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SYNTHESIS AND CHARACTERIZATION OF MESOPOROUS MATERIALS FROM CFB-FLY ASH

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FLY ASH

- **High contents of silicates and aluminosilicate suggest their susceptibility to transformation into zeolite-like materials and mesoporous materials**

- **The conversion of fly ash into zeolitic (microporous) materials is usually carried out through a hydrothermal treatment of the fly ash with an alkaline solution (NaOH or KOH)**

- **In the hydrothermal methods employed for the zeolitization of fly ash, various techniques may be used:**
  - **Classic alkaline conversion of fly ash**
  - **Fusion with sodium hydroxide prior to hydrothermal reaction**
  - **Microwave-assisted method**
  - **Two stage synthesis procedure**

FLY ASH

- **All these different processes resulted in the synthesis of sodium and potassium zeolitic material**

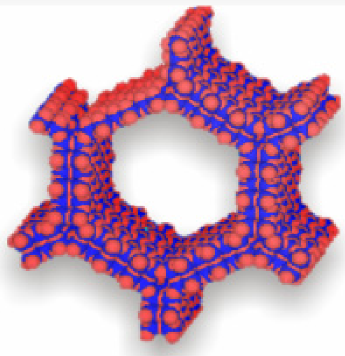
Zeolitic product	Formula
Na-P1	$Na_6Al_6Si_{10}O_{32} \cdot 12\ H_2O$
analcime	$NaAlSi_2O_6 \cdot H_2O$
sodalite	$Na_4Al_3Si_3O_{12}\ Cl$
hydroksy-sodalite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}\ .1,8\ H_2O$
chabazite	$Ca_2Al_4Si_8O_{24} \cdot 12H_2O$
zeolite X	$Na_2Al_2Si_{2.5}O_{9.6} \cdot 2H_2O$
zeolite Y	$Na_2Al_2Si_{4.5}O_{13} \cdot XH_2O$
phillipsite	$K_2Al_2Si_4O_{12} \cdot XH_2O$
gmelinite	$Na_2Al_2Si_4O_{12} \cdot 6H_2O$

- **The use of coal fly ash as a silica and aluminum source for the preparation of mesoporous materials is a new approach and has not been explored in detail**

MESOPOROUS MOLECULAR SIEVES

- **orderly-structured materials containing mesopores of identical size (2-10 nm)**
- **composites of organic (surfactant) and inorganic (silicate) species. After calcination the organic part is burned out and the remaining porous materials contain periodic pores.**
- **synthesized through a hydrothermal reaction of silicate gel in the presence of a surfactant**
- **for the synthesis of mesoporous materials a source of silicon (fumed silica, sodium silicate, tetraethyl orthosilicate) and/or aluminium and an appropriate surfactant are needed**
- **larger pore size of mesoporous sieves compared with zeolites provides greater possibilities of using these compouds for the adsorption, separation and catalytic coversion of larger molecules than are possible in the case of zeolites.**

