desulfurization of industrial flue gas stream

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Collaboration: GRE, UMR CNRS 7361 IS2M MPC, IS2M, Université Haute-Alsace, cnrs, GE

Financial support: ADEME Agence de l'Environnement et de la Maîtrise de l'Energie

Industrial SOx emissions

Production of energy

Fossil fuels combustion

Power Plant (e.g. turbines)
Industrial boilers

Gaseous pollutants

SOx (SO_2 + SO_3)

SO_X: negative impact on:

- **Environment** (acid rain, precursors of secondary aerosols)
- **Human health**

Context

Industrial SOx emissions abatement

SOx emissions → Strict Regulation at industrial level → SOx emissions abatement

Industrial Emissions Directive (IED) 2010/75/EU

↓

Traditional Desulfurization processes : wet and dry scrubbing

- Efficient
- Non regenerative
- Produce additional greenhouse gas CO_2 and large amount of solid and liquide wastes
- High energy cost

↓

Alternative solution : reversible SOx trapping on solid adsorbents

↳ promising material : supported CuO

Adsorbent requirements:

- Oxidation catalyst: $SO_2 + \frac{1}{2} O_2 \xrightarrow{CuO} SO_3$
- SO_3 chemisorption: $SO_3 + CuO \rightarrow CuSO_4$
- Regeneration: $CuSO_4 \xrightarrow{\Delta\ (600\text{-}700°C)} SO_3 + CuO$

Context

Objective

- Elaboration of a regenerable adsorbent with high SOx adsorption performances

Organized Mesoporous Silica supports →
- Inert in regards with SOx
- High specific surface aera and mesoporous volume
- Easy diffusion of SOx in the porous network

↓

SBA-15 → Copper incorporation: wet impregnation in aqueous solution

- Characterizations of the adsorbents : N_2 physisorption/XRF/XRD/ and TEM analyses

- Study of SOx adsorption capacity during cycling experiments at laboratory scale in fixed bed reactor

Context

Adsorbents synthesis

Materials and methods

SBA-15

Copper nitrate

Wet impregnation in aqueous solution : $T_{ambiant}$

+

Drying : 45°C during 12 hours

+

Calcination step:

500°C during 6 hours (ramp of 1°C.min^{-1})

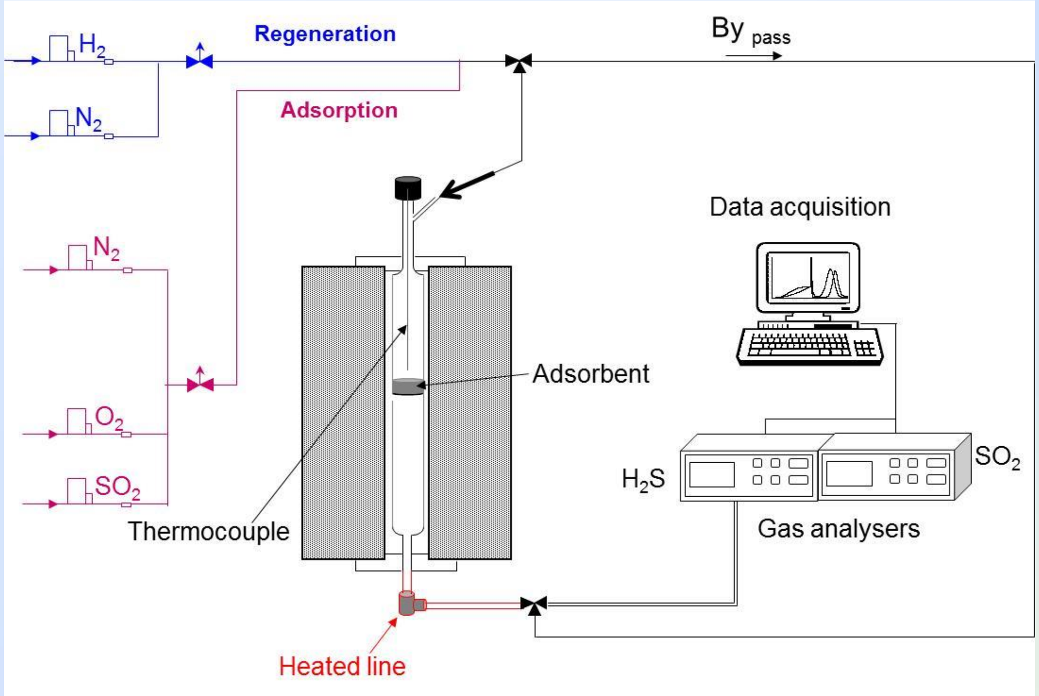
in fixed bed reactor under synthetic air flow (60 NL.$^{-1}$)

