

# A Surface Science Approach to the Preparation of Alumina-Supported Ni-Mo Catalysts in Aqueous Solution

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## Introduction

Alumina-supported Ni-Mo catalysts are widely used for hydrotreating purposes and new catalysts development is more than ever driven by stringent environmental regulations [1]. However, a molecular-level understanding of catalyst preparation is still lacking while it is a prerequisite for controlling the final properties of this class of catalysts [2]. Most studies of sorption reactions are usually performed on high surface area oxides with a number of crystallographically different surfaces and ill-defined sorption sites. A fundamental description of sorption mechanisms is thus not possible in most cases. The sorption system may be simplified by using oriented single crystals that have a limited number of well-defined surface sites. This reductionist approach applied to *aqueous deposition* is seldom used in heterogeneous catalysis where most of the studies dealing with single crystals use “surface science” deposition techniques (*i.e.* chemical vapor deposition) [3]. Although one of the most important catalyst support is  $\gamma$ - $\text{Al}_2\text{O}_3$ , it has not been prepared in single crystal form. In this work, we use a surface science approach with  $\alpha$ - $\text{Al}_2\text{O}_3$  single crystals wafers in two orientations that mimic the complexity of the surface chemistry of  $\gamma$ - $\text{Al}_2\text{O}_3$  [4] for the characterization of NiMo/ $\text{Al}_2\text{O}_3$  catalysts prepared by *aqueous deposition*.

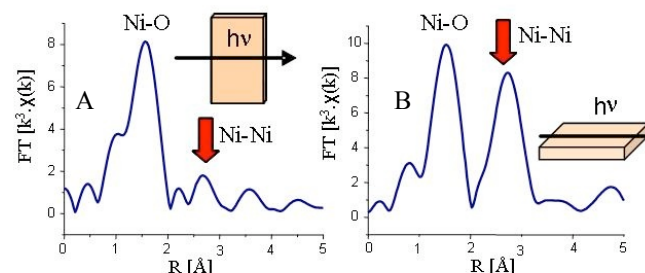
## Materials and Methods

Single crystals wafers of  $\alpha$ - $\text{Al}_2\text{O}_3$  with two orientations (0001) and (1 $\bar{1}$ 02) have been used for  $\text{Mo}^{\text{VI}}$  ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ ) and  $\text{Ni}^{\text{II}}$  ( $\text{Ni}(\text{NO}_3)_2$ ) sorption on alumina by: 1) aqueous equilibrium adsorption (the single crystal is immersed in the impregnation solution), 2) incipient wetness impregnation (a drop of metal salt solution is spread on the single crystal). Ni adsorption is carried out in the presence of a chelating ligand (ethylenediamine, *EN*) with variable *EN*/Ni ratio (1 to 3) for studying the promotional effect of chelating ligands usually observed in hydrotreating catalysts [5]. The samples were characterized by XPS, AFM and Grazing-Incidence EXAFS (GI-EXAFS). The latter technique allowed us to work at low surface coverages imposed by low surface area single crystals [6].

## Results and Discussion

$\text{Mo}^{\text{VI}}$  and  $\text{Ni}^{\text{II}}$  surface concentrations were determined by XPS in order to obtain macroscopic adsorption data. These results show that Mo adsorption is site specific since no adsorption occurs on the (0001) surface that exposes only neutral surface OH ( $\text{Al}_2\text{-OH}$ ). Hence, adsorption through hydrogen bonds can be discarded. Conversely, GI-EXAFS show that isolated  $\text{Mo}^{\text{VI}}$  species in sixfold coordination are grafted on the basic sites of the (1 $\bar{1}$ 02) face (singly coordinated surface OH) while triply coordinated surface OH ( $\text{Al}_3\text{-OH}$ ) are not reactive. These results indicate that Mo will be heterogeneously distributed over the different

surfaces of  $\gamma$ - $\text{Al}_2\text{O}_3$  particles on conventional powdered catalysts. Despite the presence of a chelating ligand (*EN*), AFM and GI-EXAFS show the heterogeneous precipitation of  $\text{Ni}(\text{OH})_2$  on the (1 $\bar{1}$ 02) surface even at low  $\text{Ni}^{\text{II}}$  concentrations. The precipitation is surface-dependent since no adsorption is observed on the (0001) surface. Moreover, thanks to the synchrotron beam polarization, GI-EXAFS allows us to show that the (1 $\bar{1}$ 02) surface induces an oriented precipitation of  $\text{Ni}(\text{OH})_2$  parallel to the surface (Fig. 1): the Ni-Ni second shell almost vanishes when EXAFS probes the bonds normal to the surface (Fig. 1A). These experiments reveal that Ni-*EN* complexes are not sufficiently stable to prevent  $\text{Ni}(\text{OH})_2$  precipitation on specific surface orientations which may explain why *EN* is not able to retard the Ni sulfidation temperature in contrast to more stable chelate ligands such as EDTA [7].



**Figure 1.** Ni K-edge Fourier transforms ( $k^3$  weighted) of GI-EXAFS data of  $\text{Ni}^{\text{II}}$  on  $\alpha$ - $\text{Al}_2\text{O}_3$  (1 $\bar{1}$ 02) wafers (*EN*/Ni = 3) in two orientations with respect to the synchrotron beam. The electric-field vector is: A) normal to the crystal surface and B) parallel to the crystal surface.

## Significance

Spectroscopic studies of the type proposed here should help developing molecular-level models of sorption products and processes for a rational design of new catalytic materials. This study allows us to distinguish molecular adsorption *vs.* precipitation for  $\text{Mo}^{\text{VI}}$  and  $\text{Ni}^{\text{II}}$  on the (1 $\bar{1}$ 02) surface while the (0001) surface is unreactive. Hence both metals, although of opposite charge (oxoanion for  $\text{Mo}^{\text{VI}}$  and cation for  $\text{Ni}^{\text{II}}$ ) appear to compete for the same type of surface alumina sites. These results should give important information for hydrotreating catalysts preparation (order of metal salt impregnation, onset of sulfidation temperature...).

## References

1. Leliveld, R.G., Eijsbouts, S.E. *Catal. Today* 130, 183 (2008)
2. Marceau, E., Carrier, X., Che, M., Clause, M., Marcilly, C. in “Handbook of Heterogeneous Catalysis” (G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Eds.) Vol. 1 p. 467. Wiley-VCH, Weinheim 2008
3. Imbihl, R., Behm, R.J., Schlögl, R. *Phys. Chem. Chem. Phys.* 9, 3459 (2007)
4. Eng, P. J., Trainor, T. P., Brown, Jr., G. E.; Waychunas, et al., *Science* 288, 1029 (2000).
5. Coulier, L., de Beer, V.H., vanVeen, J.A., Niemantsverdriet, J.W.J. *Catal.* 197, 26 (2001)
6. Towle, S.N., Brown, Jr., G. E., Parks, G.A., *J. Colloid Interface Sci.* 217, 299 (1999)
7. Cattaneo, R., Weber, T., Shodo, T., Prins, R.J. *Catal.* 191, 225 (2000)