MESOPOROUS MATERIALS- MCM-41



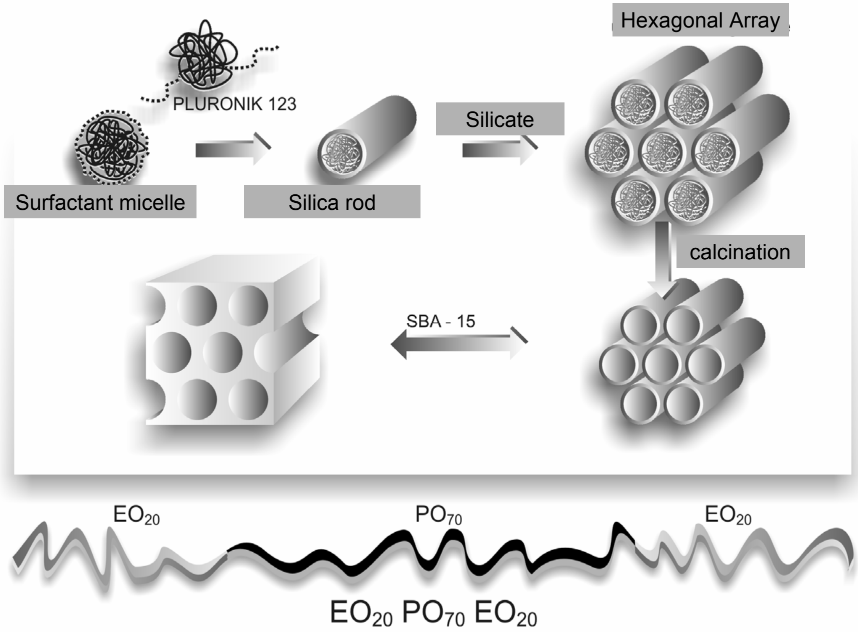
MCM-41

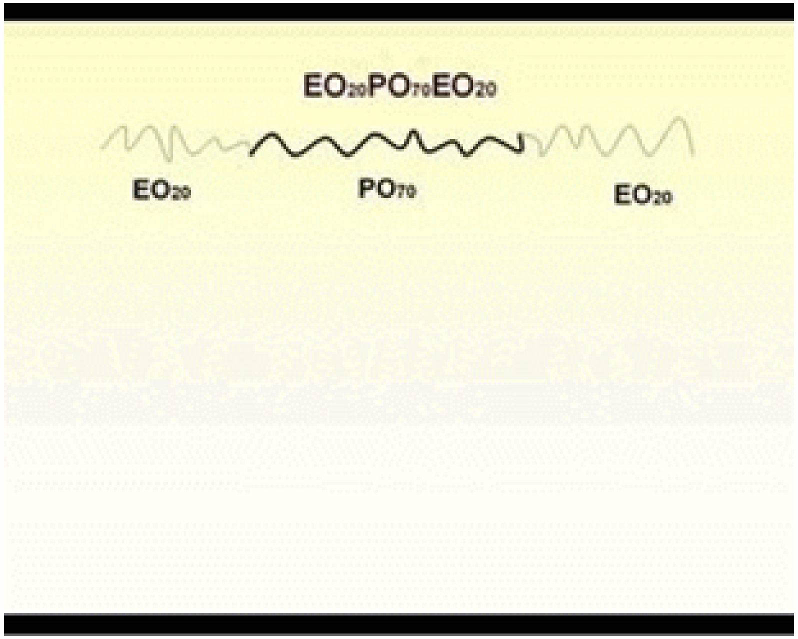
The most popular phase, MCM-41, consists of hexagonally ordered channels having amorphous silica walls (like a honeycomb)

- **Uniform, “tailorable” mesopores**
- **Narrow pore size distribution**
- **High surface area (>700m^2/g)**
- **Large pore volume**
- **High thermal stability**

MESOPOROUS MATERIALS SBA-15

Synthesis scheme for SBA-15 materials





Pluronic 123- a nonionic oligomeric alkyl-ethylene oxide surfactant

Surfactat-(structure-directing agent) has a hydrophilic (water-soluble) headgroup and a hydrophobic (water –insoluble) tail group.

Źródło: http.alpha.che.uc.edu

WHY CFB-FLY ASH ?

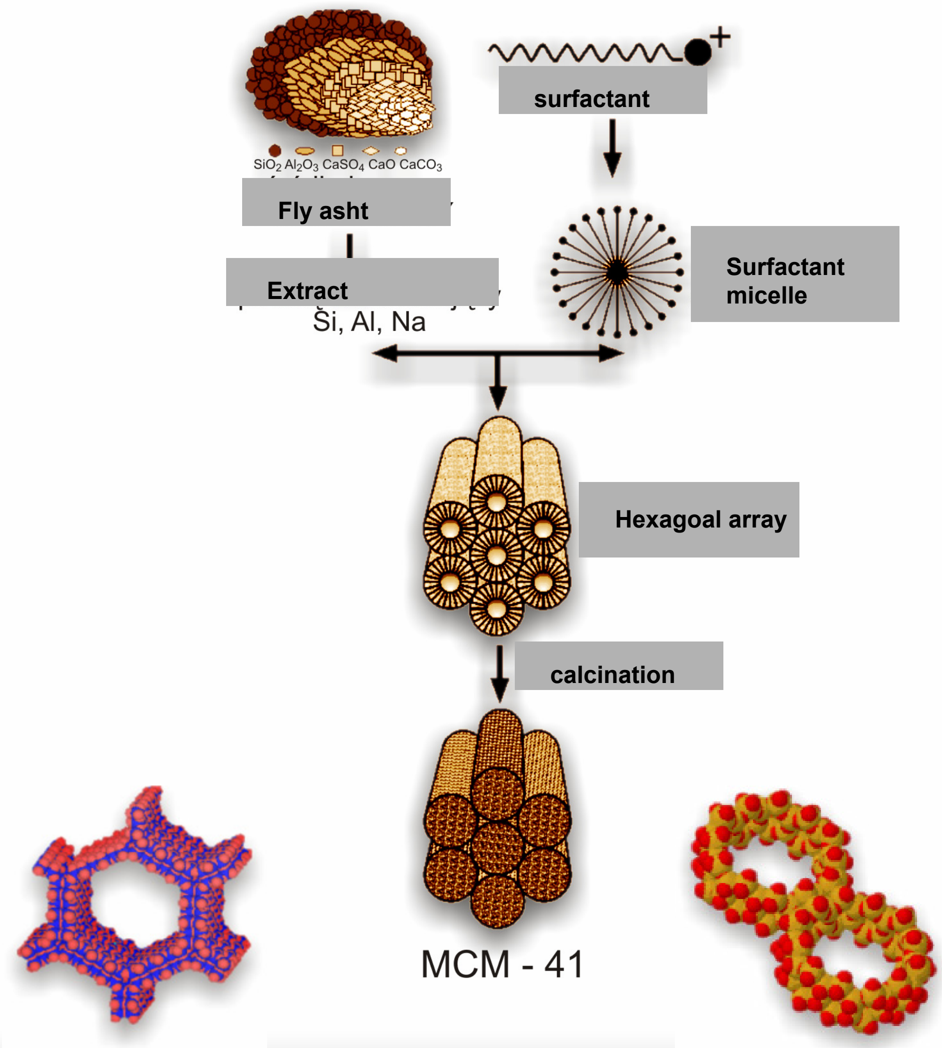
The fact of taking interest in CFB-fly ash as a starting material in the synthesis of mesoporous molecular sieves has undoubtedly had several causes

