# SYNTHESIS AND CHARACTERISATION OF MANGANESE FUNCTIONALIZED SILICA AEROGELS

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*Material characterization*
*graduate study programme*

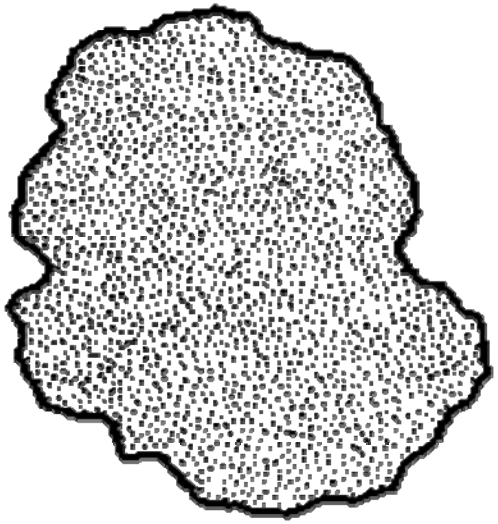
# POROUS MATERIALS

- Porous materials have highly developed internal surface area that can be used to perform specific function

- Almost all solids are porous except for ceramics fired at extremely high temperatures

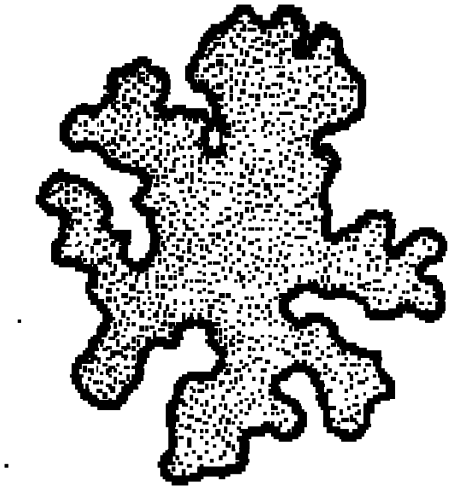
## Non-porous solid

- Low specific surface area
- Low specific pore volume

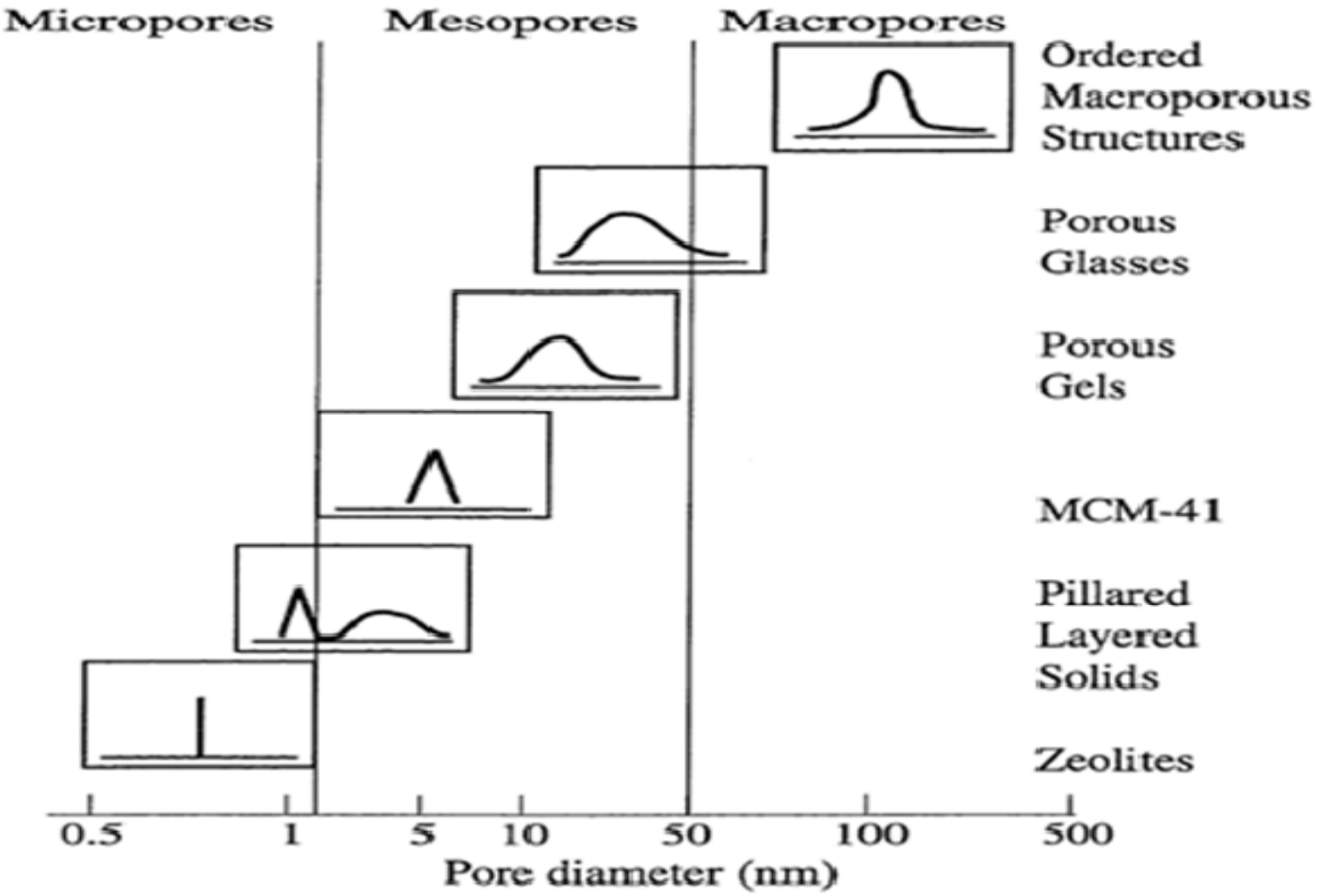


## Porous solid

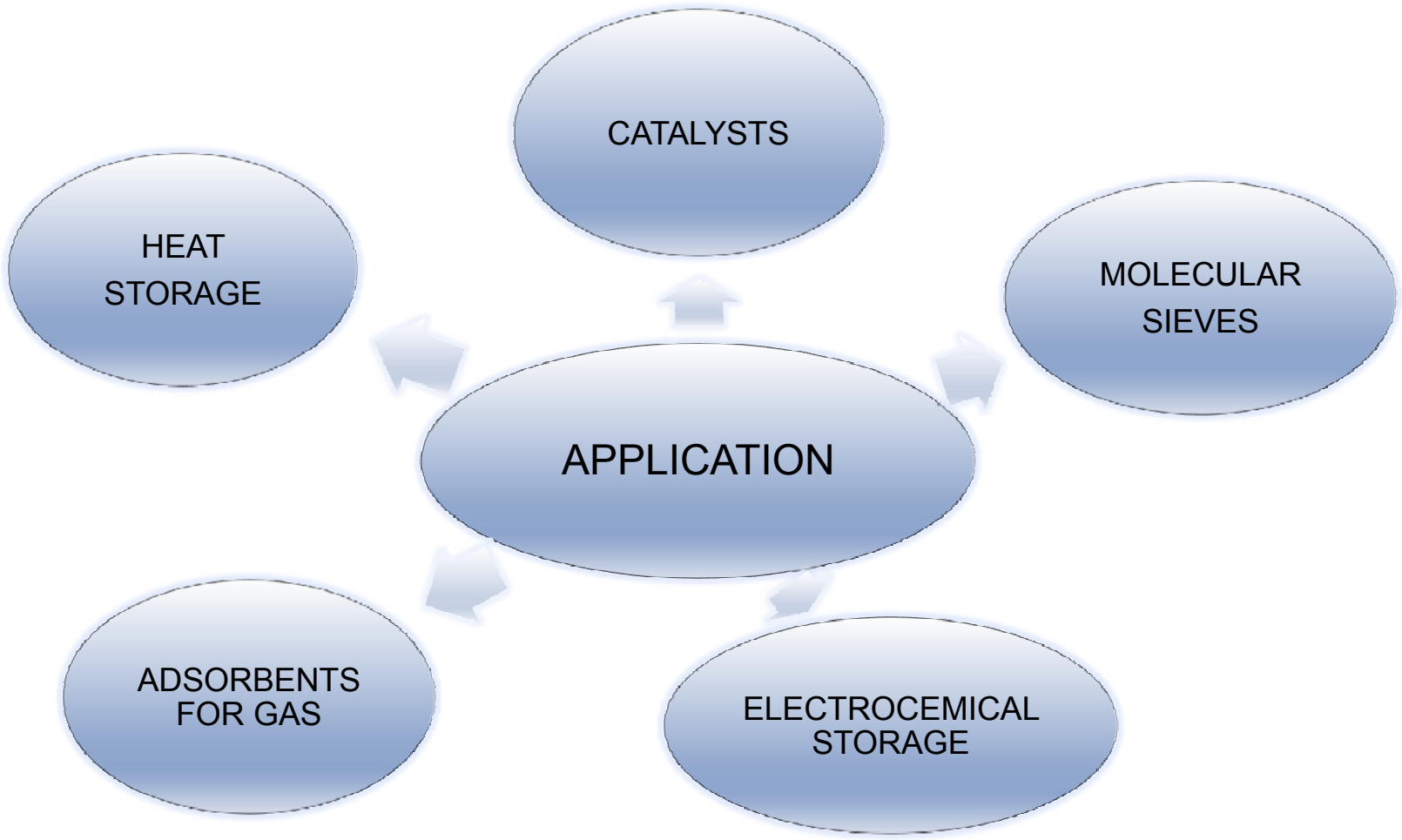
- High specific surface area
- High specific pore volume



