Novel sustainable and high-performance catalysts for hydrogen fuel cells

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Aim

To develop a new composite material consisting of a *geopolymer substrate* with incorporated *transition* or *platinum group* metals, as a potential *low-cost* ***solid electrolyte*** for application in ***solid oxide fuel cells*** that operate in intermediate temperature (***IT-SOFC***).

Outline

- Intermediate-temperature Solid Oxide Fuel Cells
- Geopolymers and Geopolymerization technology
- Development of geopolymer catalysts – characterization of materials
  - Synthesis of the geopolymeric catalytic support
  - Incorporation of active metal (Cu, Ni, Co, Pd)
  - Doping with CeO_2
- Catalytic performance of Geo-catalysts on redox reactions
- Conclusions

IT-Solid Oxide Fuel Cells

Important advantages of SOFC:

- high efficiency
- long-term stability
- low emissions
- relatively low cost

Deficiency: high operating temperature of approx. 1000 °C

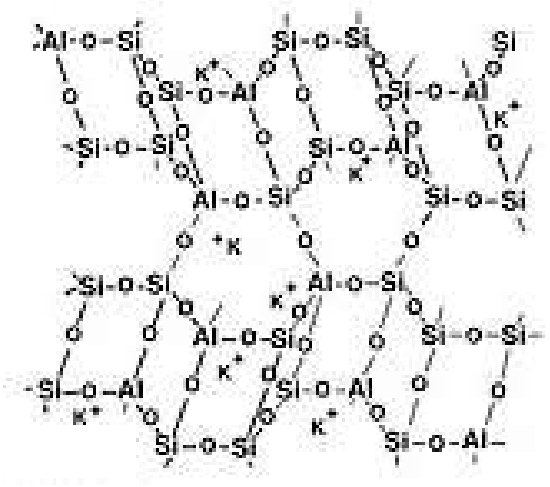
- long start-up/shutdown times
- thermal stress
- material degradation

To achieve a satisfactory performance at reduced operating temperatures:

- solid electrolytes
- high efficiency and conductivity
- Operation to temperatures 500 - 700 °C

- ceramic–matrix composites
- multidoped calcium phosphate
- alumina/YAG
- aluminosilicates / geopolymers

What are Geopolymers?



Structure of geopolymers

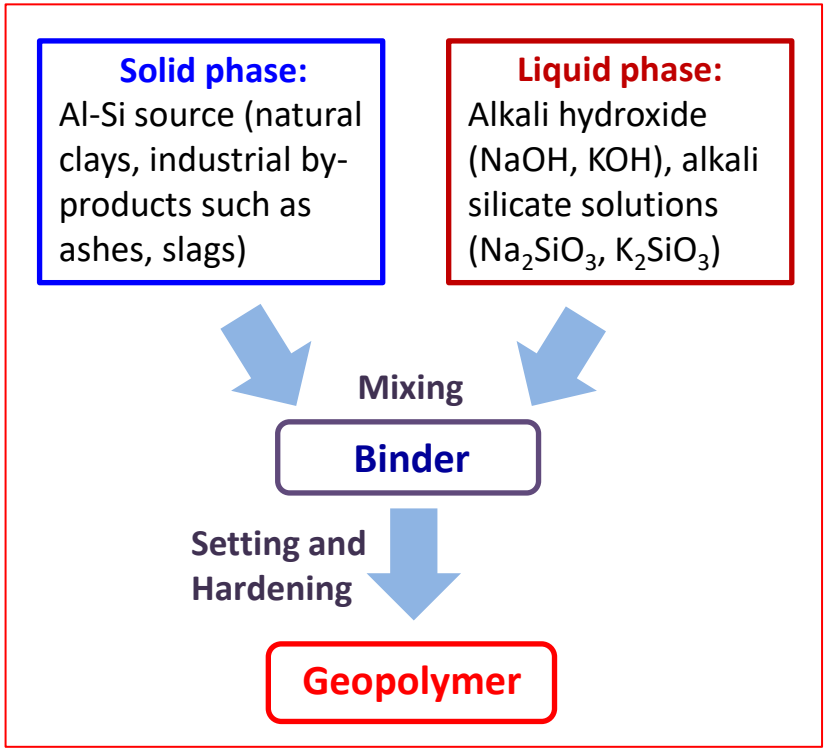
"Geopolymers" are synthetic materials produced by the alkali activation of **inorganic solid materials rich in Al and Si phases** (poly-condensation process)

The process is known as "geopolymerization"

Geopolymers are amorphous materials, with a three-dimensional aluminosilicate network, consisting of AlO_4 and SiO_4 tetrahedra connected by sharing oxygen atoms. Alkali metals also participate.

Also called as "*inorganic polymers*" and "*alkali-activated aluminosilicates*"

Preparation of Geopolymers



Geopolymerization reaction:

- Dissolution of Si and Al (formation of $Si(OH)_4$ and $Al(OH)^-_4$)
- Formation of oligomers Si-O-Si and Si-O-Al
- Poly-condensation to a 3-D network
- Hardening to a solid structure

Short time reaction / Temperature < 100 °C / Ambient pressure

Advantages of the technology:

- Low cost
- Low environmental footprint (energy demand and CO_2 emissions)

Properties and Field of applications

Properties

- Excellent mechanical strength
- Fire and heat resistance / Freeze-thaw resistance / Acid resistance
- Long-term durability
- Thermal stability / Refractoriness
- Low permeability
- Good adhesion
- Functionalization

Field of applications

- Building and Construction material
- Ceramics, Chemical industry and Metallurgy
- Fire resistant materials
- Waste stabilization and encapsulation of toxic substances
- Wastewater treatment
- Catalysis
- High-technology advanced materials

