Characterization of polynuclear Ni species at the surface of phyllosilicates, gibbsite and amorphous silica using diffuse reflectance spectroscopy

A. C. Scheinost
R. G. Ford
D. L. Sparks

Department of Plant and Soil Sciences, University of Delaware, Newark, DE 19717-1303, USA

Formation of a polynuclear Ni phase at the surface of phyllosilicates has been previously observed by EXAFS (Scheidegger et al., 1997). The exact nature of these precipitates is still in discussion (e.g. Charlet and Manceau, 1994), mainly because the second shell cations Si and Al may not be unequivocally discriminated, and because differences between the Ni-O distances of several possible structures are close to the sensitivity limit of EXAFS (O'Day et al., 1994). Thus, we investigated the potential of diffuse reflectance spectroscopy (DRS) in the UV-vis-NIR range to further elucidate the structure of these precipitates. DRS should be more sensitive to small changes in bond distances than EXAFS (Marco de Lucas et al., 1995).

Materials and methods

We used two phyllosilicates essentially without permanent charge, pyrophyllite (Si-Al) and talc (Si-Mg), a Na-exchanged montmorillonite, and amorphous silica and gibbsite. Initial reaction conditions were 1.5 mM Ni, 5 g L^{-1} suspension, I = 0.1 M. A pH of 7.5 was maintained for all experiments except silica (pH 8.2). EXAFS data were available for reaction products under very similar conditions (Scheidegger et al., 1998). DRS were taken on wet pastes after centrifugation of the suspensions. Spectra of Ni-reacted samples were ratioed against the spectra of the unreacted sorbents to separate the Ni-associated bands.

Sorption kinetics

At least 95% of the Ni was sorbed by pyrophyllite, talc and montmorillonite within 100 to 1000 hours. Silica reacted much faster, and gibbsite much more slowly than the phyllosilicates (Fig. 1).

The spectra show three main crystal field bands assignable to Ni^{2+} in Oh symmetry. The intensities of the bands increases with increasing surface loading
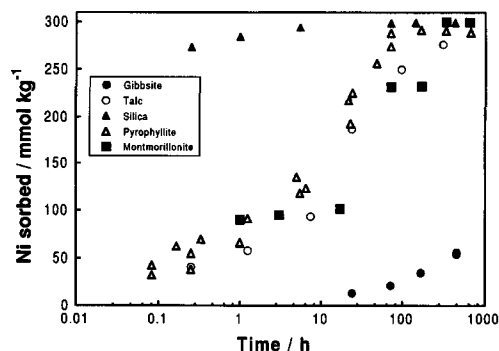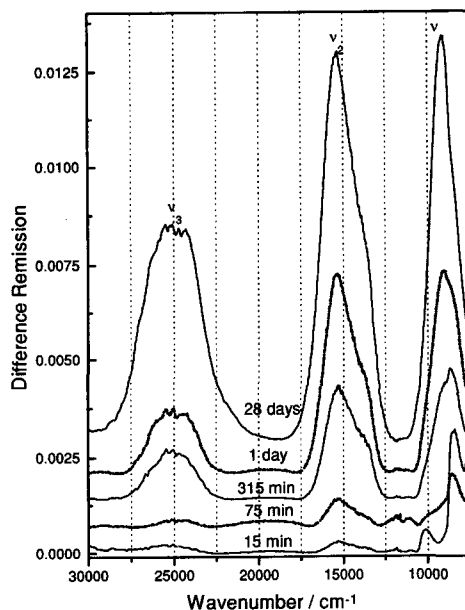

FIG. 1. Reaction kinetics of Ni.
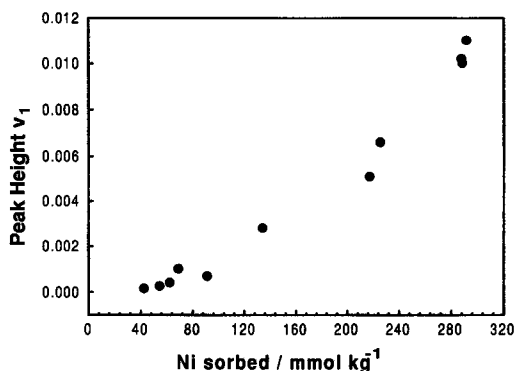

FIG. 2. DRS of Ni on pyrophylllite.