Three metal loadings : 8.8 wt.% - 15.6 wt.% - 31.7 wt.% of CuO

CuO8.8/SBA-15 | **CuO15.6/SBA-15** | **CuO31.7/SBA-15**

SO_2 adsorption tests

Cycling experiments in fixed bed reactor



SO_2 adsorption conditions:

- reactor: quartz, $Ø_{internal}$ = 6 mm
- adsorbent shaping: 250-400 µm,
- mass: 150 to 200 mg
- gas feed composition : 250 ppm SO_2 + 10 vol.% O_2 in N_2
- GHSV = 25000 h^{-1}
- temperature: 400°C

Regeneration conditions:

Two different procedures at two temperatures:

1. Under N_2 at 600°C

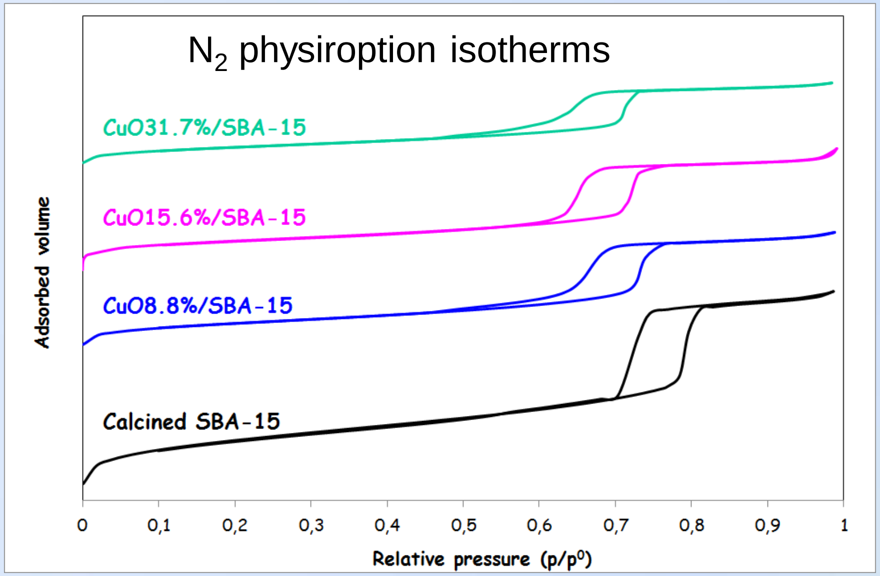
2. Under H_2 (0.5 vol.% in N_2) at 280°C

(with rege. 1 under N_2 at 600°C)

Materials and methods

Adsorbents characterizations

Textural characterization



Color, chemical composition and textural properties of materials

Sample	SBA-15	CuO8.8%/ SBA-15	CuO15.6%/ SBA-15	CuO31.7%/ SBA-15
Color	White	Light blue	Light green	Dark green
CuO (wt.%)*	/	8.8	15.6	31.7
S_{BET} (m^2/g)	825	459	356	325
Pore size(nm)	6.8	6.4	6.3	6.1
V_p (cm^3/g)	1.02	0.65	0.57	0.45

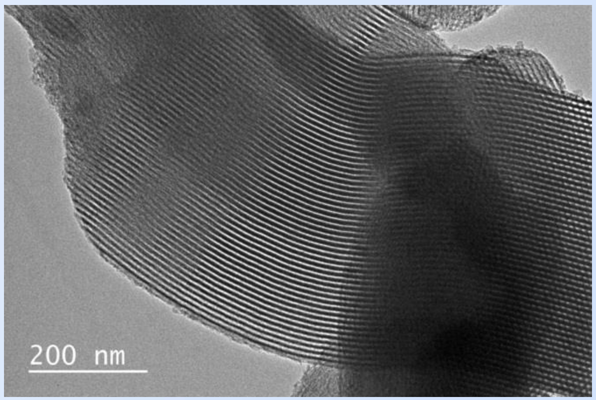
**Determined by XRF analysis*

- No alteration of the mesoporous structure after impregnation and calcination steps
- Decrease of the BET surface area, pore size and porous volume after copper incorporation, more prononced for higher copper loadings

