

dislocation storage across the entire sample. In regions with a high density of excess dislocations the diffraction spot is elongated (*i.e.* “streaked”), whereas in regions with low excess dislocation content the peak appears circular.

In the underlying studies, we demonstrated the severe impact of sample misalignments

on the storage of excess dislocations in micrometre sized compression pillars [2], the critical influence of the initial dislocation source size statistics onto the deformation behaviour at the micrometre scale during tensile testing [3] and, finally, the reversibility of dislocation movement in bending beams due to internal stress fields [4].

■ A surface science approach in aqueous phase used to rationalise the preparation of heterogeneous catalysts

The rational design of heterogeneous catalysts involves the implementation of model approaches, “surface science” being the best known. This approach aims to model a complex industrial catalyst using simple chemical systems most often presented in the form of plane monocrystalline supports capable of reproducing, at least in part, the physicochemical behaviour of a metal particle or a pulverulent metal oxide with a large specific surface area.

This study focused on catalysts using Ni on alumina ($\text{Ni}/\text{Al}_2\text{O}_3$), which can be found in many applications such as steam reforming (hydrogen production from hydrocarbons), hydrogenation and hydrotreating (removal of S, N, O and metals from petroleum fractions). To model the industrial γ -alumina oxide support (poorly crystalline and exhibiting many different crystallographic faces) we decided to use monocrystalline wafers of α -alumina in different crystallographic orientations in order to model the different surface groups (hydroxyl) of the industrial support.

The originality of this study lies in how the catalyst was synthesised. This was carried out in the aqueous phase (as done industrially) and the characterisation was carried out under ambient conditions. This is in contrast to more traditional surface science approaches, where the model catalyst is synthesised under ultra-high vacuum, industrially far less realistic.

The use of oriented monocrystals required a characterisation technique

capable of providing molecular information for very low concentrations of active phase (Ni^{II} in this case) deposited on the oxide surface. Grazing incidence EXAFS spectroscopy (grazing-incidence XAS or GI-XAS) turned out to be an ideal technique for such a study. This technique has been implemented on several complementary beamlines during this study: BM30B (FAME) and (BM08) GILDA at the ESRF and DIFFABS and SAMBA at SOLEIL.

The use of oriented monocrystals coupled with the polarisation of the synchrotron beam yielded new information about the orientation of the supported active phase and showed that the crystalline orientation of the oxide support strongly governed speciation (chemical distribution) of the active phase. When Ni^{II} was adsorbed in the aqueous phase, Ni K-edge EXAFS revealed an oriented precipitation of nickel hydroxide ($\text{Ni}(\text{OH})_2$) on the ($1\bar{1}02$) surface of α -alumina. For example, **Figure 1** shows the effect of polarisation on

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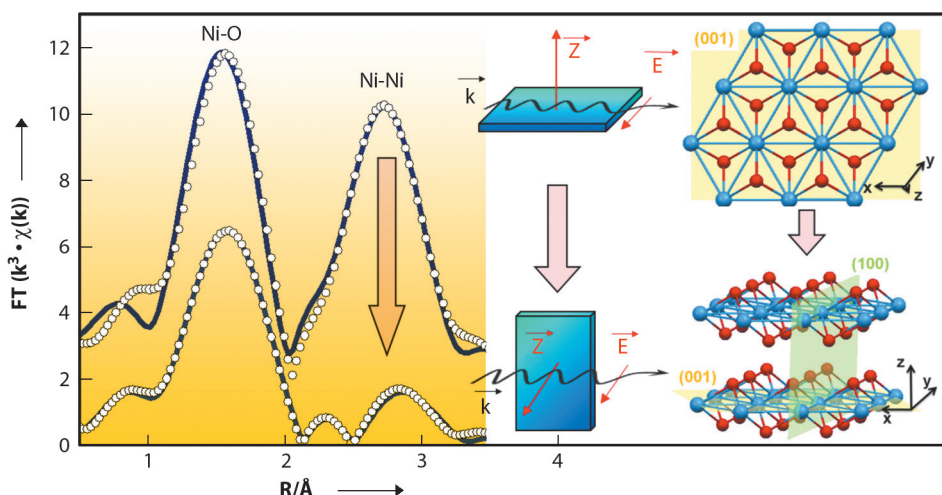
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Fig. 1: Fourier transforms of the Ni K-edge EXAFS signal (k^3 -weighted) for parallel and perpendicular polarisation of the sample obtained by depositing Ni^{II} on the ($1\bar{1}02$) surface of α -alumina. The solid blue line shows the experimental spectrum and the circle, refinement of the signal. The structure of the nickel hydroxide ($\text{Ni}(\text{OH})_2$) is shown on the right as seen from the top or on the side with respect to the (001) basal plane.





