How much can BCDI contribute to the study of heterogeneous catalysis?

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Heterogeneous catalysis

- Increases the **reaction rate**.
- Catalyst is in a **different phase** from the reactants.
- Creation of a **new** reaction path with a **lower** activation energy.
- The **selectivity** of a specific reaction can also increase.

Heterogeneous catalysis is by essence a surface process, in which each reaction step occurs near/on the catalyst surface.

Step number	Reaction
1	NH_3 + { } →{NH_3}
2	{NH_3} →NH_3 + { }
3	O_2 + 2 ( ) →2 (O)
4	2 (O) →O_2 + 2 ( )
5	{NH_3} + 3 (O) →{N} + 3 (OH)
6	{N} + {N} →N_2 + 2 { }
7	{N} + {NO} →N_2O + 2 { }
8	{NO} + ( ) →{N} + (O)
9	(OH) + (OH) →(O) + ( ) + H_2O
10	{N} + (O) →NO + ( )
11	H_2O + ( ) + (O) →(OH) + (OH)
12	NO →NO + { }
13	N_2O + ( ) →N_2 + (O)

Table 1. Dual sites reaction model for NH_3 oxidation on Pt catalyst [3]. {} denotes hollow sites, () top and bridge sites on Pt(100).

The example of ammonia oxidation

$$4NH_3 + 3O_2 \rightarrow 6H_2O + 2N_2 \quad (1)$$
$$4NH_3 + 4O_2 \rightarrow 6H_2O + 2N_2O \quad (2)$$
$$4NH_3 + 5O_2 \rightarrow 6H_2O + 4NO \quad (3)$$

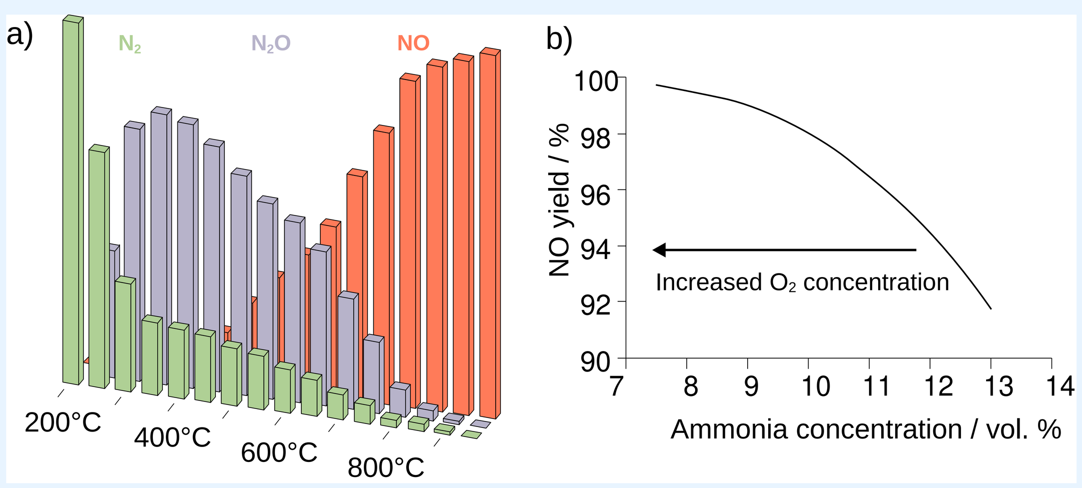

Figure 1. Only at high temperature (a), high O_2/NH_3 ratios (b), and over catalysers, is the production of NO favoured[2].

The Ostwald process relies on the production of NO *via* ammonia oxidation (first step) to produce nitric acid (second step).