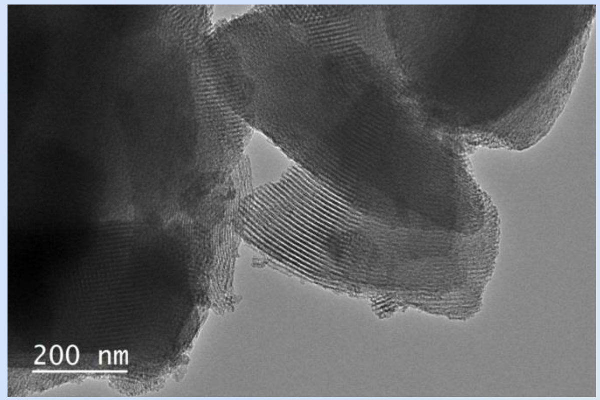
Adsorbents characterizations

TEM analyses

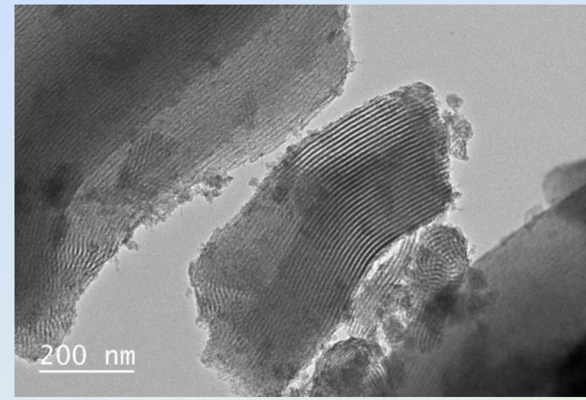
CuO8.8/SBA-15



CuO15.6/SBA-15



CuO31.7/SBA-15



- XRD analyses : no diffraction peak corresponding to a copper crystalline phase
- TEM analyses: no copper particles observed : copper highly dispersed for all materials, probably formation of Cu-O-Si species[a,b]

Synthesis conditions used prevent copper sintering phenomenon and generate copper species in strong interaction with the support SBA-15

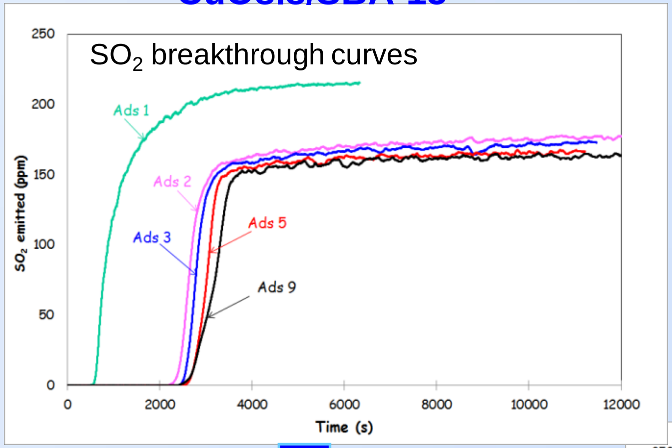
[a] Y. M. Wang, Z. Y. Wu, J. H. Zhu, Journal of Solid State Chemistry 177 (2004) 3815-3823
[b] X-C. Shao, L-H. Duan, Y-Y. Wu, X-C. Qin, W-G. Yu, Y. Wang, H-L. Li, Z-L. Sun, L-J. Song, Acta Phys. Chim. Sin. 28 (2012) 1467-1473