**Porous material are classified according to the size of pores: material with pores less than 2 nm are called micropores, materials with pores between 2 and 50 nm are called mesopores, and material with pores greater than 50 nm are macrospores**



# APPLICATION OF POROUS MATERIALS



# SOL-GEL SYNTHESIS

- **The sol-gel process** is a wet-chemical technique used for preparation of versatile materials at lower temperatures.
- **Typical materials** prepared with classical sol-gel are pure or multicomponent metal oxides or related hybrid inorganic-organic materials. Most typical precursors are metal alkoxides ($M(OR)_x$).
- The sol-gel method is based on the hydrolysis and condensation reactions which leads to formation of the extended 3D network (gel) by forming the **-M-O-M-** links

hydrolysis


(1)

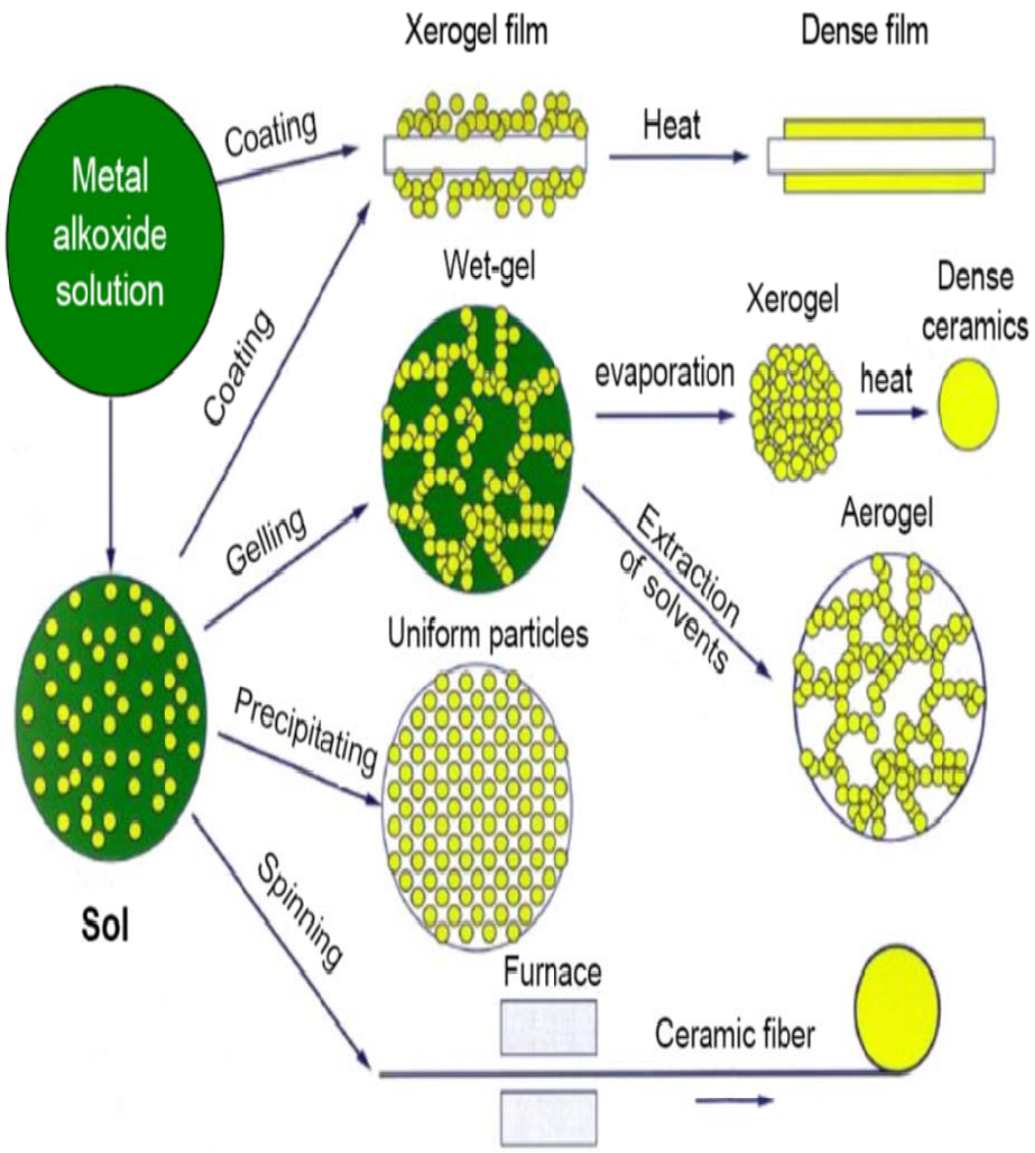
condensation reaction


(2)