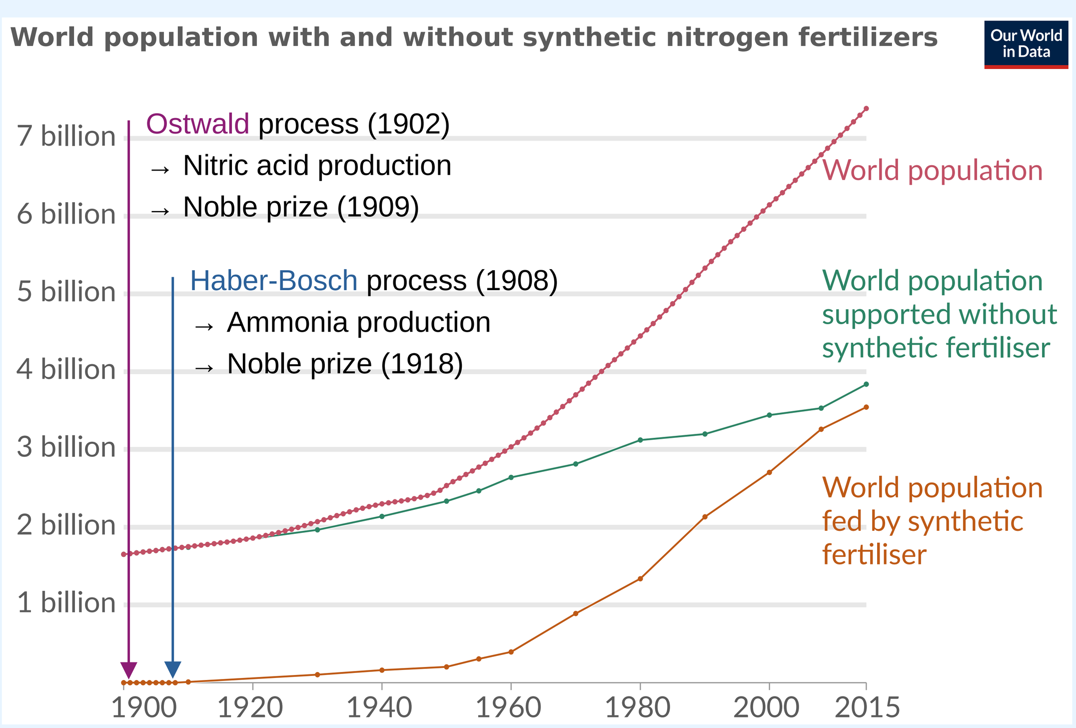

Figure 2. The production of **nitrogen fertilisers** from nitric acid is at the origin of the **selective** catalytic ammonia oxidation [1].

The material and pressure gap

"A long standing conundrum in the catalysis community emerged at the interface between surface science and heterogeneous catalysis, better known as the pressure and material gap."

Nature Catalysis editorial, 2018.

	Pressure	Material	Temperature
Industry	1 bar to 12 bar	Knitted gauzes wires (diameter ≈80 µm)	750 °C to 900 °C
Literature	UHV, mbar	Single crystals	25 °C to 900 °C
This study	Near ambient pressure (0.5 bar)	Single crystals and nanoparticles	25 °C to 600 °C

Table 2. Reproducing **relevant industrial conditions** relies on the probe, the technique, and the design of reactor cells at synchrotrons.

Observing chemical reactions indirectly

- Molecular/atomic adsorption can lead to **surface relaxation**, **roughness**, and **surface reconstruction** phenomena.
- The **electronic environment** of surface atoms can be impacted by the adsorption of reacting species.

BCDI is sensitive to structural changes

Obtain (i) the sample Bragg electronic density $\rho(\vec{r})$, and (ii) a **projection** of the **displacement field** $\vec{u}(\vec{r})$ on the **scattering vector** $\vec{G}_{hkl}$.

- Sample morphology reconstructed from BCDI measurement.
- Full **displacement field** and associated **strain tensor**.
- Few seconds measurement with nanometer resolution.

Pt particles for *in-situ* BCDI

- Particles fixed on substrate to avoid movement / sintering.
- Large distribution of particle size / morphology.
- Epitaxy impacts particle morphology and strain.