FIG. 3. Increase of v_2 peak height as a function of surface loading.

as shown for the spectra of pyrophyllite (Fig. 2). The band positions remain, however, essentially constant. The height of v_3 is curvilinearly related to the sorbed Ni (Fig. 3).

Characterization of surface species

In Fig. 4, spectra of Ni sorbed on the different minerals are shown (t = 7days, peak height of v_2 normalized). The crystal field splitting energy, 10 Dq (= v_1), increases from 9097 cm^{-1} (montmorillonite) to 9213 cm^{-1} (gibbsite), indicating a decrease in Ni-O bond distances.

The 10Dq of $NiCO_3$ (8390 cm^{-1}), an amorphous Ni silicate (8460 cm^{-1}), $Ni(OH)_2$ (8787 cm^{-1}) (Fig. 5) and the Ni-silicate kerolite (8950 cm^{-1}) (Manceau and Calas, 1985) are lower in energy than the surface species, i.e. have larger bond distances. Synthetic Ni/Al hydrotalcite has a similar 10Dq of 9207 cm^{-1}, and a similar v_2 of 15390 cm^{-1}. The position of v_3 is, however, at a lower energy than the v_3 of Ni-pyrophyllite.

Conclusion

DRS is as sensitive as EXAFS to probe low concentrations of sorbed Ni.

The 10 Dq of Ni surface species is similar to that of hydrotalcite structures, and significantly different from the 10Dq of Ni silicates, $NiCO_3$ and $Ni(OH)_2$.

There are, however, differences between the sorbents, indicating differences in Ni-O bond lengths and bond covalency. We will investigate the spectra of synthetic Ni compounds at various stages of crystallinity to better understand the spectra of surface complexes.
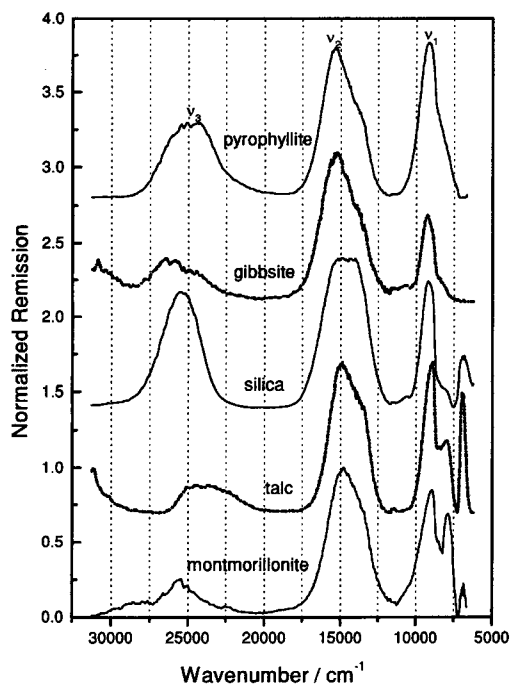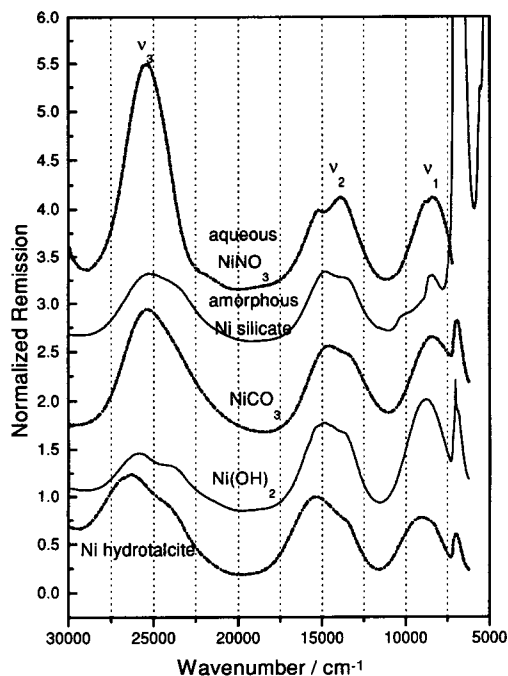

FIG. 4. Normalized DRS of Ni surface species after 7 days.

FIG. 5. Normalized DRS of reference compounds.