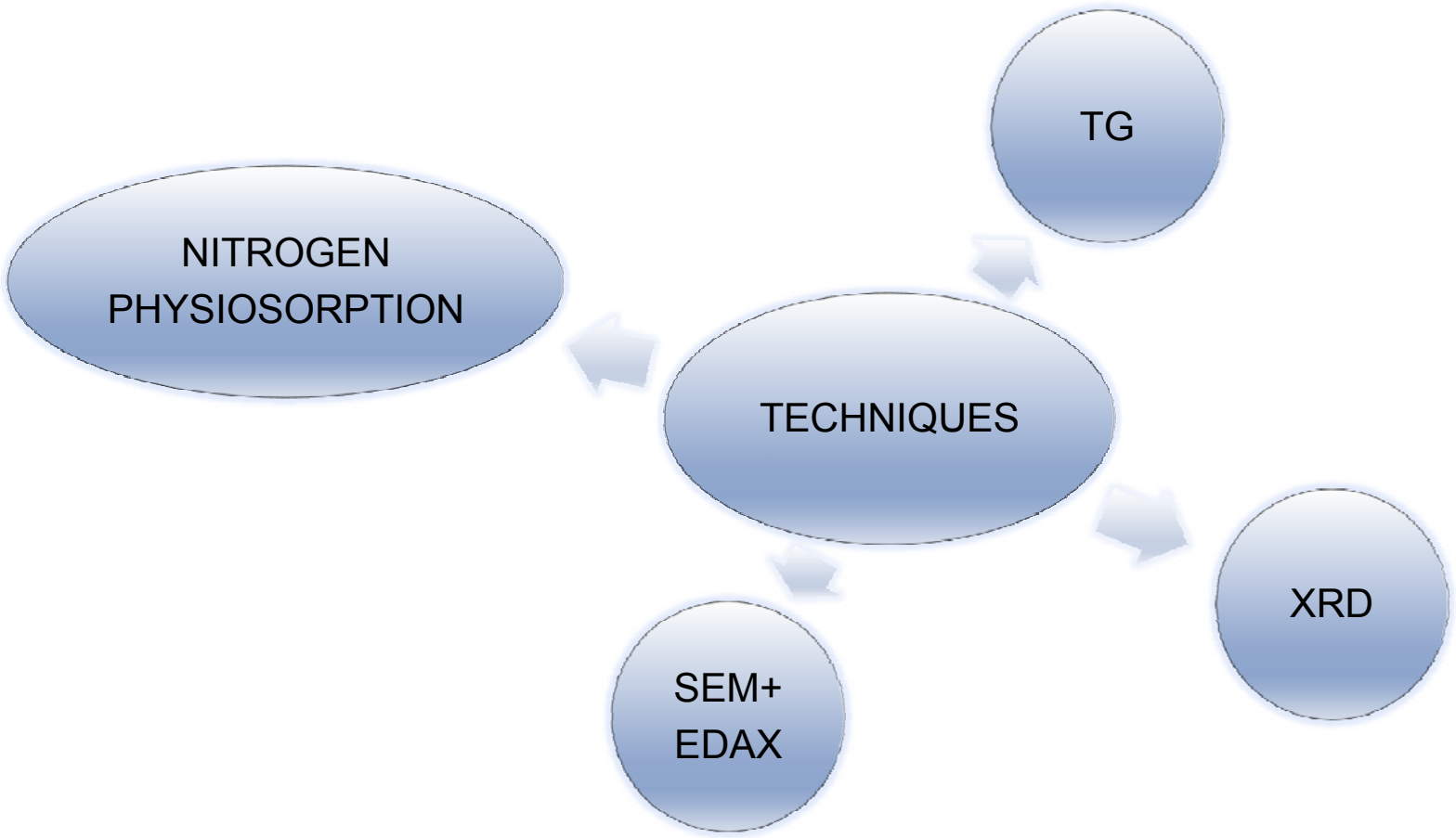

(3)

- Preparation of materials in a wide **variety of forms:**
  - ultra-fine powders
  - fibers
  - solids
  - xerogels
  - aerogels
  - thin films
  - bulk materials

- The technique is **cheap** and materials are prepared at **relatively low** or even ambient temperatures.



# BASIC CHARATERIZATION



# RECENT RESEARCH

- Porous silicates are used as catalytic supports in chemical reactions
- Manganese is one of the most intensively used elements in homogeneous oxidation catalysis
- It was shown recently that manganese-functionalized porous silicate catalyst (named **KIL**-2, synthesised at **K**emijski **I**nštitut **L**jubljana) is a highly promising heterogeneous catalytic system in catalytic water cleaning

