Surface Coprecipitation of Co(II), Ni(II), or Zn(II) with Al(III) Ions during Impregnation of γ-Alumina at Neutral pH

J. L. Paulhiac and O. Clause*

Institut Français du Pétrole
Division Cinétique et Catalyse
92506 Rueil-Malmaison Cedex, France

Received August 13, 1993

The adsorption of Co(II), Ni(II), or Zn(II) ammine complexes from aqueous solutions on γ-Al_2O_3 has been studied as a function of the pH of the impregnating solutions. Two results are noteworthy. First, the adsorption isotherms exhibit a maximum for near-neutral impregnation pH ($6.5 < pH < 8.5$), i.e., for pH values close to the isoelectric point of alumina (IEP = 7.3). Second, the adsorption in this pH range leads to the formation of surface coprecipitates with Al(III) ions. Therefore alumina should not be considered as inert during impregnation with metal ions in aqueous solutions, even under mild conditions, i.e., neutral pH and ambient temperature.

The formation of surface compounds on impregnated oxides after heat treatment has been frequently reported, for example, in the Ni(II)–SiO_2[1] or Ni(II)–Al_2O_3[2] systems. More seldom, the formation of surface compounds has been suggested to occur after drying.[3] During impregnation, the site binding model of the electrical double layer is generally thought to account for the specific or nonspecific adsorption of ions onto oxide particles.[4] Nevertheless, in a recently published study dealing with the Ni(II)–silica interactions at the oxide/liquid interface, layered silicate formation was found to have already taken place during impregnation, even with weakly basic solutions ($7 < pH < 9$).[5]

The samples were prepared by putting in contact 5 g of γ-Al_2O_3 (specific surface area, 200 $m^2\ g^{-1}$, mean pore diameter 6 nm; Na_2O content lower than 50 ppm; pretreatment in an oven at 373 K during 48 h) with 200 mL of 0.01 M Co(II), Ni(II), or Zn(II) nitrate solutions containing 1 M ammonium nitrate.[6] The suspensions were stirred at 298 K during 3 h. After centrifugation and washing with a solution containing 1 M ammonium nitrate at the same pH as the final pH of the impregnating solution, the wet samples were kept in air (or under Ar for the Co(II)-containing samples) during a fixed time, hereafter called the aging time. The samples were subsequently dried in an oven at 373 K during 12 h. The amounts of adsorbed ions were derived from the concentration differences in the impregnation solutions before and after adsorption.

The Co(II), Ni(II), and Zn(II) adsorptions as a function of pH are shown in Figure 1. The most significant result is the presence of adsorption maxima for pH in the 6.5–8.5 range, i.e., for pH values close to the isoelectric point of alumina. This intriguing feature indicates that the interaction with alumina in this pH range is not simply electrostatic.

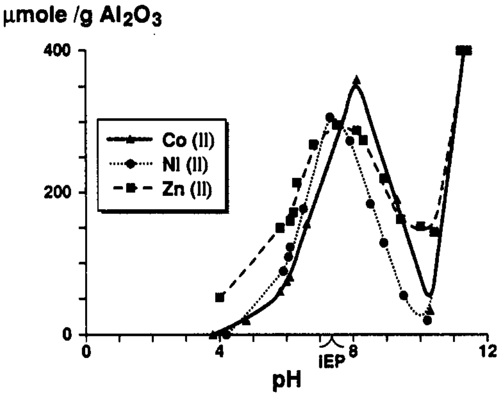

Figure 1. Adsorption of Co(II), Ni(II), and Zn(II) ammine complexes from aqueous solutions on γ-Al_2O_3 as a function of pH (contact time 3 h; ambient temperature). The isoelectric point of alumina is also reported.

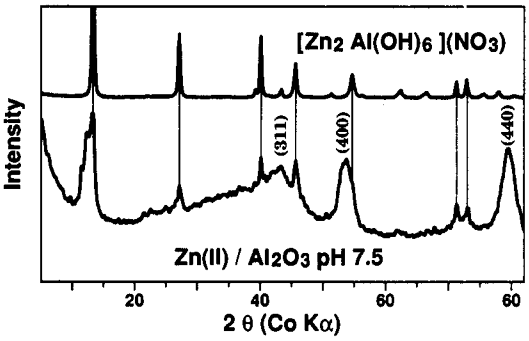

Figure 2. X-ray diffraction patterns of a wet Zn(II)/Al_2O_3 sample (see text) and of a synthetic zinc–aluminum coprecipitate with the formula $[Zn_2Al(OH)_6](NO_3)\cdot nH_2O$. The reflections indicated are those of γ-Al_2O_3.