Development of Geopolymeric catalysts

Step 1

Synthesis of the geopolymer-based catalytic support

Step 2

Loading of the active metal (Cu, Ni, Co, Pd) on Geo-support

Step 3

CeO_2 doping to improve catalytic activity

Process investigation

- Study of the process parameters
- Study of the process kinetics

Evaluation of materials

- ✓ Textural properties, SSA / TPV
- ✓ Thermal stability up to 950 ^{o}C
- ✓ Hydrolytic stability
- ✓ Catalytic performance testing redox reaction: CO and HCs oxidations

Development of Geopolymeric catalysts

(1) Synthesis of the geopolymeric catalytic support

Raw materials
- Metakaolin
- NaOH & Na_2SiO_3 or KOH & K_2SiO_3 solutions

→ **Mixing** (10 min) → **Curing** (70°C/24h) → **Hardening** (ambient / 6d) → **Grinding** (< 45μm)

Synthesis parameters

- Solid to liquid ratio
- Al/Si molar ratio
- Content of alkali in the activator

Evaluation of materials properties

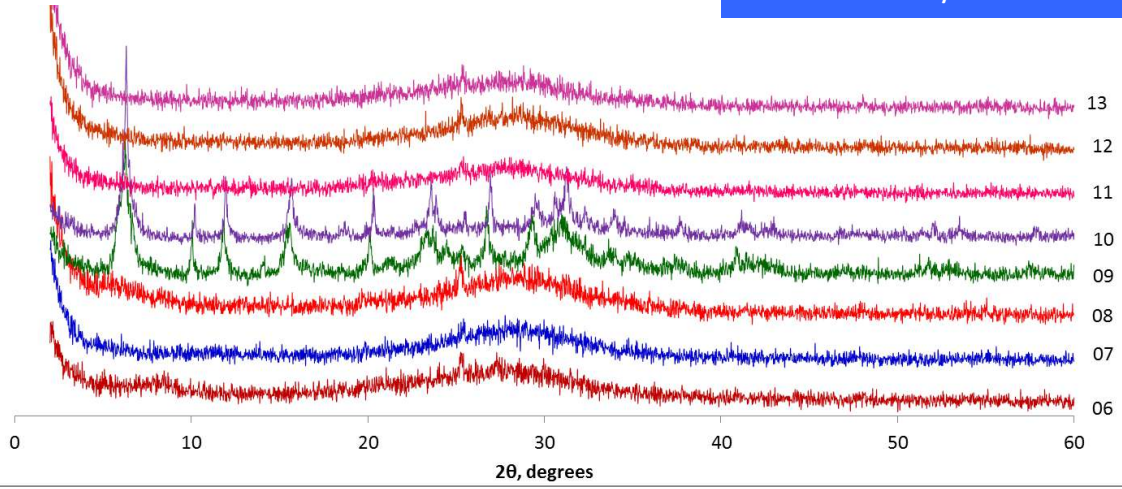
- XRD analysis
- Thermal stability up to 950 °C
- Hydrolytic stability (immersed in D.I. water for 24 h / dissolution of metals)

Development of Geopolymeric catalysts

(1) Synthesis of the geopolymeric catalytic support / Na-based materials

(06)-(08) & (11)-(13): Amorphous / "geopolymer"
(09) & (10): Zeolites

XRD analysis after curing:
70 °C / 24h

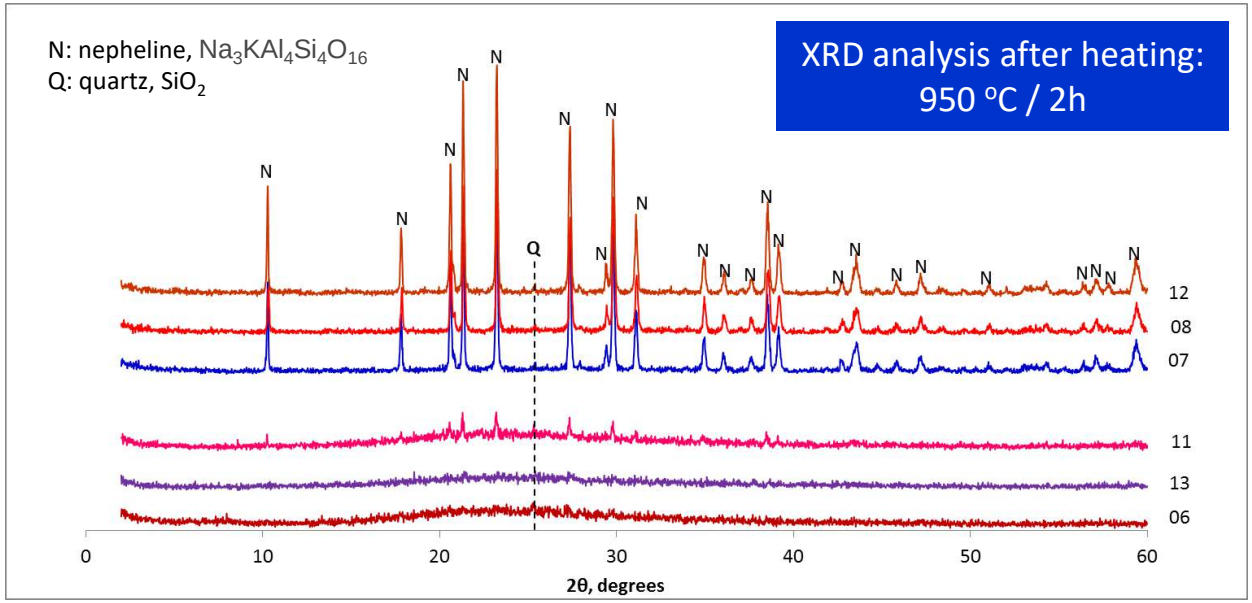


- Most of the tested synthesis conditions resulted in "Geopolymers".