- **Different sources of Si i Al can be used in the classical synthesis of mesoporous molecular sieves, which indicates that the synthesis of these compounds is not particulary sensitive to the type of those sources**

- **large-scale production of mesoporous materials is limited for both environmental and economic reasons**

- **CFB -fly ash is a cheap and evironmentally-friendly source of silicon and aluminium, and thus an appropriate substrate for the production of mesoporous materials**

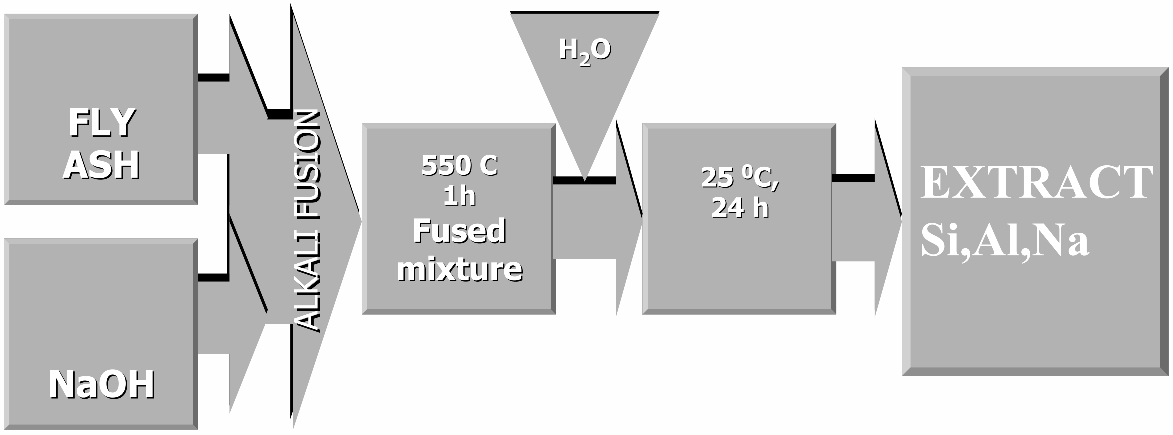
MESOPOROUS MATERIALS FROM CFB-FLY ASH



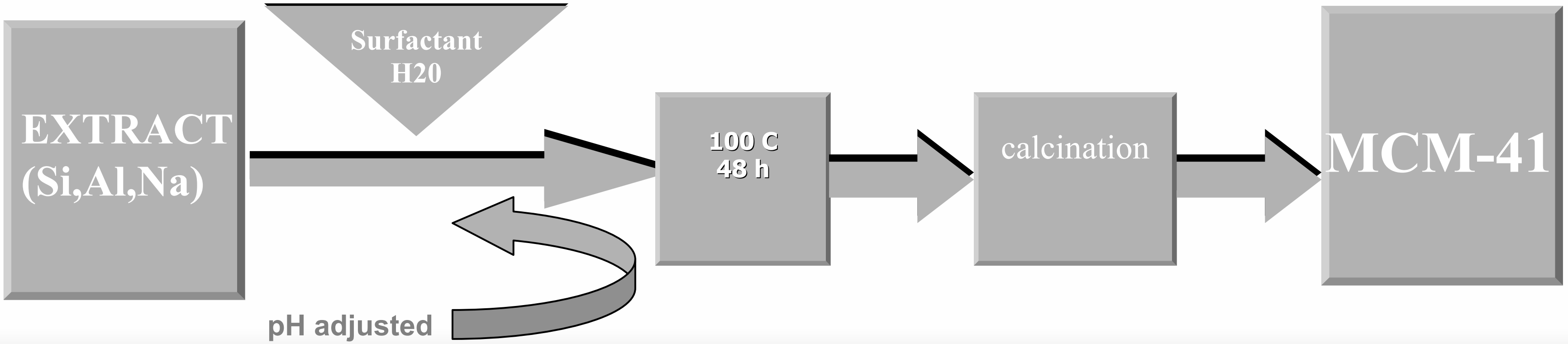
