Synthesis and Characterization of Amorphous Nickel(II) Aluminosilicates

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Amorphous aluminosilicates containing about 12 wt. $^0/_0$ nickel have been synthesized by cation exchange. Approximately $40^0/_0$ of the nickel content is present in the form of octahedral $[Ni(H_2O)_6]^{2+}$ ions while the bulk of Ni^{2+} is coordinated both by H_2O molecules and by oxygen atoms of the aluminosilicate framework. When the materials are heated in air at 350 °C, a change in the nickel coordination environment/geometry and possibly also a partial oxidation take place.

INTRODUCTION

Synthetic nickel-containing aluminosilicates have for some time been of interest since the aluminosilicate framework is a very suitable support for catalitically active nickel sites. Most attention has been directed to the zeolite--type aluminosilicates so that Ni-zeolites derived from the zeolite A, X, and Y have been extensively investigated.[1-5]

In previous papers one of us (Đ. S.) studied the amorphous aluminosilicates which are obtained if the synthesis of zeolite A is discontinued prior to the onset of crystallization.[6-8] Such amorphous aluminosilicates were then used to prepare and characterize amorphous chromium(III) aluminosilicates. In this work a study has been undertaken with the aim of synthesizing and investigating the corresponding nickel(II) derivatives.

EXPERIMENTAL

Reagents

The sodium aluminate and sodium silicate solutions were of technical grade, while sodium hydroxide, nickel(II) perchlorate, nickel(II) chloride, and sodium chloride were of p. a. purity.

Instrumentation and Chemical Analysis

The X-ray powder diffraction analysis was performed on a Siemens Kristalloflex 4 Diffractometer with the Ni-filtered CuK$_a$ radiation. The diffuse reflectance spectra were obtained on a Beckman 5240 UV Spectrophotometer in the 1400—350 nm range, using MgO as standard; the reflection values were converted into the f(R$_\infty$) values using the Kubelka-Munk relationship[9,10]. Infrared spectra were recorded on a Model 457 Perkin-Elmer spectrophotometer in the 4000—350 cm^{-1}

range with samples in the form of KBr pellets. The elemental analysis on Al, Na and Ni was performed using an Unicam SP9OB Series 2 Atomic Absorption Spectrophotometer, whereas Cl was determined by a Radiometer Selectrode F1O12Cl connected to a Radiometer M62 pH-meter; Si was determined gravimetrically. Water content was obtained from the mass loss at 1000 °C.

Preparation of Amorphous Sodium Aluminosilicate (ASAS)

This material was prepared by a previously published procedure[6], and had the following oxide formula: 1.14 $Na_2O \cdot 1.0\ Al_2O_3 \cdot 2.6\ SiO_2 \cdot 7.1\ H_2O$. Infrared spectrum ($cm^{-1}$): 3380(vs, b), 3240(sh), 2890(w), 2800(w), 2300(vw), 1620(w, b), 1100(sh), 1000(vs, b), 840(w, b), 700(s, b), 570(s, b) 420(s, b) (vs-very strong, s-strong, b-broad, m-medium, w-weak, vw-very weak, sh-shoulder).