The geopolymeric support based on this material was coded NaG4

Development of Geopolymeric catalysts

(1) Synthesis of the geopolymeric catalytic support / Na-based materials



- Most of the tested synthesis conditions resulted in "Geopolymers".
- Among the prepared materials, only one remained purely XRD-amorphous, after heating at 950 °C / 2h

The geopolymeric support based on this material was coded NaG4

Development of Geopolymeric catalysts

(1) Synthesis of the geopolymeric catalytic support / Na-based materials

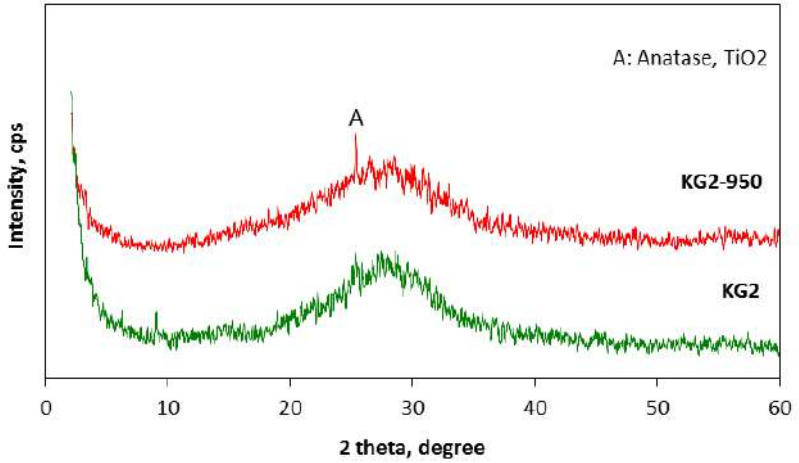
- NaG4 had low SSA and TPV compared to the other materials used in SOFC.
- After heating at 600 °C/4h, SSA and TPV remained unchangeable. However, after heating at 950 °C / 2h, SSA and TPV were significantly reduced.
- Based on the average pore diameter, it concerns for a macro-porous material.
- According to the hydrolytic stability test, Si and Al dissolution was very low (< 1%).

Property	NaG4-PURE	NaG4-600	NaG4-950
SSA, m^2/g	25.7710	23.9320	4.594
TPV, cm^3/g	0.2937	0.2556	0.012
APD, nm	45.6	42.7	-

Development of Geopolymeric catalysts

(1) Synthesis of the geopolymeric catalytic support / K-based materials

- Structural stability after heating up to 950 °C



- Better SSA and TPV than the Na-based materials
- Meso- to micro-porous materials

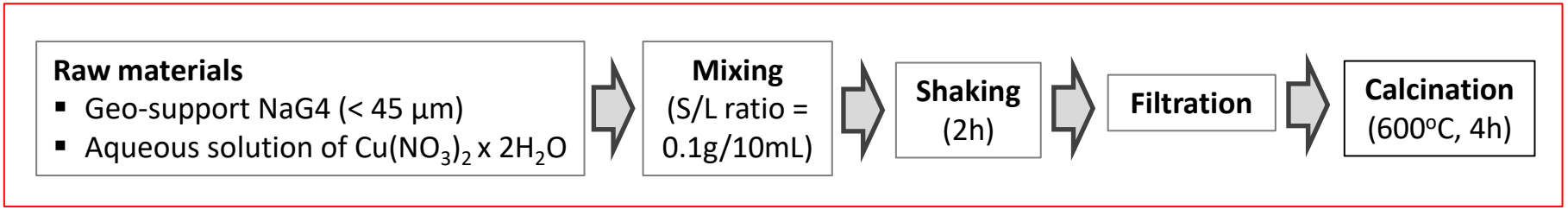
Property	KG2-PURE	KG2-950
SSA, m^2/g	30.593	9.732
TPV, cm^3/g	0.1211	0.0273
APD, nm	8.3577	8.0218

The geopolymeric support selected had the code name KG2

Development of Geopolymeric catalysts

(2a) Incorporation of transition metals (Cu, Ni, Co) as active catalytic phase

The case of copper (Cu)



Synthesis conditions

- [Me] content in the precursor
- Process kinetics

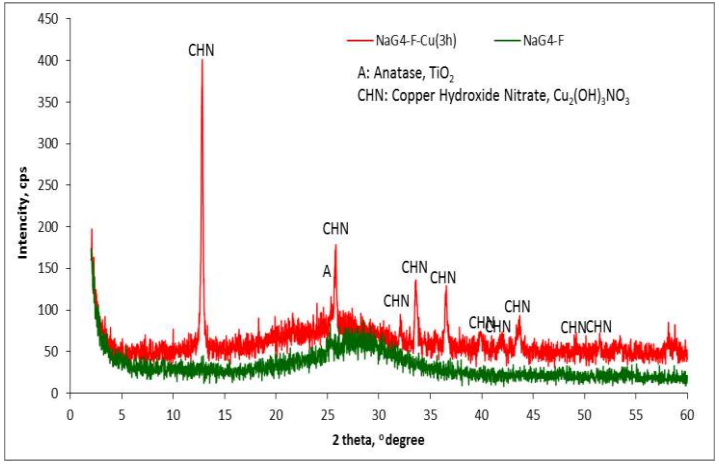
Evaluation of materials

- XRD analysis / SEM & TEM analysis
- Catalytic performance testing (CO and HCs oxidations)