  N.N.Tušar, A.Ristić, G.Mali, M.Mazaj, I.Arčon, D.Arčon, V.Kaučič, N.Z. Logar, *Chem.Eur.J*., **2010**, 16, 5783-5793
- However, MnKIL-2 is not recycable, because of the manganese leaching from the silicate support.
- The problem could be solved using aerogels as silicate supports for manganese.

# CASE STUDY FOR SYNTHESIS of manganese functionalized porous silicate MnKIL-2

## REACTION GEL IN ALCALINE CONDITIONS

1 TEOS : 0,5 TEA : 0,1 TEAOH : 11 $H_2O$


solvothermal treatment
ethanol

first step

second step

thermal treatment

calcination at 500 $^oC$ in the air flow

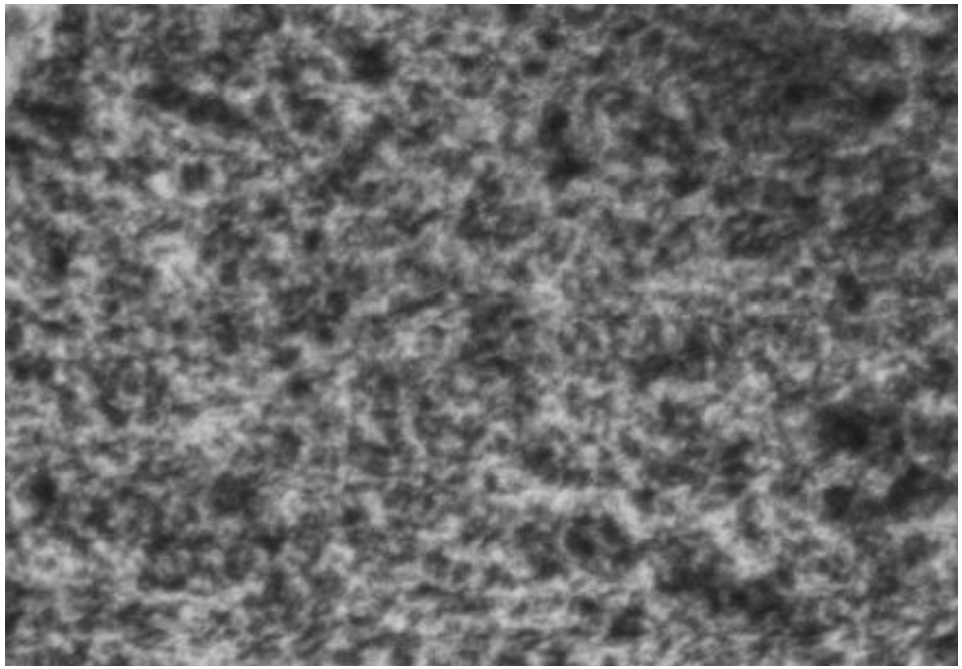
# CASE STUDY FOR CHARACTERIZATION of manganese functionalized porous silicate MnKIL-2