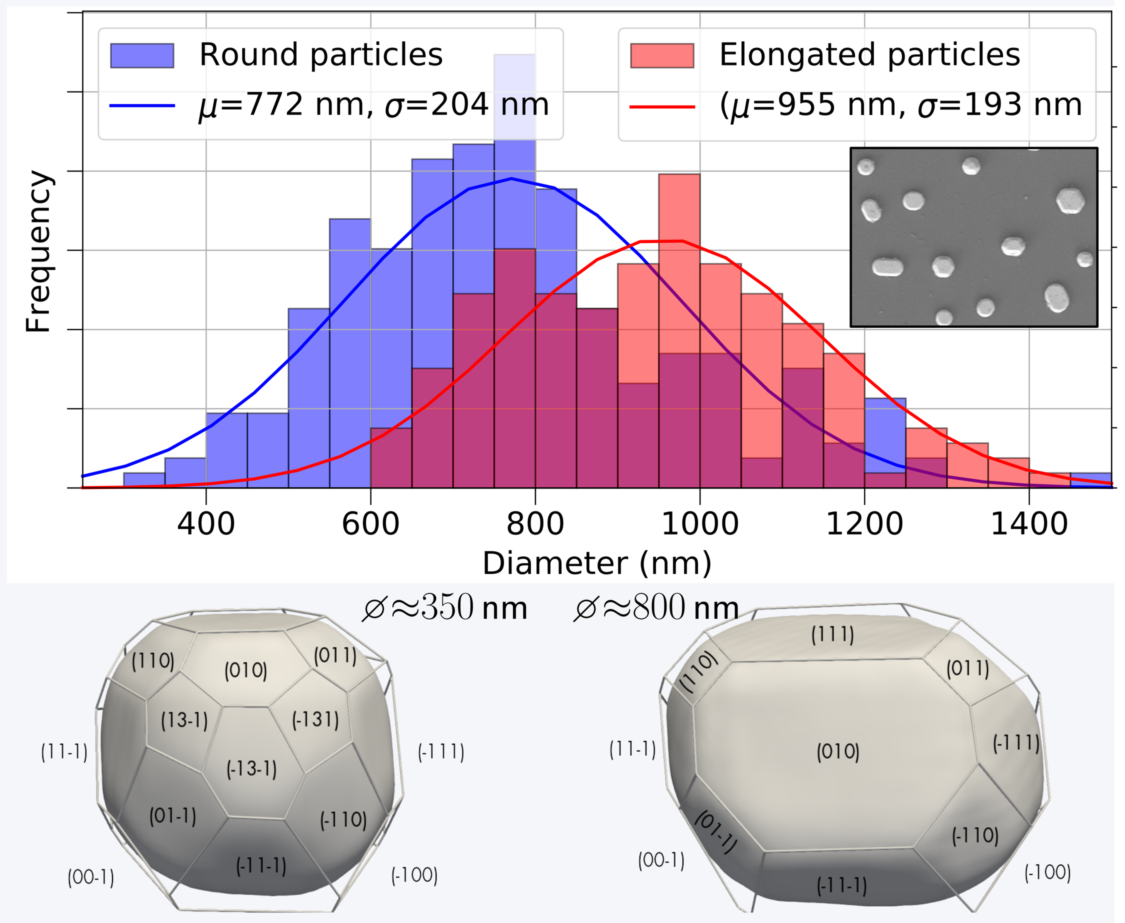

Figure 3. Top: Histogram of particle size distribution from Scanning Electron Microscopy (SEM). Bottom: BCDI reconstructions.