Development of Geopolymeric catalysts

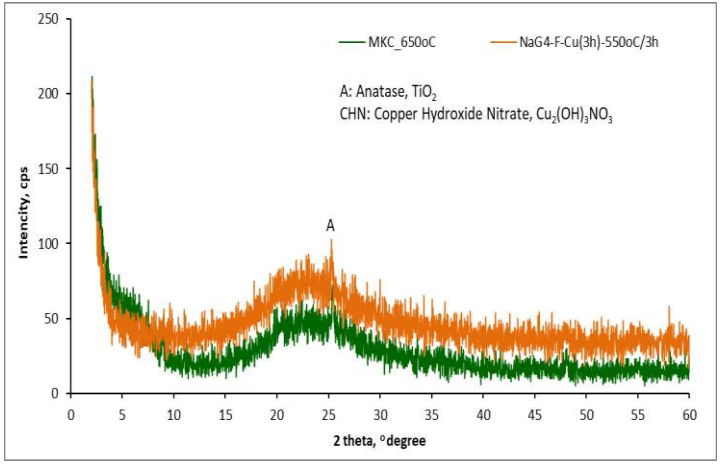
XRD analysis

Before calcination



- Copper is incorporated in geopolymer as a mixed hydroxide-nitrate salt

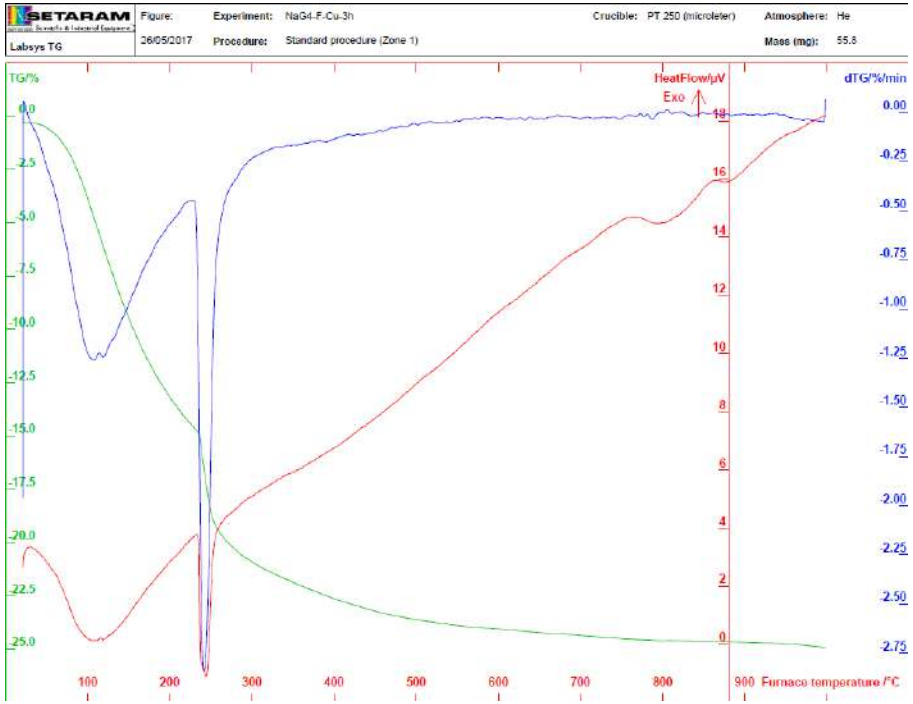
After calcination (600 °C, 4h)



Copper salt is transformed to an XRD-amorphous phase (nano-sized Cu oxide)

Development of Geopolymeric catalysts

TG analysis of NaG4 geopolymer



Thermal decomposition at 230 ^{o}C:

$4Cu_2(OH)_3NO_3 = 8\mathbf{CuO} + 6H_2O + 4NO_2 + O_2$

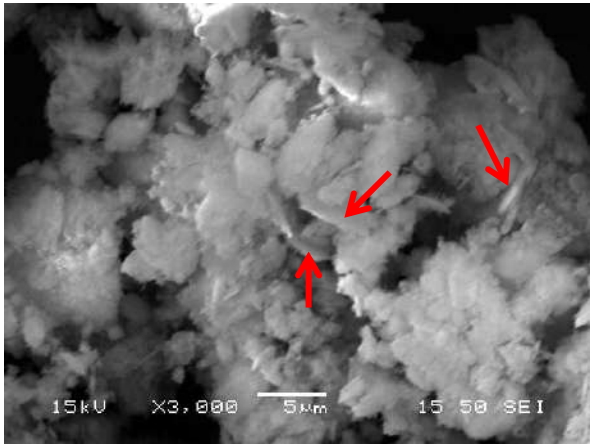
Mass loss (25 – 230 ^{o}C) = 14.5 %

Mass loss (230 – 550 ^{o}C) = 9%

Development of Geopolymeric catalysts

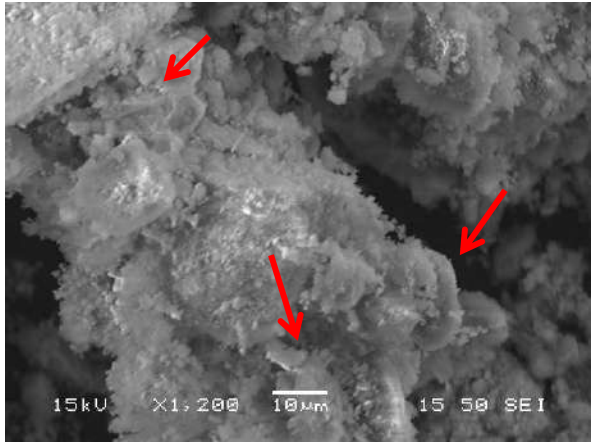
SEM analysis / Elemental analysis (EDS)

Before calcination



Copper salt is surface precipitated forming characteristic “flakes”

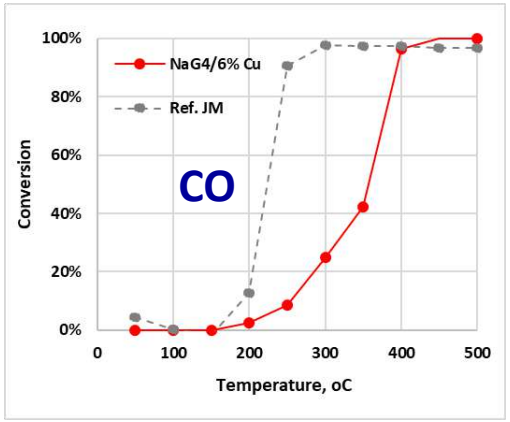
After calcination (600 °C, 4h)