- Basic structure characterization:

XRD, SEM and nitrogen physisorption

- Characterization of local enviranment of manganese are: XAS (EXAFS, XANES).

# SCANNING ELECTRON MICROSCOPE (SEM)



SEM micrograph suggests that the main type of porosity in the sample is the so-called interparticle mesoporosity

**Figure 1.** SEM micrograph of the template-free Mn/KIL-2.

# X-RAY POWDER DIFFRACTION (XRD)

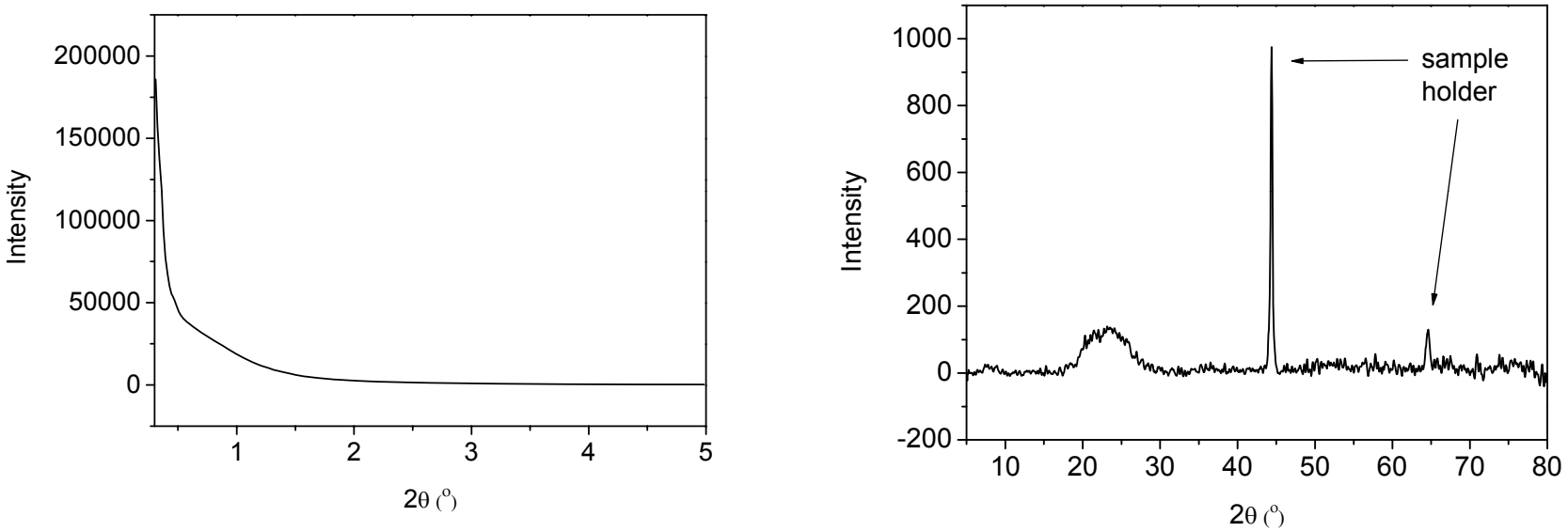



Figure 2: XRD patterns of the template-free sample of Mn/KIL-2: a) the left figure shown: at low angles in the 2θ range from 0.3° to 5° and right figure at high angles in the 2θ range from 5° to 80°.