Of the importance of particle morphology

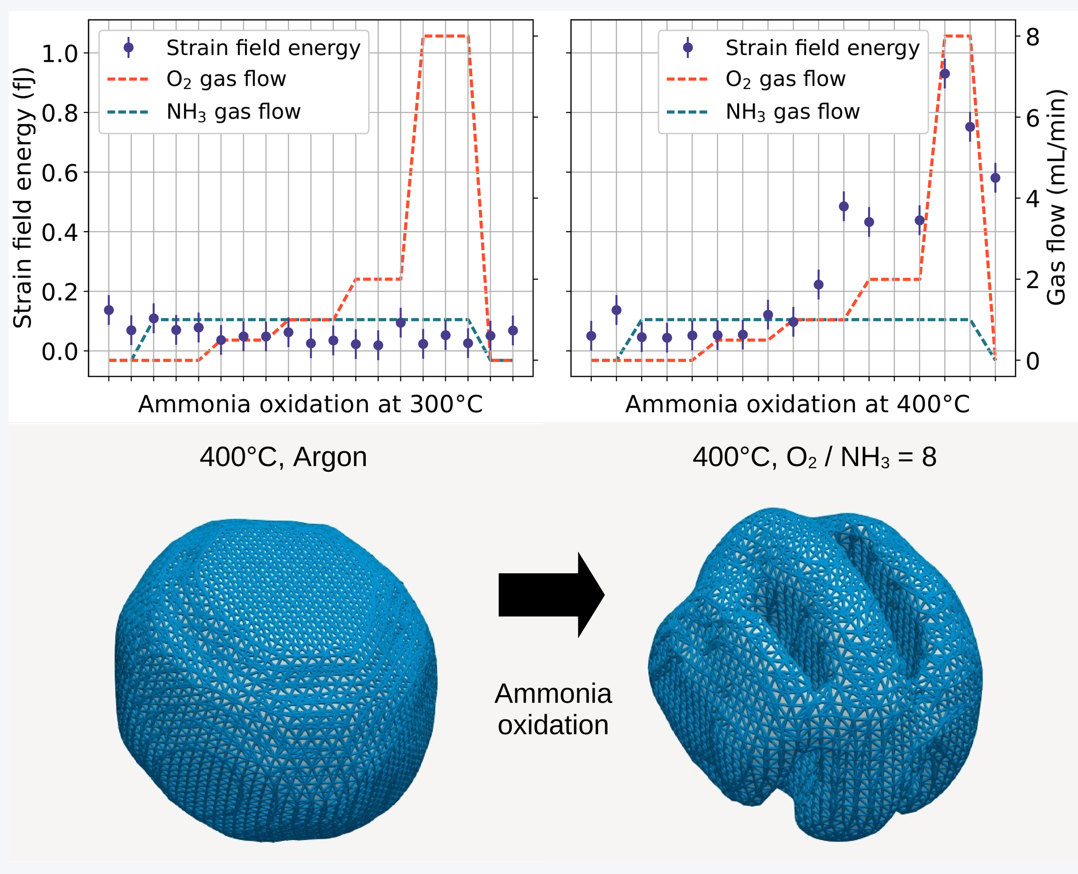

Figure 4. *In-situ* round particle morphology evolution at 400 °C.

- Different evolution for particles of **different size, morphology (facets), and initial strain state.**
- Structural changes at 400 °C above O_2 / NH_3 : 1 on round particle, conditions favouring NO, defects appear.
- Ammonia adsorption poisoning on elongated particle.

BCDI offers a limited picture...

- Sample size from 100 nm to 1000 nm.
- **Single** measurement process →far from collective behaviour.
- **Anisotropic** spatial resolution, **sample specific**.
- Difficult to observe the formation of **active surface phases**.

How to correlate strain changes to facet specific absorption / adsorption phenomena?