Synthesis scheme for MCM-41 materials

EXPERIMENT
SYNTHESIS OF MCM-41

Extraction of Si from CFB fly ash



Synthesis of MCM-41 on the basis of the obtained extract

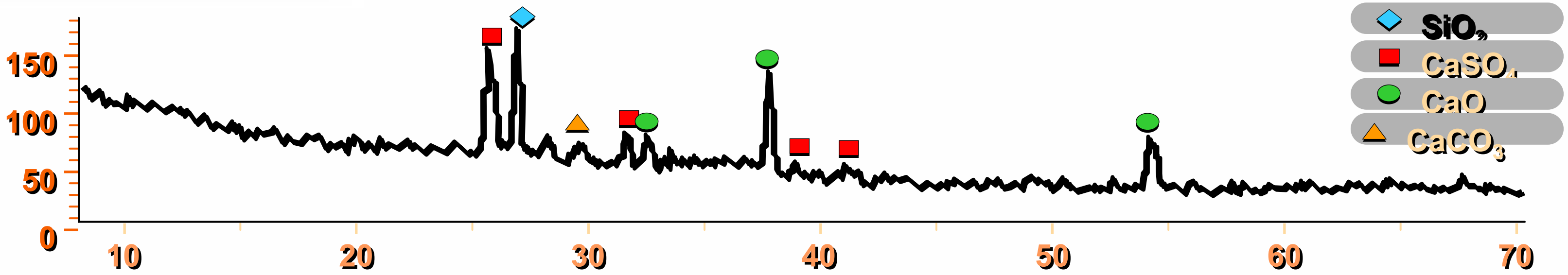


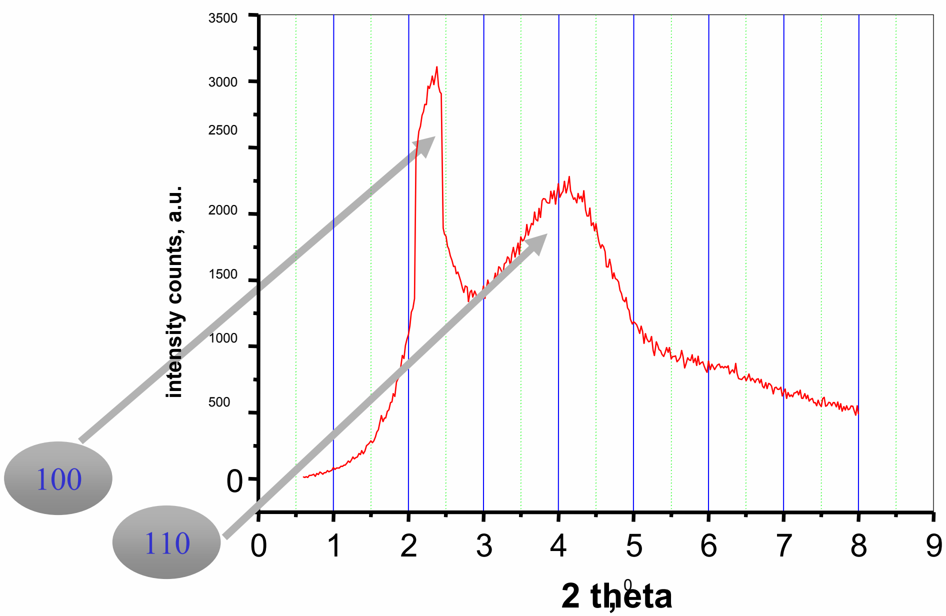
EXPERIMENT

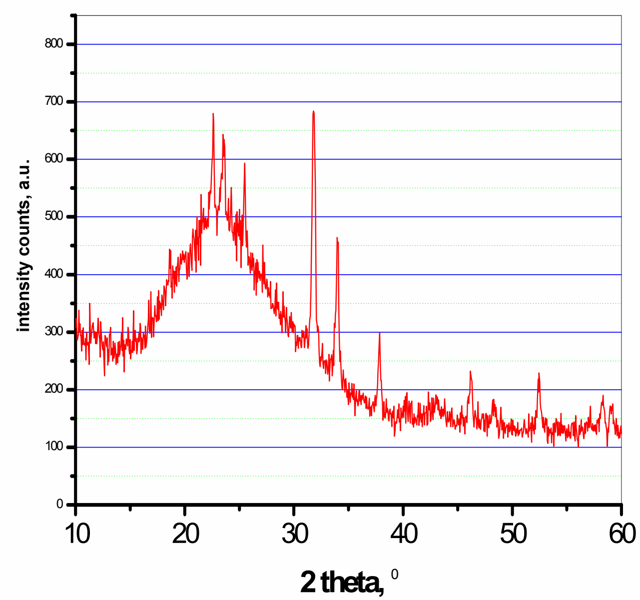
CHARACTERIZATION OF MCM-41

XRD analysis

CFB-FLY ASH







X-ray diffraction patters of the MCM-41 prepared using fly ash as the starting material

Bruker AXS D8 Advance (CuKα λ = 0.154 nm)

EXPERIMENT

CHARACTERIZATION OF MCM-41