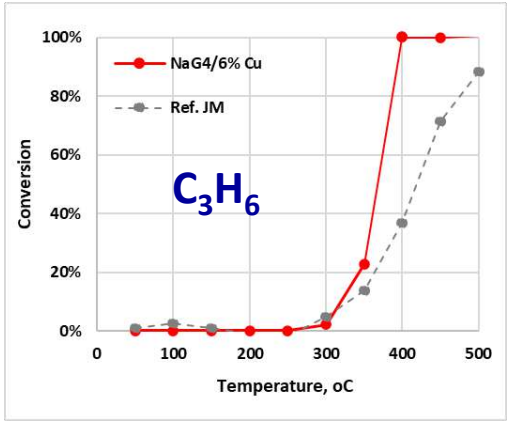


CuO nano-size particles are formed

Development of Geopolymeric catalysts

Catalytic performance testing (6 %wt. of Cu)



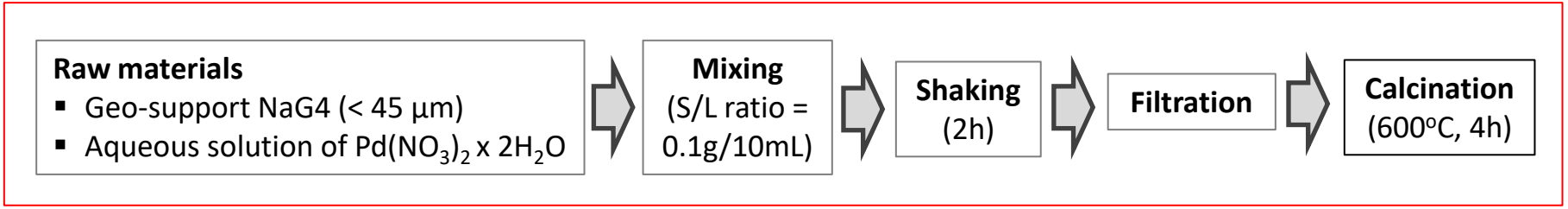


- ***Experimental conditions:***
  200mg of catalyst, feed = 200Nml/min, λ=1 (stoichiometry), GHSV 60000, pre-treatment: 2 h at 500 °C under stoichiometric feed, measurements taken at steady state conditions every 50 °C.
- ***Tested oxidations:***
  The new catalysts were tested against the oxidation of CO, C_3H_8, C_3H_6 and CH_4.
- An automotive catalyst based on ***γ-alumina and Pd/Rh was used as reference***.

- ✓ Oxidation of CO and C_3H_6 in an adequate efficiency
- ✓ No any activity for C_3H_8 and CH_4 oxidation

Development of Geopolymeric catalysts

(2b) Incorporation of PGMs (Pd) as the active phase / catalyst



Synthesis conditions

- Pd content in the precursor
- Process kinetics

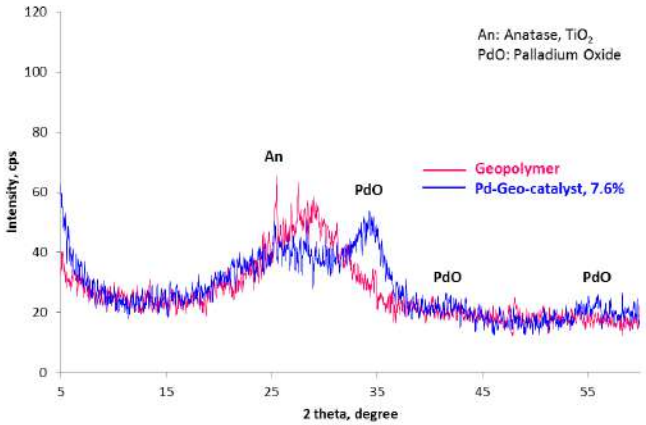
Evaluation of materials

- XRD analysis / SEM & TEM analysis
- Catalytic performance testing (CO and HCs oxidations and NOx reductions)

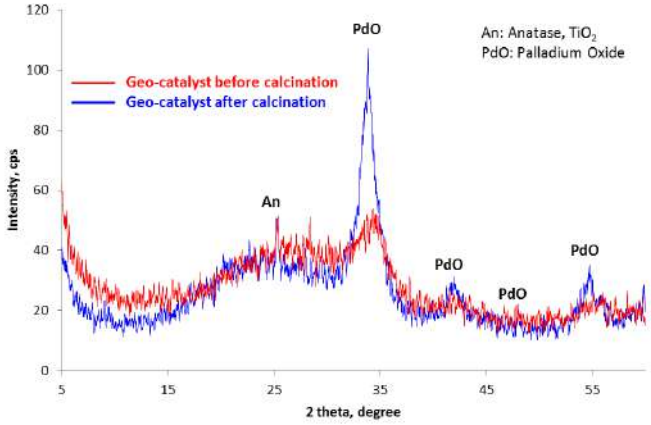
Development of Geopolymeric catalysts

XRD analysis

Before calcination



After calcination (600 °C, 4h)



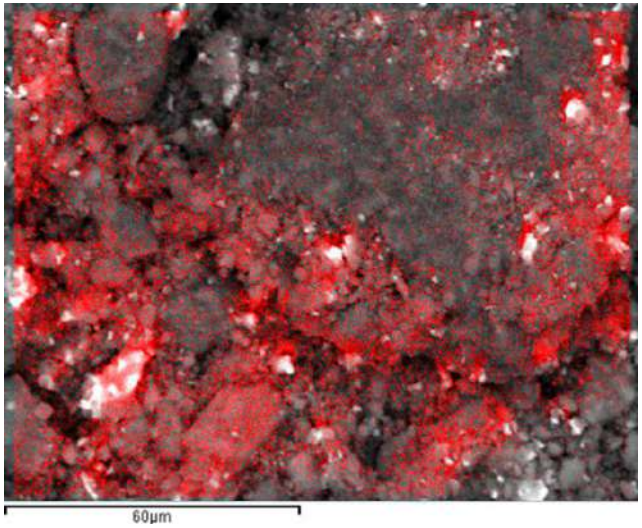
- Pd is incorporated in geopolymer as PdO
- Surface precipitation mechanism resulting in the formation of PdO nano-crystals