Preparation of Amorphous Nickel-Substituted Aluminosilicate

I. Using nickel(II)perchlorate. — ASAS (50 g, 0.110 mol) was suspended into 1.0 dm^3 of aqueous $Ni(ClO_4)_2$ (c = 0.4 mol/dm^3), and the suspension was kept in a closed flask for five days at room temperature with occasional stirring. The suspension was then filtered through a filter of B-3 porosity, the solid thoroughly washed with water and dried in air at room temperature to a constant mass. This gave 58 g of a light-green powder. Anal. found (%): Al 10.06; Na 0.64; Ni 11.46; Si 13.60; mass loss at 1000 °C, 36.37%. This composition corresponds to the following oxide formula: 1.0 $NiO \cdot 0.1\ Na_2O \cdot 1.0\ Al_2O_3 \cdot 2.6\ SiO_2 \cdot 10.9\ H_2O$ (product I). The X-ray powder diffraction pattern of I shows it to be an amorphous material (no diffraction maxima are present in the 2 Θ range of 7—65 °C). Diffuse reflectance spectrum (nm): 1140, 692, 650, 380. Infrared spectrum (cm^{-1}): 3380(vs, b), 3180(sh), 2880(m), 2780(m), 2300(w), 1620(m, b), 1430(w, b), 1370(w), 1070(sh), 1000(vs, b), 850 (s, b), 610(s, vb), 420(s, b) (vb-very broad).
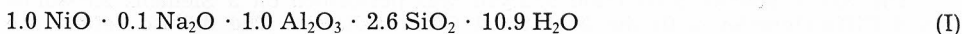
II. Using nickel(II)-chloride. — The procedure was the same as that under I except that $NiCl_2$ instead of $Ni(ClO_4)_2$ was employed. The work-up yielded 58 g of a light-green powder. Anal. found (%): Al 10.11; Na 0.51; Ni 12.51; Si 13.77; Cl — not found; mass loss at 1000 °C, 34.38%. This corresponds to the following oxide formula: 1.1 $NiO \cdot 0.05\ Na_2O \cdot 1.0\ Al_2O_3 \cdot 2.6\ SiO_2 \cdot 10.4\ H_2O$ (product II). The X-ray powder diffraction pattern as well as the diffuse reflectance and IR spectra of II were the same as those of I.
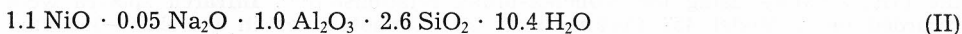
Treatment of I with Aqueous NaCl

A sample of I (10 g, 0.002 mol) was suspended into 1.0 dm^3 of aqueous NaCl (c = 2 mol/dm^3) and the suspension was kept in a closed flask for five days at room temperature with occasional stirring. The suspension was then filtered (yielding a light-green filtrate), the solid thoroughly washed with water and dried in air at room temperature to a constant mass. This gave 8.4 g of a light-green product. Anal. found (%): Al 11.48; Na 2.93; Ni 7.99; Si 15.48; mass loss at 1000 °C, 31.01%. The corresponding oxide formula is: 0.64 $NiO \cdot 0.3\ Na_2O \cdot 1.0\ Al_2O_3 \cdot 2.6\ SiO_2 \cdot 8.1\ H_2O$.

RESULTS AND DISCUSSION

Amorphous nickel-substituted aluminosilicates have been obtained by treating an amorphous sodium aluminosilicate of the composition 1.14 $Na_2O \cdot 1.0\ Al_2O_3 \cdot 2.6\ SiO_2 \cdot 7.1\ H_2O$ (ASAS) with aqueous $Ni(ClO_4)_2$ or $NiCl_2$ while having in the reaction system the Ni : Na molar ratio of 3 : 2. The products are: with $Ni(ClO_4)_2$:

$$1.0\ NiO \cdot 0.1\ Na_2O \cdot 1.0\ Al_2O_3 \cdot 2.6\ SiO_2 \cdot 10.9\ H_2O \qquad (I)$$

with $NiCl_2$:

$$1.1\ NiO \cdot 0.05\ Na_2O \cdot 1.0\ Al_2O_3 \cdot 2.6\ SiO_2 \cdot 10.4\ H_2O \qquad (II)$$