Results

SO_2 adsorption tests: cycling experiments

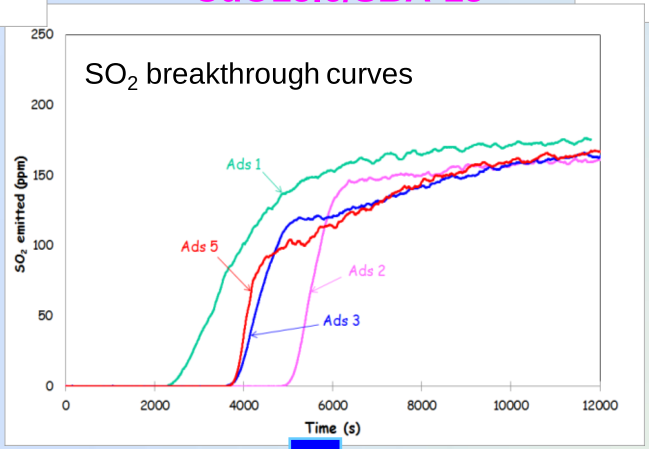
Regeneration under N_2 at 600°C

CuO8.8/SBA-15

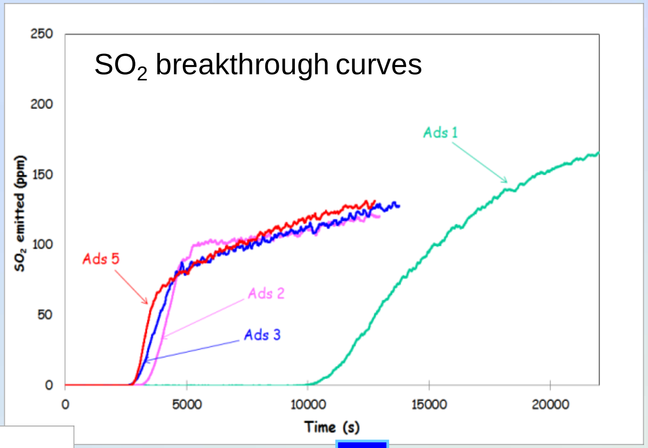


- No deactivation, even after 9 cycles
- Strong increase of performances from the 2nd SO_2 chemisorption

CuO15.6/SBA-15



CuO31.7/SBA-15



- The best SO_2 adsorption capacity during adsorption 1
- Important deactivation from adsorption 2

- Interesting SO_2 adsorption capacities obtained along cycling experiments with a relatively weak deactivation
- The best performances after 5 cycles

SO_2 adsorption tests: cycling experiments

Regeneration under N_2 at 600°C

Adsorbent	SO_2 adsorption capacity at 75 ppm ($mg_{SO2}.g_{ads}^{-1}$)*					Copper sulfation rate at 75 ppm (%)**				
	Cycle					Cycle				
	1	2	3	5	9	1	2	3	5	9
CuO8.8/SBA-15	21	37	39	42	44	30	52	55	59	62
CuO15.6/SBA-15	44	75	60	57		35	60	48	45	
CuO31.7/SBA-15	162	54	51	49		63	21	20	19	

* *SO_2 adsorption capacity calculated by integration of the SO_2 curve until the outlet SO_2 concentration reaches 75 ppm*
** *Ratio of SO_2 chemisorbed at 75 ppm/total Cu content (mol/mol)*

The best adsorbent

Adsorbents CuO/SBA-15 behavior strongly depends on copper loading

Low and intermediate copper loadings

Formation of Cu^+ species during the first regeneration, more efficient in the desulfurization reaction

High copper loading

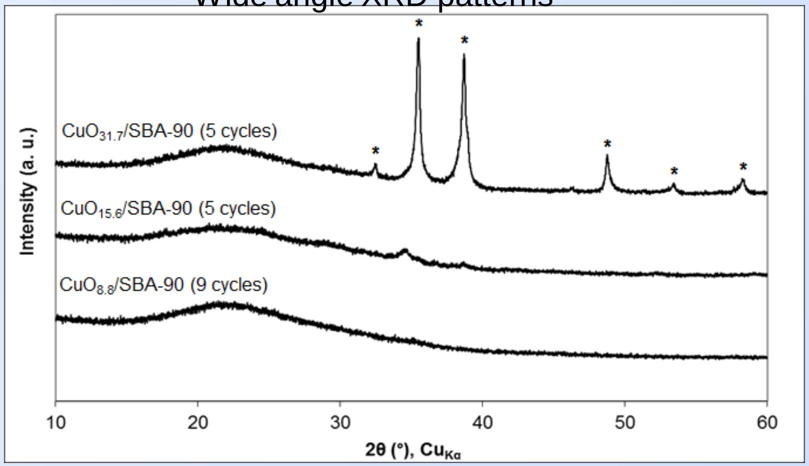
High SO_2 storage capacity during cycle 1
Strong deactivation during cycle 2 due to strong copper sintering