The diffraction peaks of PdO became sharper and higher, indicating increase of the size of PdO nano-crystals

Development of Geopolymeric catalysts

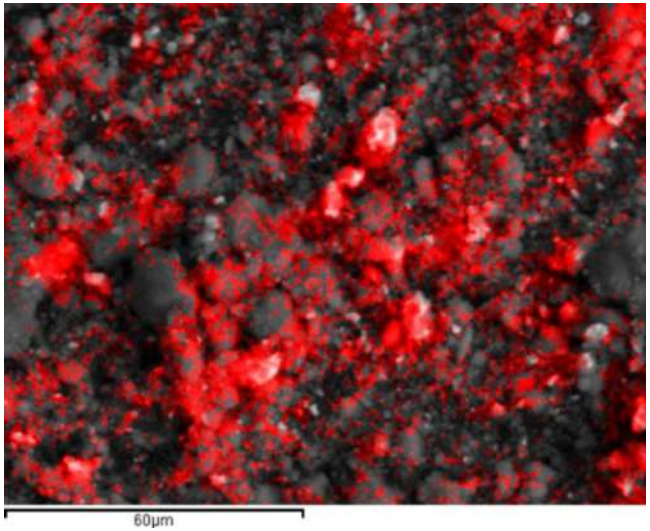
SEM analysis / Elemental mapping

Before calcination



Good dispersion of Pd particles on the whole area of the geopolymeric support

After calcination (600 °C, 4h)

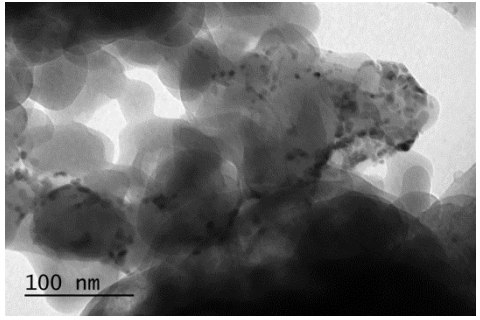


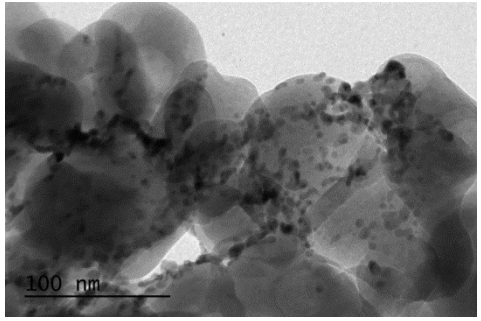
Agglomeration of Pd particles

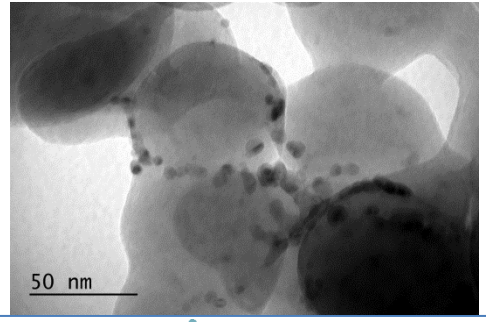
Development of Geopolymeric catalysts

TEM analysis

Before calcination

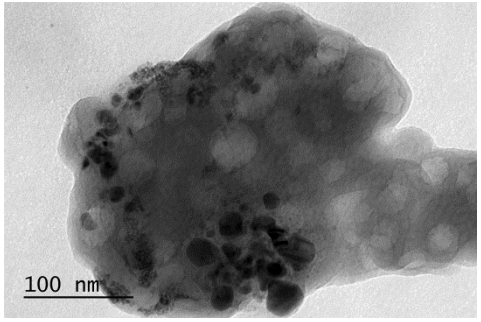


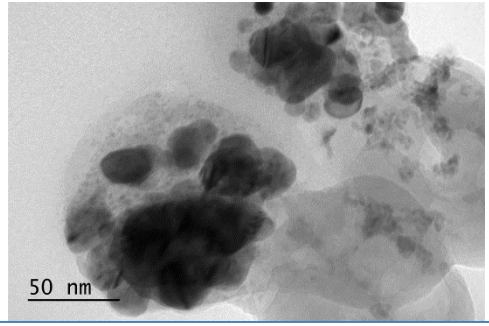




- Nano-size particles of Pd
- Very good dispersion of Pd in the geopolymeric mass

After calcination (600 °C, 4h)

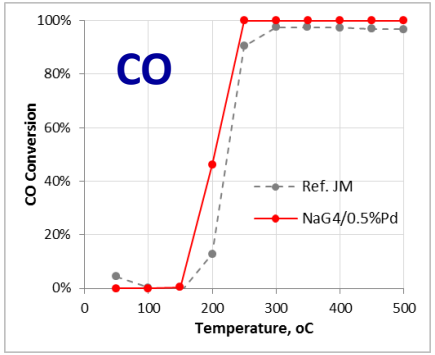


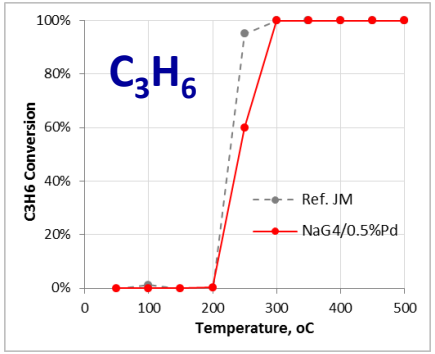


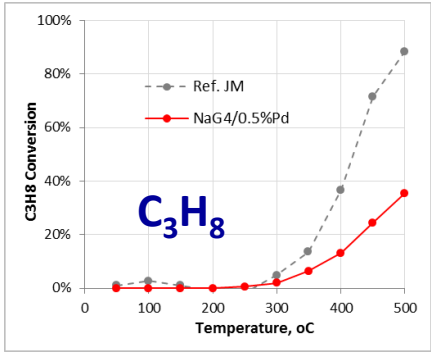
- Pd particles agglomerated

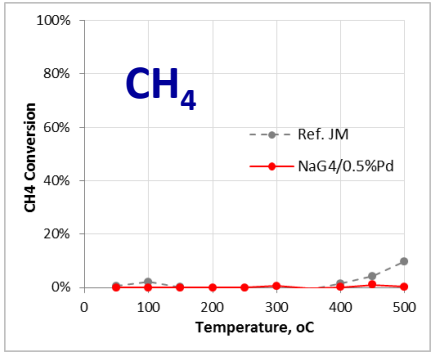
Development of Geopolymeric catalysts

Catalytic performance testing (0.5 %wt. of Pd)