the second peak in the Fourier transform of the EXAFS signal (Ni-Ni distances): this peak is very pronounced for a monocrystal orientation parallel to the electric field vector, \vec{E} , whereas the intensity of the same Ni-Ni peak decreases sharply when the sample is oriented perpendicular to the electric field vector \vec{E} . In contrast, for the (0001) surface of α -alumina, no Ni deposit was observed, which shows the importance of the type of surface group exposed by the oxide for controlling the adsorption of the active phase.

These results demonstrate at the molecular level that the oxide support does not merely act as a physical container of the active phase and that the nature of specific surface sites plays a key role in the formation and orientation of the

nickel hydroxide precipitate. The fact that $\text{Ni}(\text{OH})_2$ precipitated only on the (1 $\bar{1}$ 02) face can be explained by the minimisation of surface energy between the alumina and the nickel hydroxide.

The use of a model system shows that the Ni dispersion on individual oxide particles is highly heterogeneous for an industrial catalyst as it will depend on the type of face exposed and therefore on the morphology of the oxide support. These findings also highlight the fact that each face of the alumina has a specific reactivity depending on which OH groups are exposed. Controlling the morphology of γ -alumina is therefore a key factor at the industrial scale in order to be able to control the deposition and dispersion of the active phase.

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■ Design of zeolite by inverse sigma transformation: Cut and paste zeolites

Zeolites are crystalline microporous aluminosilicates which consist of corner-sharing TO_4 tetrahedra. They are workhorses in industry for adsorption, separation and catalysis. Heteroelements are often inserted to enhance desired properties such as catalytic activity and selectivity. The introduction of germanium however results in stability problems.

Germanosilicate IM-12 zeolite (UTL topology) consists of dense silicate layers connected by double-four rings (D4Rs), the preferential location of germanium (**Figure 1**). The systematic instability of the UTL zeolite can be used to harvest building units that can be rearranged to transform UTL zeolite into a new and stable zeolite. Acid leaching removes the germanium from the UTL framework while preserving the dense silicate layers and reconnects these layers to form new zeolite topologies –COK-14 or COK-14. –COK-14 is a new all-silica interrupted framework topology with a two-dimensional channel system and interconnecting 8-, 10- and 12-membered rings (**Figure 1**). Upon drying in the absence of water, silanol condensation takes place and COK-14 is formed (**Figure 1**). The transformation from UTL zeolite to COK-14 involves the systematic removal of one layer of T-atoms and as

such is the first experimentally observed inverse sigma transformation.

To verify if a true inverse sigma transformation occurred, an intermediate state was captured named Ge-COK-14. This sample was synthesised by reducing transformation time. ^{29}Si -NMR and ^1H -NMR indicated this sample contained Q^3 silicon environments, associated with silanol groups, while still having Si-O-Ge bonds. Approximately 50 wt% of the original germanium content was still present in Ge-COK-14. High-resolution powder X-ray diffraction data and X-ray absorption spectra for Ge-COK-14 were collected at room temperature at beamline BM01B (the Swiss Norwegian Beamline SNBL) in collaboration with beamline BM26 (DUBBLE) (**Figure 2**). Indexing of the powder pattern of Ge-COK-14 resulted in a unit cell of $a = 24.43 \text{ \AA}$, $b = 13.90 \text{ \AA}$, $c = 12.28 \text{ \AA}$ and a monoclinic angle of 108.97° compared to $a = 24.64 \text{ \AA}$, $b = 13.92 \text{ \AA}$, $c = 12.26 \text{ \AA}$ and $\beta = 109.20^\circ$ for –COK-14 and $a = 29.00 \text{ \AA}$, $b = 13.98 \text{ \AA}$, $c = 12.45 \text{ \AA}$ and $\beta = 104.91^\circ$ for the parent UTL zeolite. This indicated that Ge-COK-14 already had the interlayer spacing of –COK-14 but still contained germanium. Ge K-edge EXAFS spectra revealed the local environment