We focused on the adsorptions at near-neutral pH. The X-ray diffraction pattern of an alumina sample impregnated at pH 7.5 with a Zn(II) ammine solution (contact time 3 h; no aging; temperature 298 K; no drying; 6.5 Zn wt %) is shown in Figure 2. The pattern of a synthetic zinc–aluminum coprecipitate, $[Zn_2Al(OH)_6](NO_3)\cdot nH_2O$, is also provided. The presence of water in the sample is visible and raises the background in the 20–50 2Θ range. The (311), (400), and (440) reflections of γ-alumina are observed. Well-defined reflections additional to those of alumina are also observed. The additional reflections cannot be attributed to zinc hydroxide nor to a zinc(II) basic salt. Good agreement is found with the pattern of the synthetic zinc–aluminum mixed hydroxide. While other phases may also be present in the sample, even though they are not identified by X-ray diffraction, the main point is that a coprecipitate including Al(III) ions is formed after impregnation at near-neutral pH and ambient temperature. A similar result is attained after impregnation with Co(II) or Ni(II) ions and demonstrated by X-ray diffraction for metal loadings higher than 10 wt %: a coprecipitate is formed on alumina before aging and drying.

The results obtained on the solids with metal loadings above 10 wt % may or may not apply to solids having lower metal loadings. Unfortunately, it is not possible to specify whether the broad reflections observed by XRD for low metal content are due to hydroxides, basic salts, or coprecipitates. Therefore, the EXAFS technique was used to characterize the local environment about adsorbed Co(II), Ni(II), or Zn(II) ions for wet and dried samples with lower metal loadings, typically in the 2.0–6.0 wt % range.

The normalized EXAFS at the Ni K-edge of nickel hydroxide, a nickel–aluminum synthetic coprecipitate with the formula [Ni_2-

---

* To whom correspondence should be addressed.

(1) See, for example: Trambouze, Y. *C. R. Hebd. Seances Acad. Sci.* **1948**, *227*, 971–972. Tohji, K.; Udagawa, Y.; Tanabe, S.; Ueno, A. *J. Am. Chem. Soc.* **1984**, *106*, 612–617.

(2) See, for example: Lo Jacono, M.; Schiavello, M.; Cimino, D. *J. Phys. Chem.* **1971**, *75*, 1044–1050. Wu, M.; Hercules, D. M. *J. Phys. Chem.* **1979**, *83*, 2003–2008. Houalla, M.; Delannay, F.; Delmon, B. *J. Phys. Chem.* **1981**, *85*, 1704–1709.

(3) See, for example: de Bokx, P. K.; Wassenberg, W. B. A.; Geus, J. W. *J. Catal.* **1987**, *104*, 86–98. Mile, B.; Stirling, D.; Zammitt, M. A.; Lovell, A.; Webb, M. *J. Catal.* **1988**, *114*, 217–229.

(4) A comparison of electrostatic models for the oxide/solution interface is given in the following: Westall, J.; Hohl, X. *Adv. Colloid Interface Sci.* **1980**, *12*, 265–294. See also: Lyklema, *J. Electroanal. Interfacial Electrochem.* **1968**, *18*, 341–348.

(5) Clause, O.; Kermarec, M.; Bonneviot, L.; Villain, F.; Che, M. *J. Am. Chem. Soc.* **1992**, *114*, 4709–4717.

(6) The concentrations of particles in solution having a size larger than 2 nm were found to be negligible by small angle X-ray scattering (SAXS) at any pH in the solutions before impregnation.

0002-7863/93/1515-11602$04.00/0

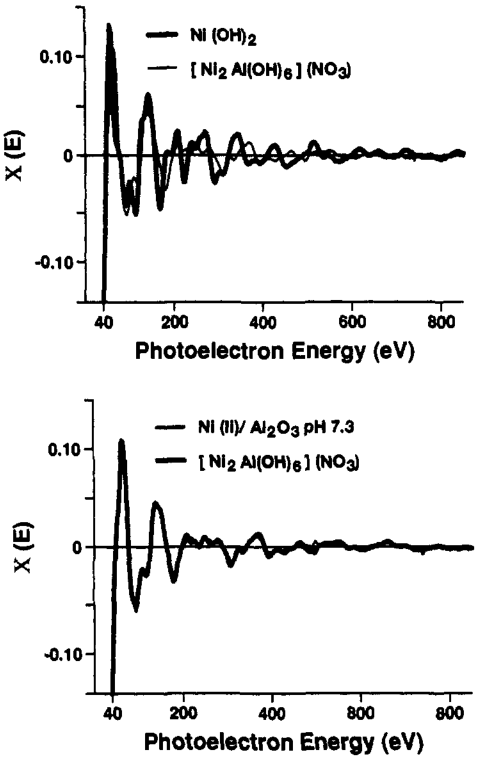

Figure 3. (a) Normalized EXAFS at the Ni K-edge of $[Ni_2Al(OH)_6](NO_3)\cdot nH_2O$ and of $Ni(OH)_2$. (b) Normalized EXAFS at the Ni K-edge of $[Ni_2Al(OH)_6](NO_3)\cdot nH_2O$ and of a dried $Ni(II)/Al_2O_3$ sample (see text).