- **The formation of the mesoporous structure has also been confirmed by the sorption examination of a synthesized sample, which has enabled the determination of the specific surface, pore size and sorption capacity**

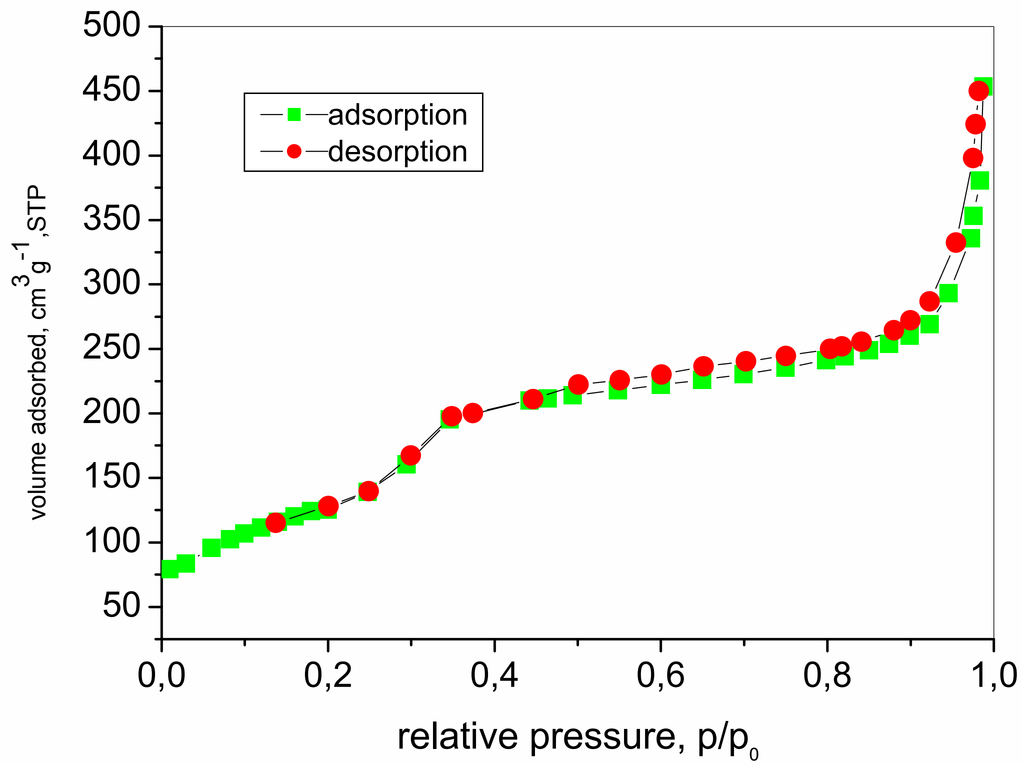
materials	$S_{BET} m^2/g$	Pore volume cm^3/g	Pore diameter, nm
Fly ash	4.26	0.023	21.7
MCM-41 from fly ash	510	0.7	4.25

- **The values of structure parameters, obtained for the fly ash MCM-41 are similar to the results obtainable for the MCM-41 material synthesized from chemically pure Si sources**

EXPERIMENT

CHARACTERIZATION OF MCM-41

N_2 adsorption/desorption isotherms for MCM-41 prepared using fly ash as the starting material



