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Neof ormation of DLH During Impregnation of γ -Alumina

J.-B. d'Espinose de la Caillerie and O. Clause

*Ecole Supérieure de Physique et de Chimie Industrielles, Laboratoire de Physique Quantique,
URA 1428 du CNRS, 10 rue Vauquelin, 75231 Paris cedex 05, France*

** Institut Français du Pétrole, Division Cinétique et Catalyse, BP. 311, 92506 Rueil-Malmaison cedex,
France*

Abstract: The adsorption of Co(II) or Ni(II) ammine complexes from aqueous solutions onto γ -alumina at neutral pH and ambient temperature was investigated. The formation of coprecipitates including Al(III) ions extracted from the support was demonstrated by EXAFS for contact times and Ni or Co loadings higher than 0.5 h and about 2.0 wt %, respectively. The EXAFS technique makes it possible to distinguish the Ni or Co hydroxides and basic nitrates from coprecipitates with a double layer hydroxide (DLH) structure. Not only is EXAFS shown to be sensitive to the presence of aluminum in the coprecipitates, but in most cases, the M(II)/Al(III) ratio (M= Ni or Co) in the supported coprecipitates can be estimated. Thus, alumina should not be considered systematically as inert even at pH values close to its isoelectric point. It is suggested that a dissolution-precipitation mechanism is involved and that the rate of alumina dissolution is promoted by adsorbed Ni(II) or Co(II) ions. Site-binding models have a considerable value for the early stages of impregnation, whereas a geochemical approach involving surface rehydration and coprecipitation have probably a greater validity for the later stages.

1. INTRODUCTION

The understanding of the nature of the interaction between solvated ions and solid oxides surfaces is fundamental to diverse areas of chemistry such as heterogeneous catalyst preparation, geochemistry, and environmental chemistry. A solid catalyst usually consists of a chemically active species dispersed by impregnation or adsorption of a solvated precursor on an oxide solid surface chosen for its textural and mechanical properties. The system to be described when studying the first stage of catalyst preparation therefore consists of an aqueous solution / solid oxide interface. While geochemists studying weathering and the interaction of minerals with hydrothermal fluids have focused on the solubility of minerals and surface leaching, phenomena invoked for the fixation of solvated metal cations during the preparation of supported catalysts have relied exclusively on electrostatic [1] and ligand exchange models [2] developed within the framework of colloid chemistry. In the field of catalyst preparation, the formation of surface phases involving both the dispersed species and elements of the support has mainly been considered to occur during the later stages of preparation such as drying or activation at high temperature [3]. However, we have recently submitted evidence for the formation of lamellar surface species during impregnation of divalent cations at room temperature and near-neutral pH on silica [4] and alumina [5]. Here we focused on the alumina/water interface during impregnation with Ni(II) or Co(II). In this paper the EXAFS technique is shown to be well adapted to the determination of the species formed on alumina during impregnation.

2. EXPERIMENTAL

2.1 Sample Preparation

The preparation of the reference double layer hydroxide (DLH), hydroxides, and basic salts has been reported previously [5]. Impregnated samples were prepared by stirring during 1.5 h 5 g of Al_2O_3 powder in 200 mL of Co(II) or Ni(II) nitrate solutions containing 1 M ammonium nitrate. The pH was adjusted to 7.2 and 8.1 for Ni(II) and Co(II) respectively by bubbling ammonia.

2.2 XAS measurements

EXAFS measurements at the Ni and Co K edges were performed at the LURE radiation synchrotron facility (Orsay, France) using the D44 X-ray beamline emitted by the DCI storage ring (positon energy 1.85 GeV; ring current 300 mA). The spectra were recorded at 77 K in the transmission mode using two air filled ionization chambers. A Si(331) monochromator was used. Data analysis was performed using the University of Washington XAFS analysis package.