$Al(OH)_6](NO_3)\cdot nH_2O$, and a $Ni(II)/Al_2O_3$ sample (contact time at pH 7.3 3 h; no aging; temperature 298 K; after drying; 3.0 Ni wt %) are shown in Figure 3.[7] The EXAFS of nickel hydroxide and of the nickel–aluminum hydrotalcite-type coprecipitate are readily distinguishable from each other, in particular in the 100–300-eV energy range. For energies higher than 500 eV, there is a phase opposition between the signals. Thus, the EXAFS technique is very sensitive to the presence of aluminum ions in the precipitate. The normalized EXAFS of the sample and that of the coprecipitate are nearly indistinguishable. Accordingly, the presence of a nickel–aluminum coprecipitate in the sample is clearly demonstrated. Since EXAFS averages over all Ni(II) ions in all phases in the sample, the possibility that large amounts of nickel are present as nickel hydroxide or as nickel basic salt can be ruled out. Conclusions very similar to those drawn with the $Ni(II)/Al_2O_3$ sample were reached in the case of a $Co(II)/Al_2O_3$ sample (contact time at pH 8.2 3 h; no aging; temperature 298 K; after drying; 2.4 Co wt %) using EXAFS at the Co K-edge: the presence of a cobalt–aluminum coprecipitate was readily demonstrated in the $Co(II)/Al_2O_3$ sample.

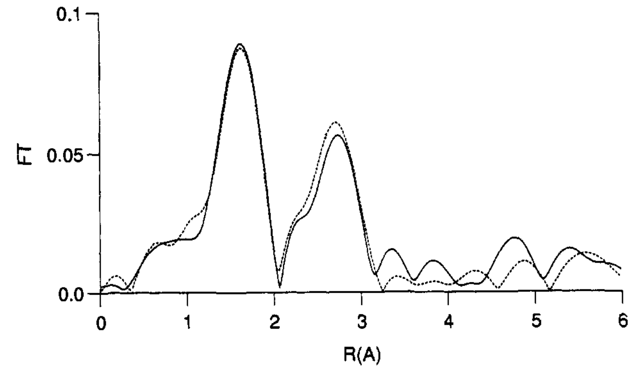

Figure 4. Fourier transformed EXAFS spectra (k^3 weighted; without phase correction) at the Ni K-edge of a wet $Ni(II)/Al_2O_3$ sample before drying (full line; see text) and of $[Ni_2Al(OH)_6](NO_3)\cdot nH_2O$ (dashed line).

We also performed EXAFS measurements on undried $Co(II)/Al_2O_3$, $Ni(II)/Al_2O_3$, and $Zn(II)/Al_2O_3$ samples prepared by impregnation at near-neutral pH in order to investigate the role of drying. The Fourier transformed EXAFS spectra at the Ni K-edge of the $Ni(II)/Al_2O_3$ wet sample before drying (without aging) and of the NiAl hydrotalcite-type coprecipitate are shown in Figure 4. The presence of the coprecipitate in the wet sample was clearly demonstrated. Thus, coprecipitates were found when the EXAFS measurements were performed immediately after filtration and washing. The same result was obtained with Co(II) or Zn(II) ions and with a great number of other γ-Al_2O_3 samples. Drying was not found to have a significant effect on the formation of coprecipitates. As expected, aging greatly enhanced the coprecipitate crystallinity. Some kind of aging may also occur during the impregnation process, i.e., during the contact time or during washing.

In the hydrotalcite structure, the di- and trivalent cations are homogeneously distributed in brucite-type layers. Thus, the formation of such coprecipitates during impregnation requires the breaking of Al–O–Al bonds in the surface region of alumina.[8] Alumina reacts with adsorbing cations.

---

[7] The EXAFS experiments were performed at the LURE (Orsay) synchrotron radiation facilities using the D44 beam line. The spectra were recorded in the transmission mode using two argon-filled ionization chambers as detectors. The spectra of the dried samples were recorded at liquid nitrogen temperature.

[8] Clause, O.; Rebours, B.; Merlen, E.; Trifiro, F.; Vaccari, A. *J. Catal.* **1992**, *133*, 231–246.