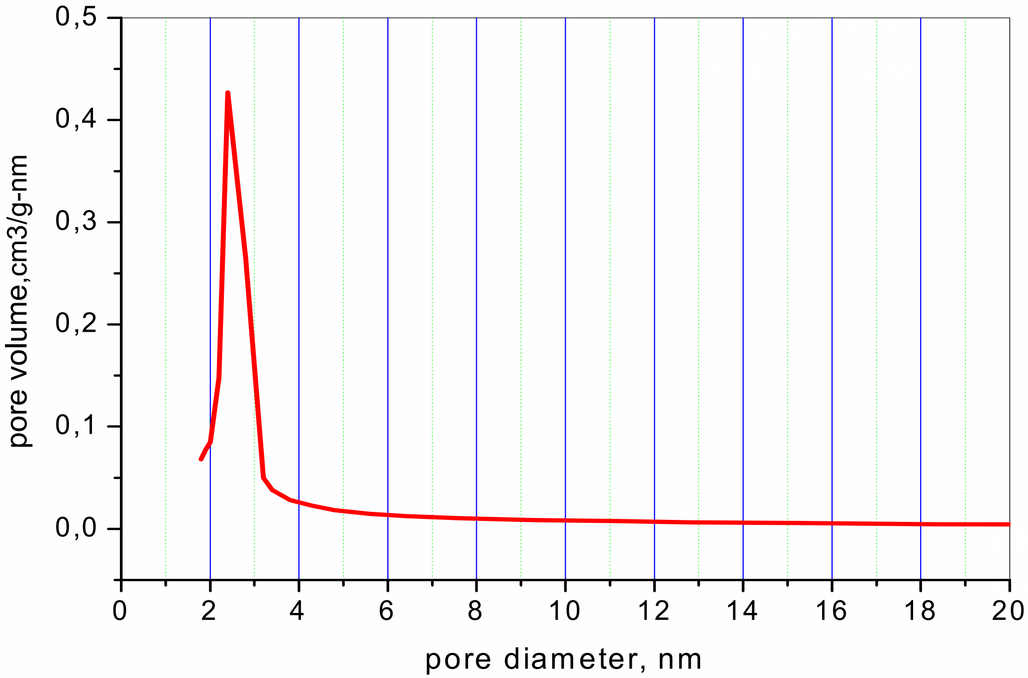
The nitrogen adsorption isotherm is IV type isotherm according to the IUPAC classification with the inflection point at p/p_0 =0.3 which confirms the mesoporous structure of the obtained fly-ash based material

ASAP 2010 Instruments

EXPERIMENT

CHARACTERIZATION OF MCM-41

Pore size distribution of the MCM-41 prepared using fly ash as the starting material



The greatest share of the overall pore (mesopore) volume belongs to pores of a diameter of 2.7 nm

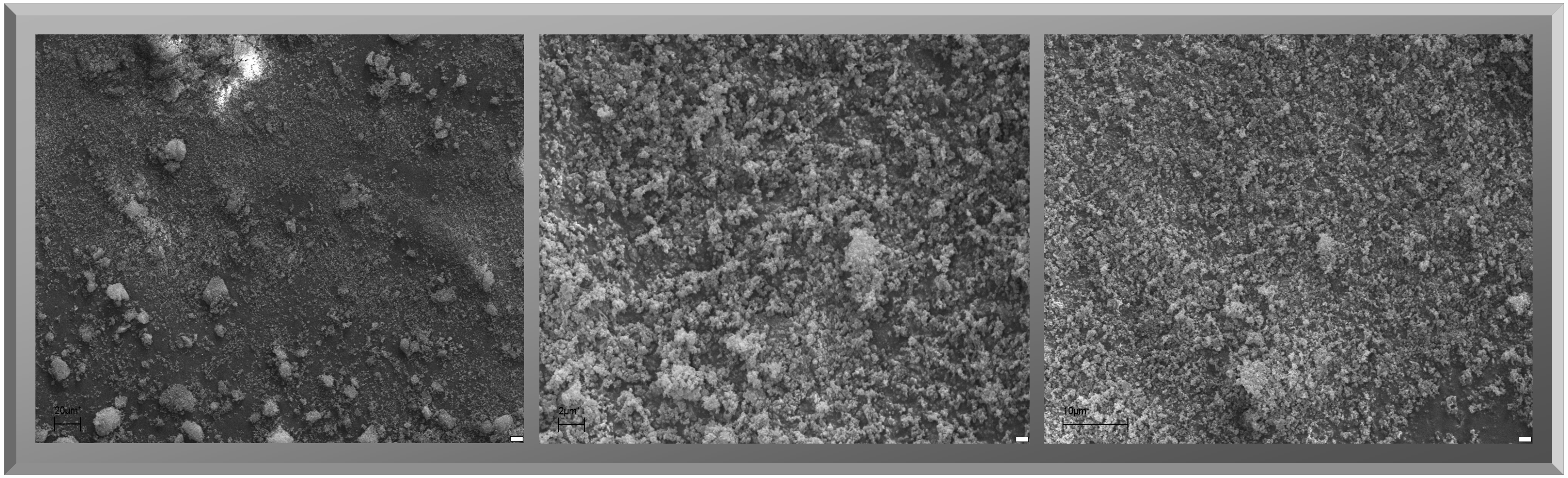
The narrow distribution of mesopore sizes indicates a homogenity of pores