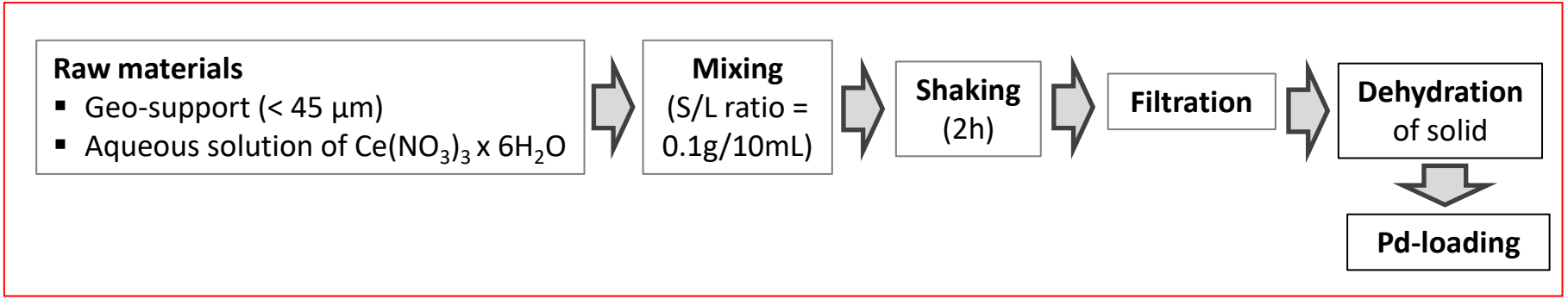


- ✓ Similar or better performance for CO and C_3H_6 oxidations
- ✓ Good performance for C_3H_8 oxidation
- ✓ No any activity for CH_4 oxidation

- ***Experimental conditions:*** 200mg of catalyst, feed = 200Nml/min, λ=1 (stoichiometry), GHSV 60000, pre-treatment: 2 h at 500 °C under stoichiometric feed, measurements taken at steady state conditions every 50 °C.
- ***Tested oxidations:*** *The new catalysts were tested against the oxidation of CO, C_3H_8, C_3H_6 and CH_4.*
- An automotive catalyst based on ***γ-alumina and Pd/Rh was used as reference.***

Development of Geopolymeric catalysts

(3) Doping with CeO_2 (before the incorporation of Pd)



Synthesis conditions

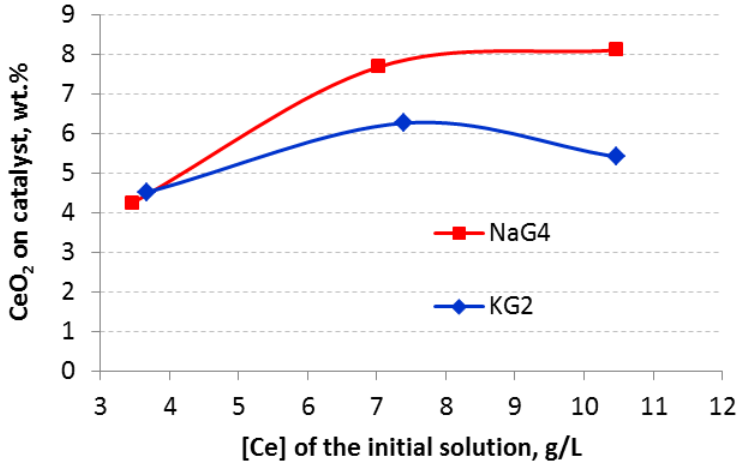
- Ce content in the precursor
- Process kinetics