# NITROGEN PHYSISORPTION

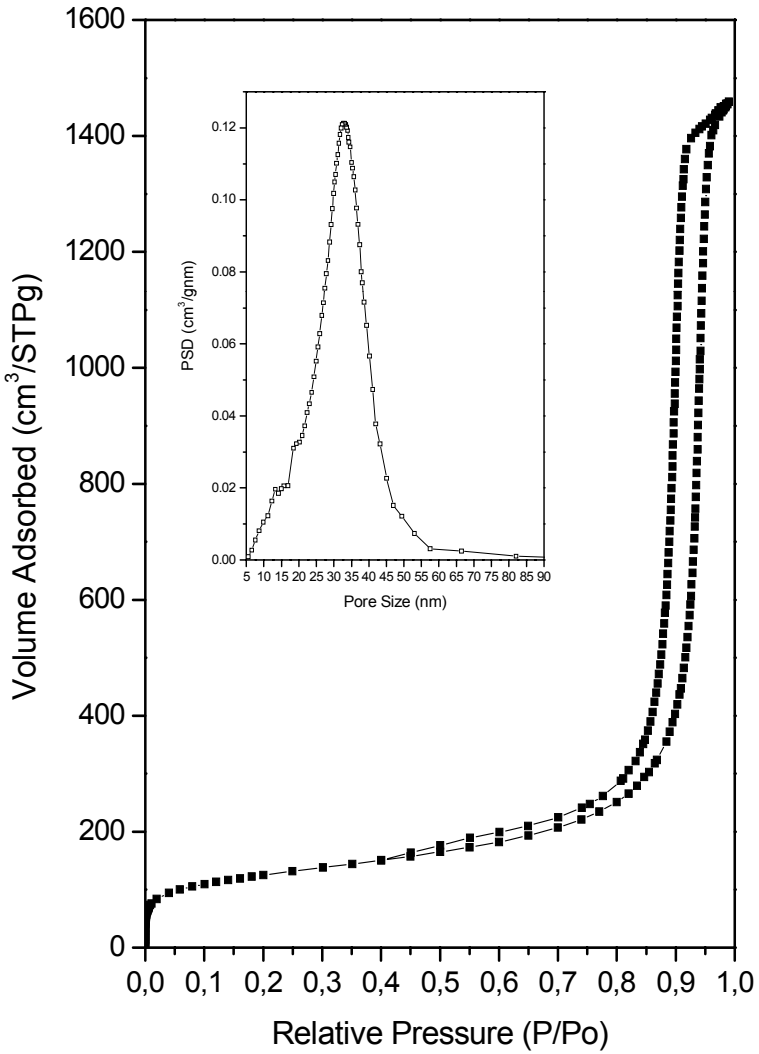



Figure 3. Nitrogen sorption isotherm with pore size distribution curve (Inset) of Mn/KIL-2.