It is seen that the Na^+ by Ni^{2+} ionic exchange is not accompanied by any change in the SiO_2/Al_2O_3 molar ratio, which indicates that no degradation of the aluminosilicate framework occurs in the process. This is contrasted with the analogous preparation of the amorphous chromium(III)-substituted aluminosilicate[6] where dealumination of the framework takes place to a considerable degree. The difference in behavior can be attributed to a significantly lower acidity of aqueous nickel(II), as compared to aqueous chromium(III).[11,12] An increase in the water content relative to that found in ASAS is observed for both I and II. A similar increase has been reported for the analogous conversion of crystalline sodium aluminosilicates (zeolites) into crystalline nickel-substituted aluminosilicates (nickel zeolites).[13] This increase can be explained by the fact that the trend in the size of hydrated ionic radii is generally opposite to that found for crystal ionic radii[14] (Ni^{2+} having a smaller crystal radius than Na^+ [15]).
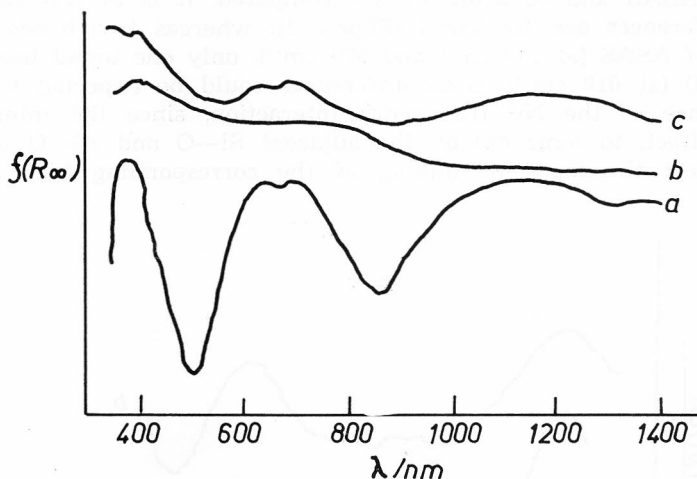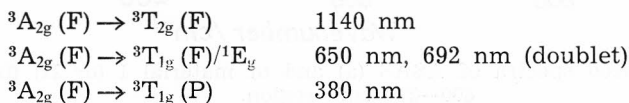

Figure 1. Electronic spectra of I (or II): a) prior to heat treatment; b) after heat treatment at 350 °C; c) after heat treatment at 800 °C.

Diffuse reflectance spectra of I and II (Figure 1a) exhibit in the 350—1400 nm spectral range four absorption maxima: at 380 nm, 650 nm, 692 nm, and 1140 nm. The position of the maxima is in accord with octahedrally coordinated Ni^{2+}, i. e. with the following band assignments:[16]

$$^3A_{2g}\,(F) \rightarrow\, ^3T_{2g}\,(F) \qquad 1140\ nm$$
$$^3A_{2g}\,(F) \rightarrow\, ^3T_{1g}\,(F)/^1E_g \qquad 650\ nm,\ 692\ nm\ (doublet)$$
$$^3A_{2g}\,(F) \rightarrow\, ^3T_{1g}\,(P) \qquad 380\ nm$$

The splitting of the middle band is due to spin-orbit coupling which mixes the $^3T_{1g}\,(F)$ and ^1E_g states,[17] and it has also been found in some other octahedral Ni^{2+} comlexes with oxygen ligands, e. g. in nickle zeolites.[18] The spectra of I and II differ somewhat from the spectrum of the free $[Ni(H_2O)_6]^{2+}$ ion, the latter having maxima at 1110 nm, 715 nm, 660 nm, and 400 nm.[19] This suggests that the Ni^{2+} species in I and II is not coordinated

exclusively by H_2O molecules as it is usually assumed for nickel zeolites,[12,20-22] but that at least some of the nickel(II) is also coordinated by the oxygen atoms of the aluminosilicate framework. Such mixed coordination provides an explanation for the fact that only about 40% of Ni^{2+} can be replaced by Na^+ when I is treated with a concentrated NaCl solution. Namely, as the aluminosilicate framework can coordinate transition metal ions in bidentate fashion,[6] it is the chelate effect that prevents the complete replacement of Ni^{2+} by Na^+. It, therefore, follows that ~60% of the total nickel content is coordinated simultaneously by H_2O and the framework O-atoms, whereas the rest (i. e. the exchangeable part) is coordinated only by H_2O molecules.