... completed by other techniques

Surface X-ray diffraction

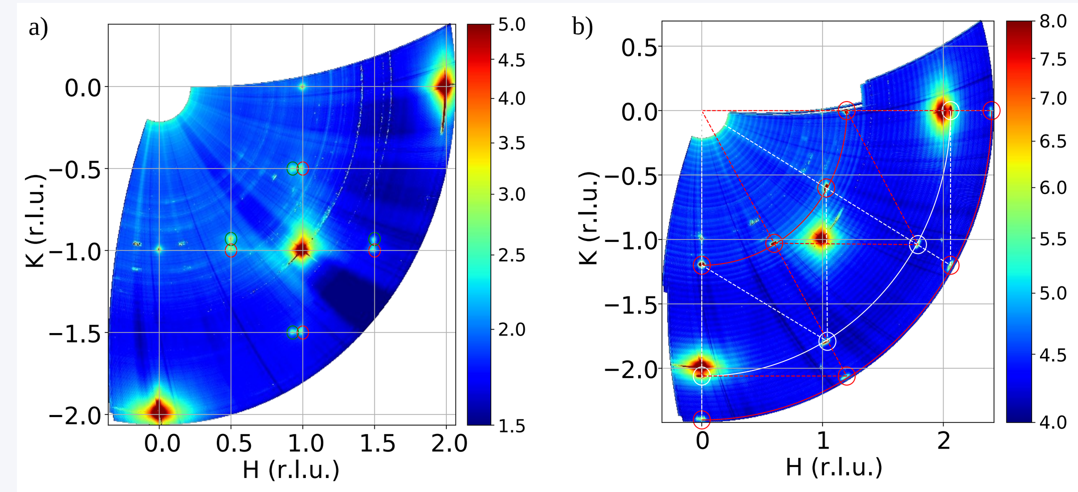

Figure 5. Pt(100) reciprocal space in-plane maps →**Presence of active surface phases such as surface oxides (a) and surface reconstructions (b) during ammonia oxidation at** 450 °C.

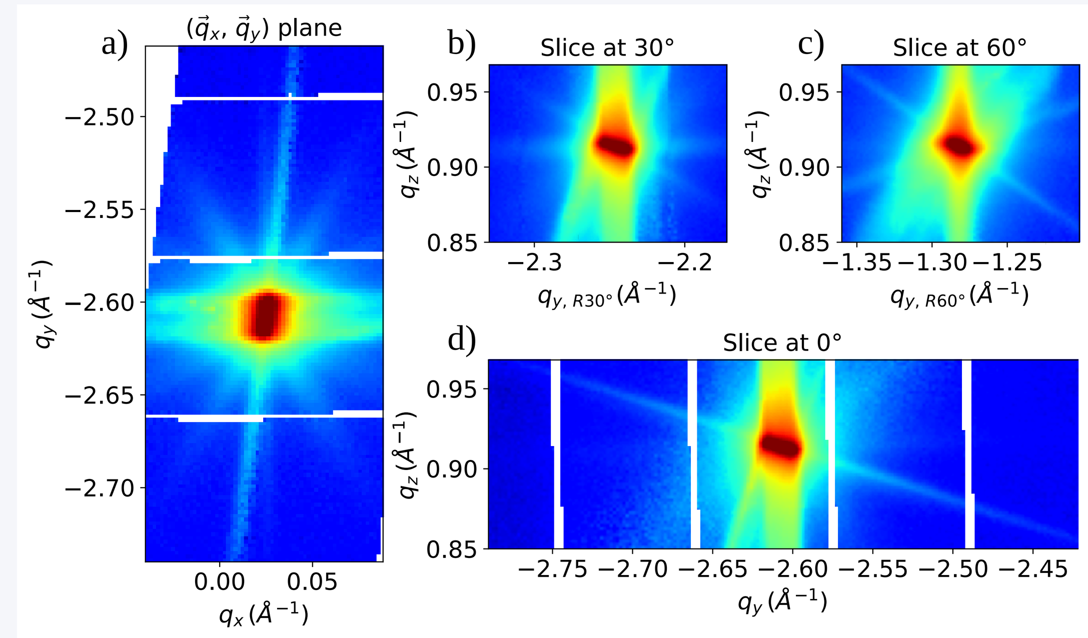

Figure 6. Crystal truncation rods from facets on Pt particles →**Collective behaviour such as particle reshaping.**