EXPERIMENT

CHARACTERIZATION OF MCM-41

CFB fly ash

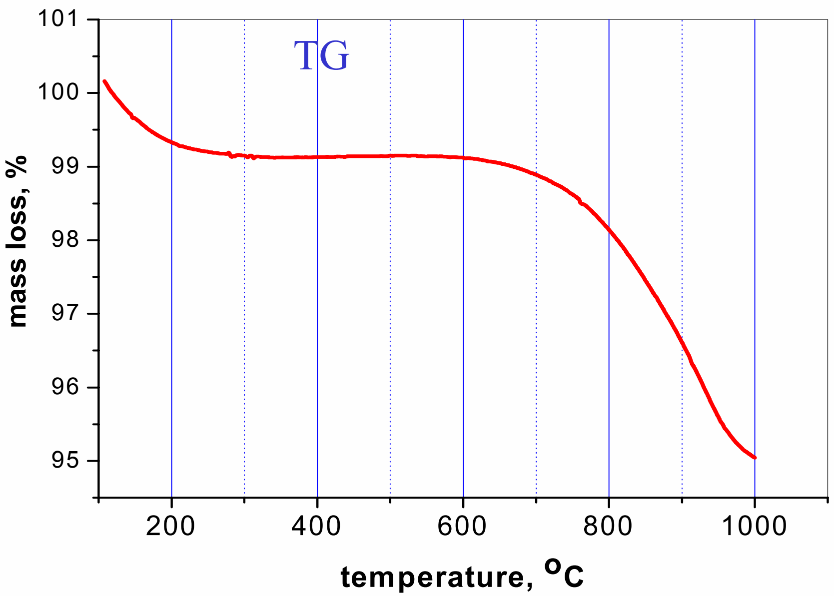
SEM analysis

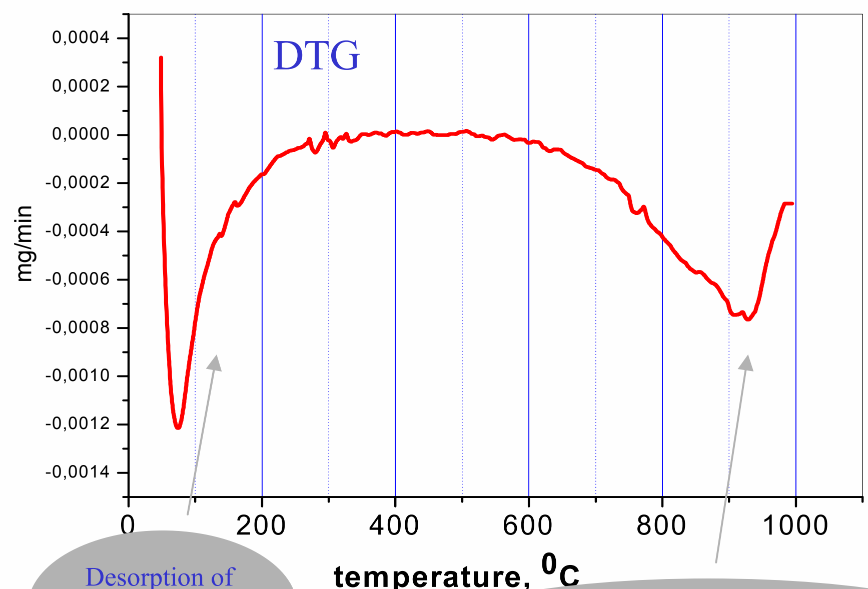


SEM image of calcined MCM-41 prepared using fly ash as the starting material

CHARACTERIZATION OF MCM-41

TG and DTG curves of calcined MCM-41
prepared using fly ash as the starting material





Desorption of adsorbed water 1,5%

Decomposition of organic species -4% and/or fly ash residue

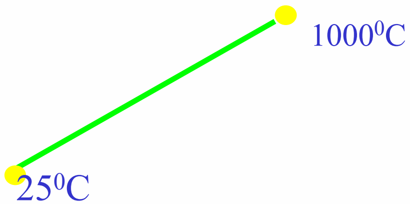
Dynamic test:

Weight::5 mg

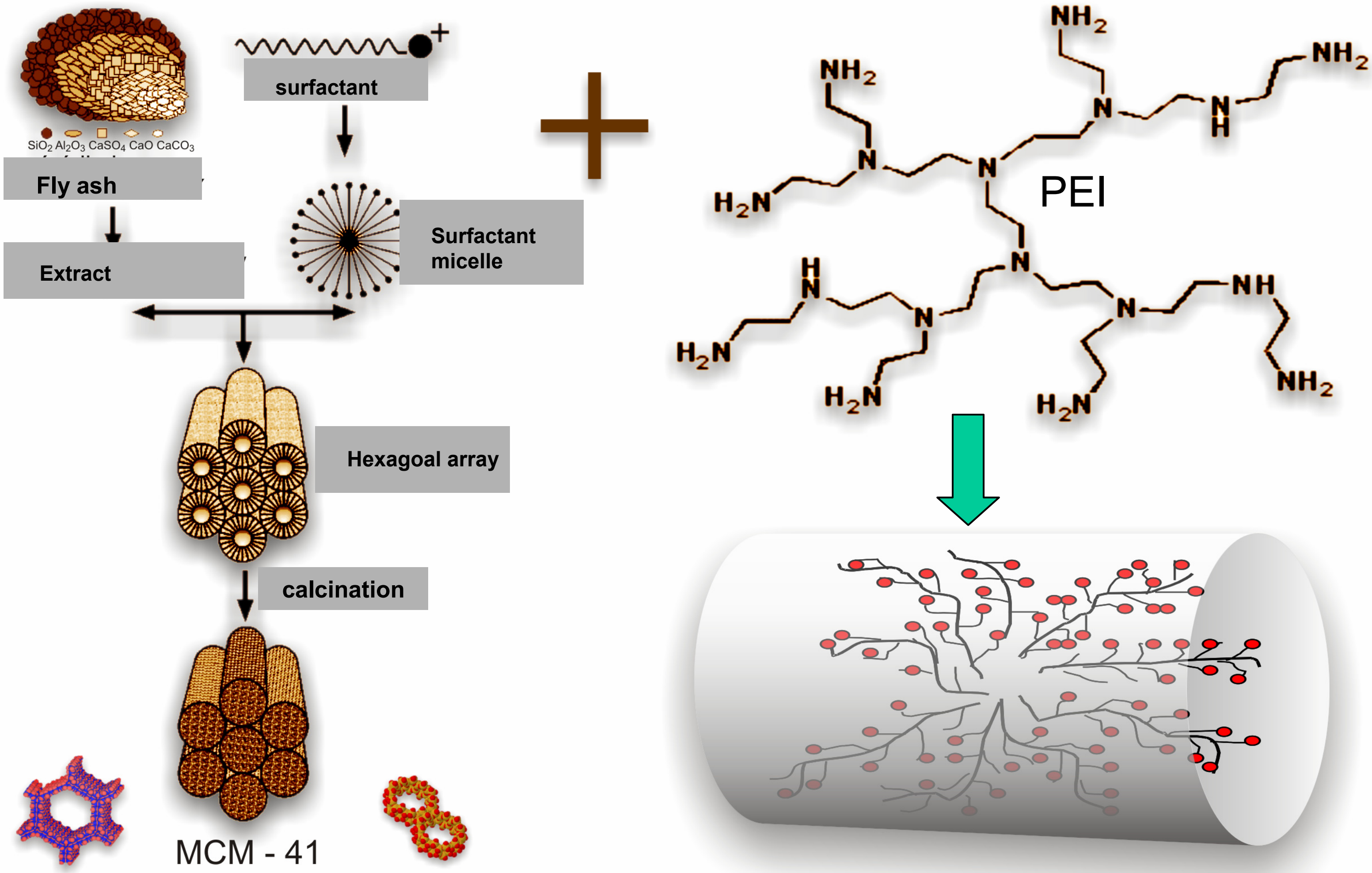
Gas: N2

Heating rate: 20^{0}C/min

Flow rate: 50ml/min



Modified mesoporous materials from fly ash-
-novel sorbents for post-combustion capture of CO2



Modified mesoporous materials (MCM-41) from fly ash

CONCLUSIONS

- **From the investigation carried out it can be concluded that the CFB - fly ash extract is a useful starting substrate for the synthesis of MCM-41 mesoporous materials**

- **The high content of sodium ions in the filtrate obtained from fly ash, proved to be a factor interfering with the formation of the MCM-41 and resulted in the obtained material being admixed with a zeolite. That effect of the Na content can be eliminated by the control of pH during the running of the process**

- **The BET specific surface and volume of pores of the MCM-41 mesoporous material obtained on the basis of fly ash have proved to be slightly lower for samples obtained from more reactive (commercial) silicon sources and indicate high overall porosity of obtained samples, thereby confirming the possibility of obtaining orderly-structured mesoporous materials based on fly ash Si and Al**