Results

Characterizations after SO_2 adsorption experiments

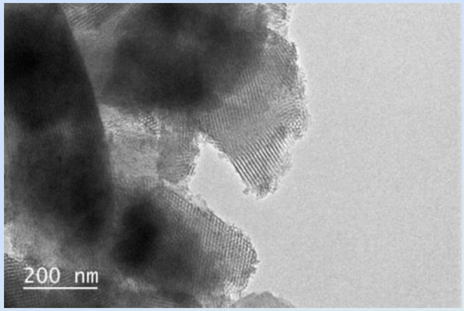
XRD analyses

Wide angle XRD patterns

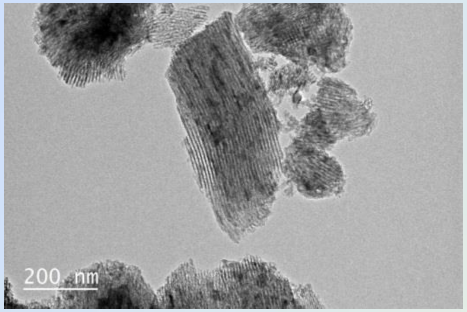


TEM analyses

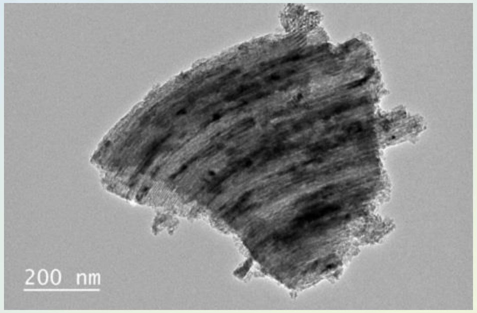
CuO8.8/SBA-15



CuO15.6/SBA-15



CuO31.7/SBA-15

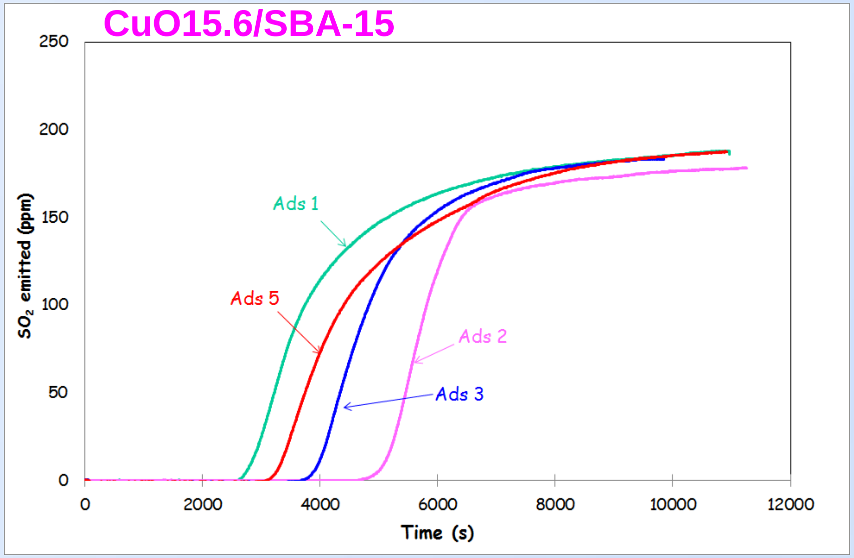


- CuO8.8/SBA-15 : after 9 cycles, copper species remain highly dispersed
- CuO15.6/SBA-15 : small XRD peaks of CuO
- CuO31.7/SBA-15 : sharp XRD CuO peaks : presence of large CuO crystallites in high quantity

Results

SO_2 adsorption tests: cycling experiments

Regeneration under H_2 at 280°C



CuO15.6/SBA-15	SO_2 adsorption capacity at 75 ppm ($mg_{SO2}.g_{ads}^{-1}$)*			
	Cycle			
	1	2	3	5
Regeneration under N_2 600°C	44	75	60	57
Regeneration under H_2 280°C	38	63	51	45

* *SO_2 adsorption capacity calculated by integration of the SO_2 curve until the outlet SO_2 concentration reaches 75 ppm*

- Regeneration at low temperature (280°C) under H_2 (0.5 vol.%) is efficient
- No H_2S is emitted during regeneration under H_2
- Energetic and financial advantages

Results

Conclusions

✓ Synthesis of CuO/SBA-15 based adsorbents with highly dispersed copper species by wet impregnation in aqueous solution

✓ Interesting SO_2 chemisorption capacities along cycling experiments

✓ Significant increase of the adsorbent efficiency after thermal treatment at 600°C : generation of Cu^+ species, more active in desulfurization reaction

✓ The adsorbents' behavior strongly depends on copper loading : deactivation increases with copper loading

✓ Optimum copper loading to ensure sufficient SO_2 adsorption capacity and weak deactivation

✓ Total regeneration under H_2 at 280°C without H_2S emissions

Thanks for your attention!

Acknowledgments:

- Philippe Fioux
- Loïc Vidal
- Damaris Kehrli
- All my colleagues!

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