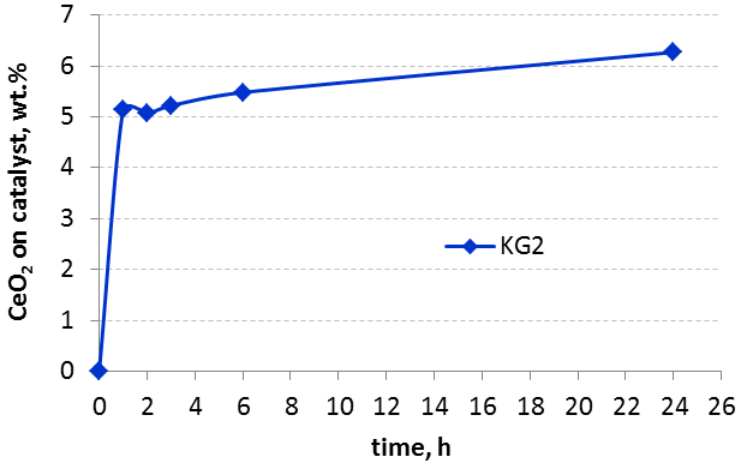
Evaluation of materials properties

- XRD analysis / SEM analysis / BET analysis
- Catalytic performance testing

Development of Geopolymeric catalysts

Synthesis conditions / process kinetics

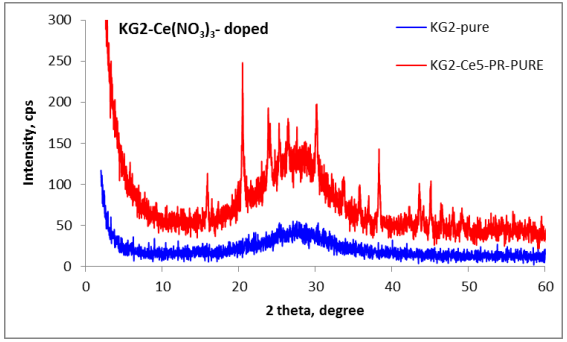


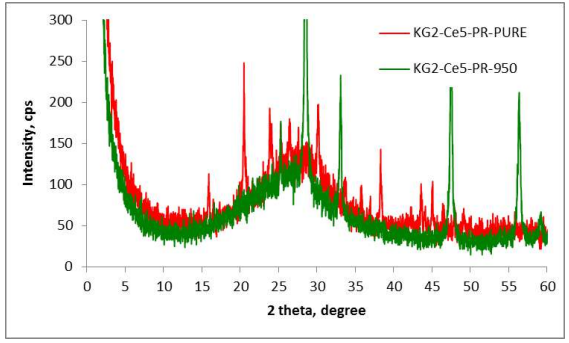


- CeO_2 doped forms a plateau at ~8%wt. for the **Na-Geo** supports and optimizes at ~6% wt. for the **K-Geo** supports
- The kinetics of Ceria doping process is very fast (85% is completed in 1h)

Development of Geopolymeric catalysts

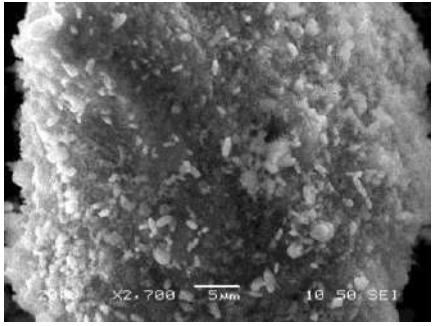
XRD analysis





- Precipitation as Cerium Oxide Carbonate Hydrate $Ce_2O\cdot(CO_3)_2\cdot H_2O$ that transforms to CeO_2 after heating at 600 °C/4h.

SEM analysis



- Ce is homogeneously dispersed on the geopolymer forming surface precipitants of nano- to micro-size

BET analysis

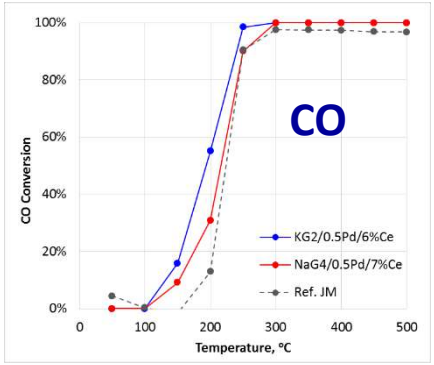
MATERIAL	SSA m2/g	Total PV cc/g	Average PD nm
KG2-pure	30.593	1.21E-01	9.2
KG2-950	9.732	2.73E-02	8.8
KG2-Ce5-600	16.536	3.76E-02	9.1
KG2-Ce5-950	12.711	2.47E-02	7.8

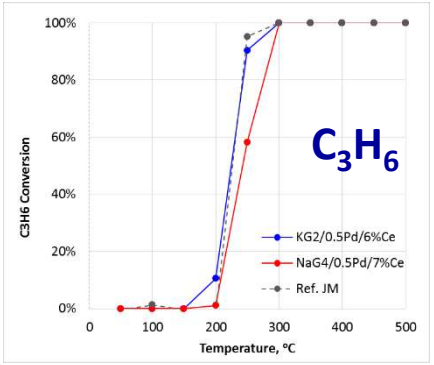
- Ce-doped geopolymer had lower SSA and TPV.
- The difference between SSA and TPV in the thermally treated geopolymers are importantly reduced.

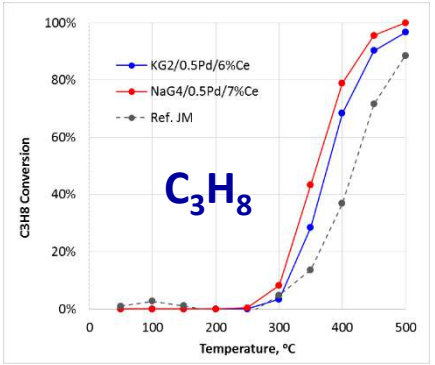
Development of Geopolymeric catalysts

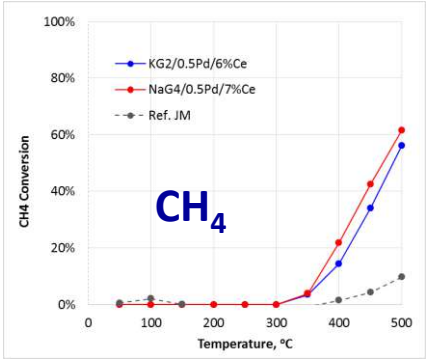
Catalytic activity testing of CeO_2 doped Geo-Pd catalysts (5% CeO_2 and 0.5% Pd)

- Na-Geo/Ce5/Pd0.5
- K-Geo/Ce5/Pd0.5









- ✓ Excellent performance for all oxidations
- ✓ K-Geo catalyst has a better activity than the Na-Geo catalyst

Conclusions

- Geopolymer catalysts suitable to be used in Intermediate-Temperature Solid Oxide Fuel Cells were developed.
- The geopolymeric catalytic supports based on sodium are macroporous with limited structural stability up to 950 ^{o}C
- The geopolymeric catalytic supports based on potassium are mesoporous with very good structural stability up to 950 ^{o}C
- Active metals were successfully incorporated in the geopolymer through a hydro-chemical process and following a surface precipitation mechanism (PdO nano-particles)
- Ceria-doping improved the catalytic activity of Geo-catalysts
- Geopolymers are promising materials for applications in the field of energy production

Thank you for your attention!

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