# AEROGELS
# HYSTORY

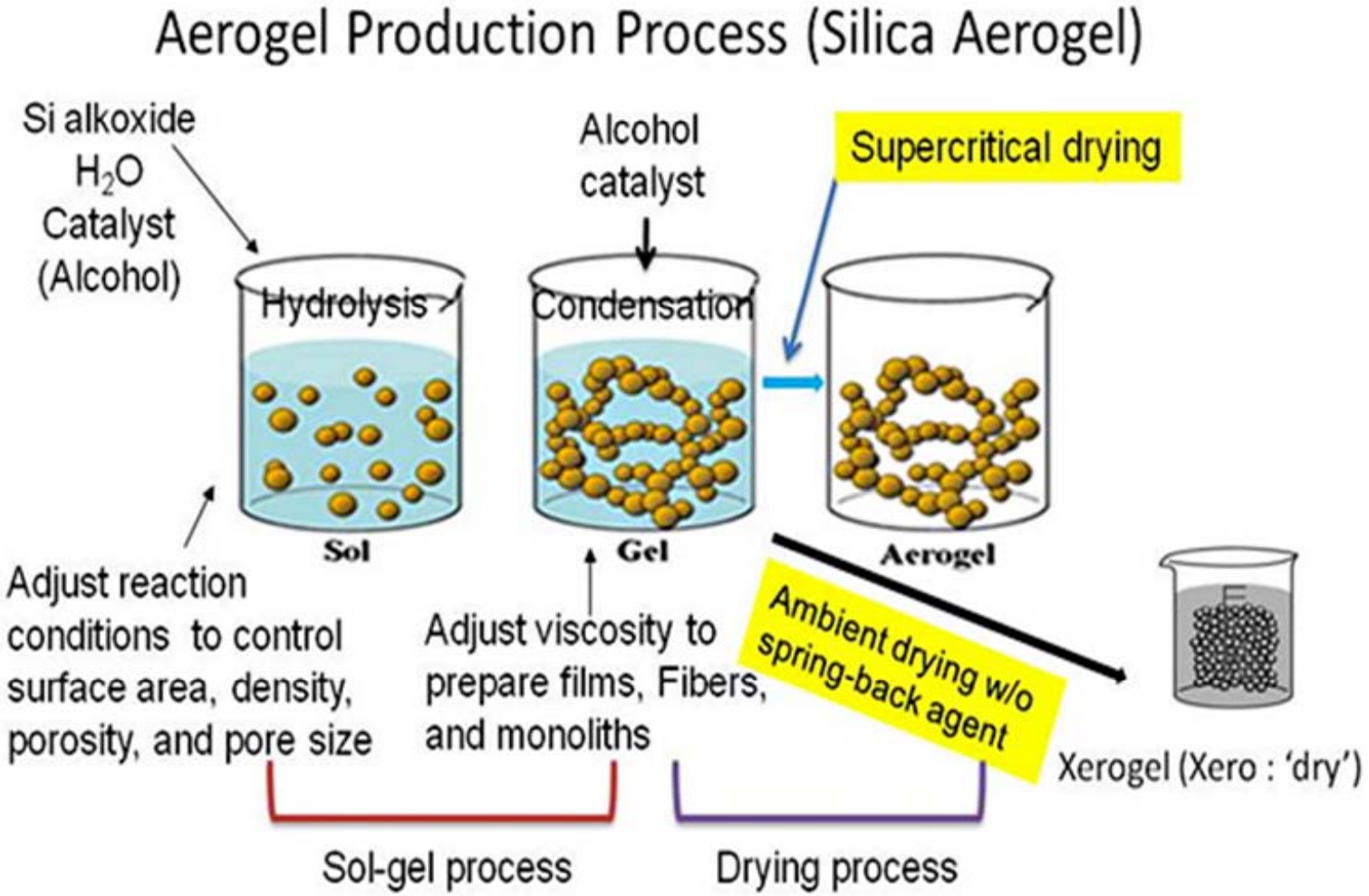
- Steven S. Kistler prepare aerogels in 1931

- In the 70th years of the previous century, it was used for storing oxygen and rocket fuel

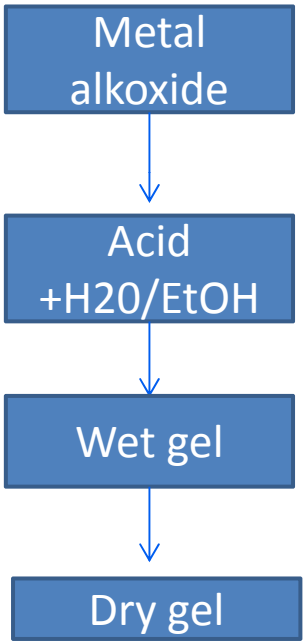
# PROPERTIES

- extremely high porosity
- large area of
- low density
- high optical conductivity
- low thermal conductivity
- low dielectric constant

# SYNTHESIS


Aerogel Production Process (Silica Aerogel)
Si alkoxide
$H_2O$
Catalyst
(Alcohol)
Alcohol
catalyst
Supercritical drying
Hydrolysis
Condensation
Sol
Gel
Aerogel
Adjust reaction conditions to control surface area, density, porosity, and pore size
Adjust viscosity to prepare films, Fibers, and monoliths
Ambient drying w/o spring-back agent
Xerogel (Xero : 'dry')
Sol-gel process
Drying process

- Mn functionalized Aerogel prepared by the sol-gel synthesis



# CHARACTERIZATION

- Basic structure characterization are: XRD,SEM and nitrogen physiosorption

- Characterization of local environment of manganese are: TEM, EPR

# ACKNOWLEDGEMENTS

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