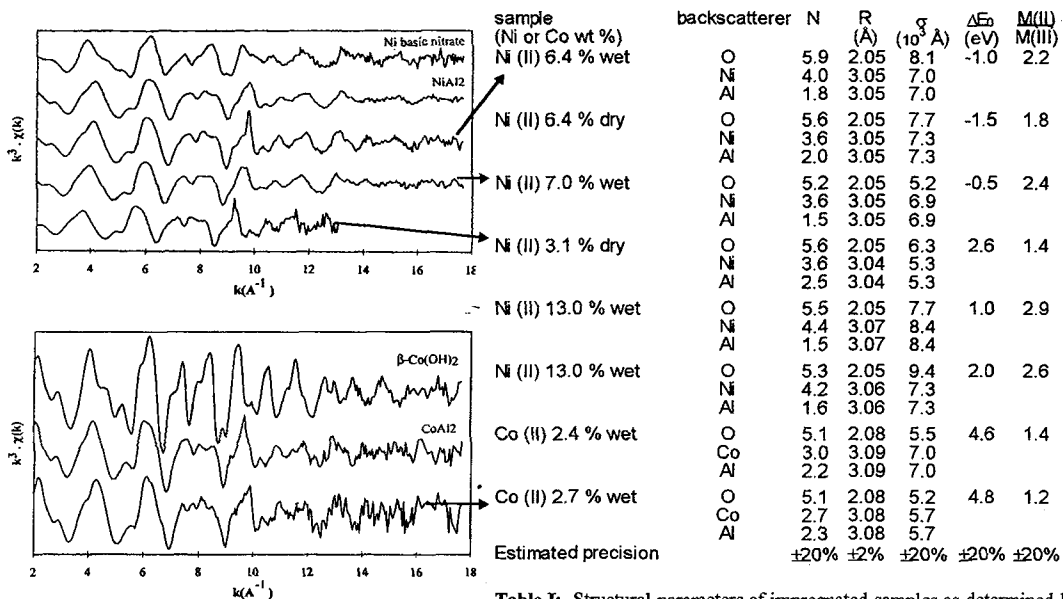


Table I: Structural parameters of impregnated samples as determined by EXAFS at the Ni and Co K edge.

Figure 1: k^3 weighed EXAFS at the Ni (above) and Co (below) K edges of hydroxides, basic nitrates, reference DLH of atomic ratio M(II)/Al(III) = 2, and impregnated samples (arrows point to the corresponding sample in the table).

3. RESULTS AND DISCUSSION

Direct examination of the spectra in Figure 1 showed that the signal of the DLH reference compounds can be readily distinguished from that of hydroxides and basic salts, in particular in the 4-6 \AA^{-1} and the 7-9 \AA^{-1} ranges. This demonstrated that EXAFS is sensitive to the presence of aluminum in the precipitates. The spectra of the impregnated samples were similar to the ones of DLH, supporting the assumption that DLH was formed in these samples.

Data analysis led to absorber-backscatterer distances consistent with X-ray data, while the M(II)/Al(III) atomic ratio determined for the DLH reference compounds was in agreement with the samples compositions (not shown). Therefore detailed analysis of the EXAFS data of the impregnated samples was performed. The structural information extracted from the EXAFS data is presented in Table I. In all impregnated samples, the formation of DLH was confirmed and the amount of aluminum incorporated from the support was estimated. An important point is that these observations are unambiguous whatever the crystallinity of the structures may be.

4. CONCLUSION

EXAFS clearly demonstrated that even at pH close to neutrality, aluminum is extracted from the alumina support and incorporated in a secondary DLH phase. We suggest that three phenomena occur simultaneously at the oxide/water interface in the presence of metal ions: (1) adsorption of the originally solvated ions, (2) dissolution of alumina which is rate-limiting but may be accelerated by the metal ion adsorption, and (3) the coprecipitation of cations released from the support, Al^{3+} , with the metal ion in solution leading to the DLH structure. Thus, alumina should not be considered systematically as inert even at pH values close to its isoelectric point.

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