

# The Application and Characterisation of Nickel Nanoparticles Inside the Mesopores of MCM-41

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## Introduction

The recent development of several structured mesoporous materials has received much attention from the field of catalysis. The textural and structural properties of these materials make them suited for use as support for the catalytically active phase(s). However, stability limitations of MCM-41 and related materials call for dedicated catalyst synthesis procedures.

Here we present a study on the influence of the precursor of the catalytically active phase on the ultimate properties of supported nickel (oxide) catalysts. To arrive at a high loading of well-dispersed nickel nanoparticles inside the mesopores a chelating citric acid precursor was applied. This nickel precursor leaves a strongly adhering thin film on the surface of the pore walls, which upon drying, calcination and reduction breaks up in small nickel nanoparticles. As a reference precursor the commonly used nickel nitrate was used.

## Experimental

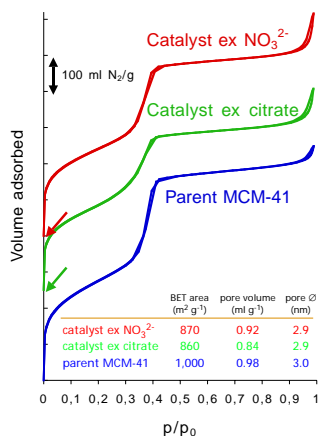
### MCM-41

All-silica MCM-41 was obtained from a synthesis gel with composition 1 SiO<sub>2</sub> (Aerosil 380) : 0.27 CTABr : 0.19 TEAOH : 40 H<sub>2</sub>O. After ageing for 24 hours (RT) this gel was transferred to an autoclave and aged hydrothermally for 2-3 days at 150°C. Template was removed by calcination in air (6 hours 550°C).

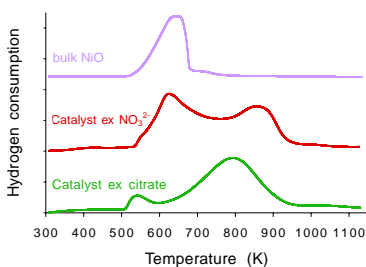
### Catalysts

Powdered MCM-41 material was impregnated to incipient wetness with solutions of Ni(NO<sub>3</sub>)<sub>2</sub> and Ni<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub> (citrate-precursor) respectively, dried (12 hours 120°C) and calcined (4 hours 450°C, air). Nickel loading = 10% by weight.

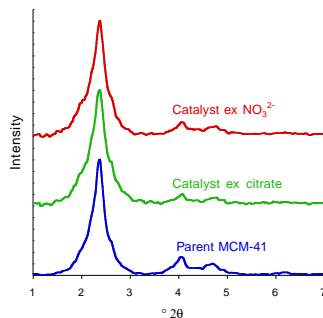
## Results



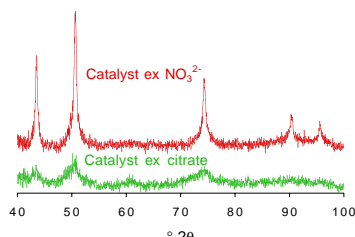
Nitrogen physisorption data of the parent MCM-41 material and calcined catalysts.



TPR patterns of the calcined catalysts and bulk NiO.

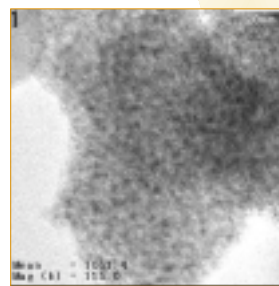


X-ray diffraction patterns at low angles of the parent MCM-41 material and calcined catalysts. Upon application of nickel the hexagonal order of the support, reflected by the (100), (110) and (200) diffractions, is retained.

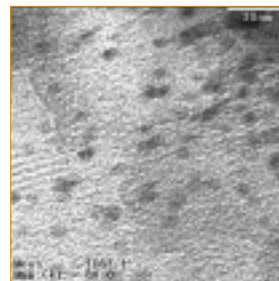


X-ray diffraction patterns showing NiO reflections in the calcined catalysts.

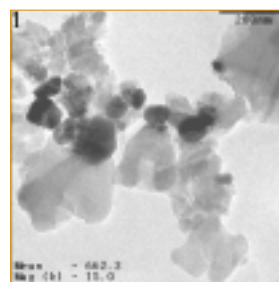
With XPS a notably higher Ni:Si ratio was measured for the catalyst *ex citrate* (0.09) vs. *nitrate* (0.05), indicating a higher dispersion of nickel resulting from the use of a film-forming precursor.



TEM micrograph showing the nickel nanoparticles inside the mesopores of the catalyst *ex citrate* after reduction.



TEM micrograph showing some nickel nanoparticles inside the mesopores of the catalyst *ex nitrate* after reduction.



TEM micrograph showing very large nickel particles on the MCM-41 support after reduction of the catalyst *ex nitrate*.

## Conclusions

- ✓ Upon application of nickel the favourable structural and textural properties of MCM-41 have been retained, independent of the nickel precursor used.
- ✓ With a non-adhering, common nickel nitrate precursor the mobility during drying and calcination results in the formation of large nickel (oxide) particles at the external support surface.
- ✓ The use of a chelating nickel citrate precursor results in the deposition of a thin film strongly fixed to the mesopore surface. Upon drying, calcination and reduction this thin film breaks up, leaving a high dispersion of nickel nanoparticles, exclusively situated inside the mesopores of the MCM-41 support.

## Future work

SAXS will be used to study in more detail the processes occurring during the various stages of catalyst synthesis. Catalytic performance will be tested in the hydrodesulphurisation of thiophene.

## Acknowledgements

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