Infrared spectra of I and II also indicate that coordinative bonds exist between Ni^{2+} and the framework O-atoms. The 800—500 cm^{-1} region in the IR spectra of aluminosilicates is considered to be particularly sensitive to changes in the mode of linking of SiO_4 and AlO_4 tetrahedra.[23,24] If the IR spectra of ASAS and of I (or II) are compared, it is in this region that notable differences can be found (Figure 2): whereas two bands are characteristic of ASAS (at 700 cm^{-1} and 570 cm^{-1}), only one broad band is seen for I (or II) (at 610 cm^{-1}). Such differences could be expected to arise as a consequence of the Ni^{2+}-framework interaction, since the interaction is bound to affect, to some extent, the adjacent Si—O and Al—O bonds and thereby affect the mode of linking of the corresponding SiO_4 and AlO_4 tetrahedra.
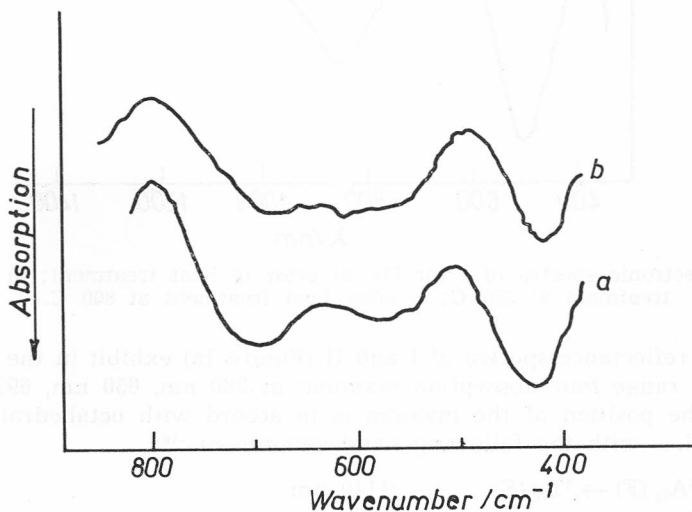

Figure 2. Infrared spectra of ASAS (a) and of material I (or II) (b) in the 800—350 cm^{-1} region.

When products I or II are heated in air at 350 °C for 2 h their color changes from light-green to brown; the same behavior had been reported for nickel zeolites.[25] The brown material exhibits only one absorption maximum (at 400 nm) in its electronic spectrum (Figure 1b). The color change primarily reflects the change in the nickel coordination geometry and

environment caused by the departure of water from the system during the thermal treatment.[18,21] However, in view of the basicity of the aluminosilicate medium, a partial oxidation of nickel(II) to Ni(III) or Ni(IV) could be yet another cause of the color change.[25] Further heating of the brown material at 800 °C results in a decomposition of the aluminosilicate framework[26] yielding a light-yellow product. The electronic spectrum of the latter (Figure 1c), again shows four absorption maxima (at 1130 nm, 700 nm, 620 nm, and 400 nm) characteristic of octahedral Ni^{2+} coordination by oxygen ligands. The spectrum differs somewhat from the spectrum of NiO (NiO having maxima at 1163 nm, 741 nm, 671 nm, and 406 nm[27]), so that the product of the 800 °C treatment can not be described as a simple mixture of oxides (NiO, Al_2O_3, and SiO_2) but rather as a mixed oxide.

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SAŽETAK

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Amorfni aluminosilikati sa oko 12 mas. % nikla dobijeni su jonskom izmenom. Oko 40% nikla nalazi se u obliku oktaedarski koordiniranih jona $[Ni(H_2O)_6]^{2+}$, a preostali nikal koordiniran je sa molekulima vode i kiseonikovim atomima iz aluminosilikatne rešetke. Zagrevanjem na vazduhu, na oko 350 °C dolazi do promena u koordinaciji, odnosno geometriji nikla, a moguće je da dolazi i do delimične oksidacije nikla.