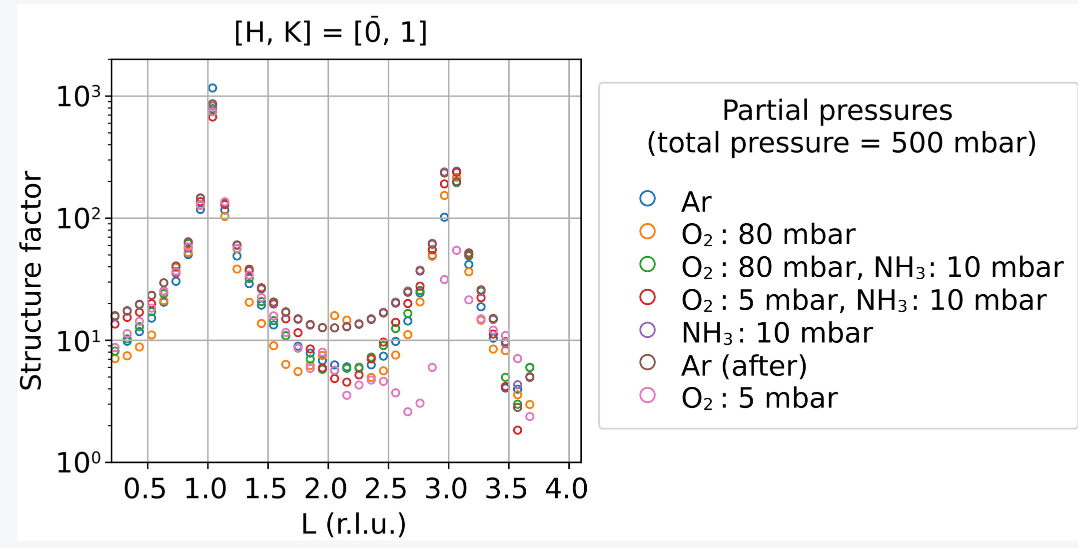

Figure 7. Pt(100) crystal truncation rods →**Surface roughness and relaxation effects.**

X-ray photoelectron spectroscopy

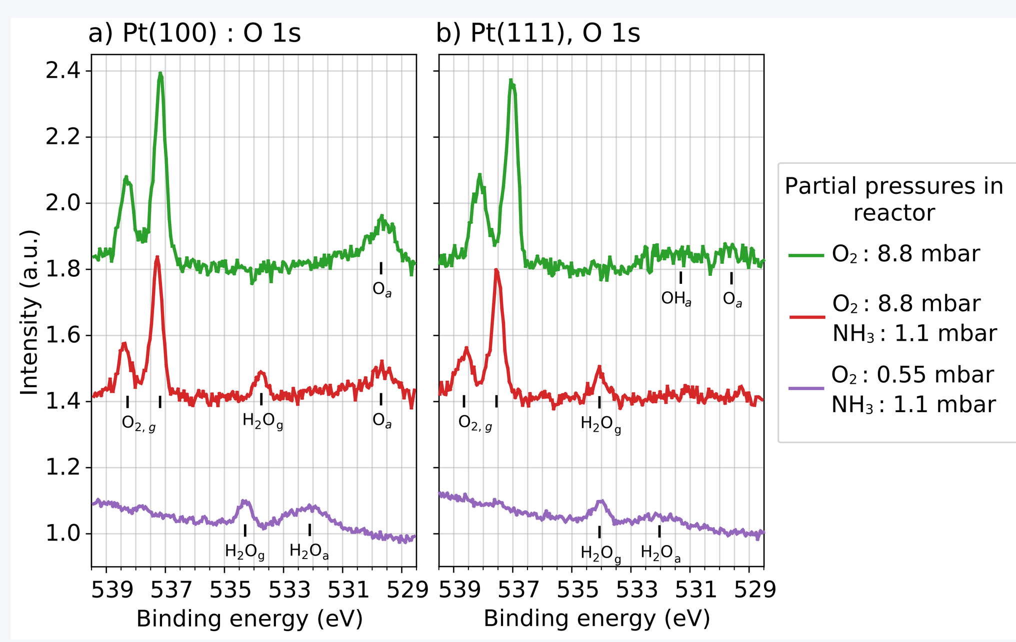

Figure 8. XPS spectra collected at the O 1s (a) and N1 s (b) levels under different atmospheres at 450 °C →**Difference in quantity / nature of adsorbed active surface species.**

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