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Properties of nickel (II) doped silica xerogels

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Silica xerogels doped with varying content of Ni^{2+} are prepared using a sol–gel method based on acid-catalyzed hydrolyzation of tetraethylorthosilicate (TEOS) and gelation at 50 ^{o}C. The samples are investigated by differential scanning calorimetry, DSC, thermo gravimetry, TG and X-ray diffraction. Detailed thermal analyses up to 500 ^{o}C demonstrate a strong effect of the Ni content on the crystallization behavior of doped xerogels. A sharp endotherm of dehydration is observed in the vicinity of 150 ^{o}C. The activation energy related to this endotherm is evaluated to E_a = *80* [kJ/mol]. Additional two endotherms are observed depending on both Ni amount and heating rate.

Keywords: nickel doping, silica xerogels, thermal analysis, activation energy

INTRODUCTION

Nanostructured materials are of increasing interest because of their physical properties and technological applications. Mechanical, thermal, optical, electrical, magnetic and catalytic properties are size-dependent and diverse for nano and bulk materials [1–3]. A number of works is focused on new methods of synthesis of NiO nanoparticles [4–7]. They have been prepared by decomposition of nickel hydroxide [2,5], by decomposition of nickel acetate [6], or by oxidation of Ni nanoparticles [7]. Crystalline NiO is obtained by decomposition of nickel (II) nitrate hexahydrate through pyrolysis of its aerosol nitrate [8].

The sol-gel process is a method for synthesizing new materials [9-17]. Sol-gel chemistry offers possibility for preparation of transparent ceramic materials like xerogels. The sol-gel incorporation of high amounts of rare-earth ions using tetraethoxysilan (TEOS) and nitrate solutions of rare earth ions was recently described [9–20]. The monoliths obtained in our recent papers display interesting optical properties [17,18]. In our previous paper [21] we described for the first time, in detail, the thermal behaviour of Sm^{3+} doped silica xerogels. Strong influence of Sm content on the thermal properties of xerogels was demonstrated. Two different activation energies related to dehydration and chemical decomposition of $Sm(NO_3)_3 \cdot 6H_2O$ were evaluated: E_a = 38 kJ/mol, and E_a = 210 kJ/mol [18]. The aim of this study is to investigate thermal behavior of nickel (II) doped silica xerogels.

EXPERIMENTAL

Xerogels doped with Ni(II) were prepared at room temperature by acid-catalyzed hydrolyzation of tetraethylorthosilicate (TEOS), dissolved in ethanol (EtOH) and hydrolyzed with HCl at *pH=2*. It was followed by gelation and subsequent drying at 50 ºC (Boeco dry block). Prior to hydrolysis a 0.55 M $Ni(NO_3)_2$ solution was added to the TEOS / EtOH solution. The initial molar composition for all samples was TEOS / H_2O = 1/4, with Ni/Si contents of 0, 0.01, 0.03, 0.05, 0.1, 0.2 and 0.45, respectively, and a starting amount of 5 ml TEOS. The duration of the different sol-gel steps was 1 h for room - temperature hydrolysis, 48 h for gelation in closed glass containers and 100 h for drying at 50ºC in open glass containers.

Nickel doped silica xerogels were characterized by X-ray diffraction and thermal analysis. A standard powder diffractometer Philips PW 1050 was applied for this study.

The thermal properties of nickel doped silica xerogels were studied systematically by differential scanning calorimetry (DSC) and thermogravimetry (TG) using a Mettler TA 3000 system. All experiments were performed in aluminum pans, in the temperature range from 25 to 500ºC with samples of about 10 mg. The heating rates applied for the DSC study were: 3, 5, 10, 15, 20, 25, 30, and 40 K/min. The weight losses and corresponding temperature maxima were estimated from TG curves.

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RESULTS AND DISCUSSION

Solid grains with typical sizes bellow 1 cm were formed during drying. The undoped gels, as well as samples with low nickel content were transparent while the Ni containing samples were slightly translucent due to the dispersed microcrystallines. This is in line with the structural model discussed in our previous publications, according to which the nitrate complexes are distributed between the SiO_4 tetrahedra [17,19–23].

The DSC study of nickel doped sol-gel samples showed a strong influence of the concentration of Ni^{2+} on the type and shape of the curves. The influence of the heating rate was studied at constant composition. Data from the DSC study were compared with the results of TG analysis and the results are summarized in Table 1.

All Ni-doped xerogels are characterized by three peaks of weight losses (see Fig.1): a first one in the vicinity of 150 ºC, a second one at about 300 ºC and a third one at about 400ºC. The first peak position depends on the concentration of nickel, as well as on the scan rate. On Table 1 data for a heating rate $q = 20$ [K/min] are given.

Table 1 The dependence of the temperatures and enthalpies of the three peaks on the Ni content. The first and the third peak of weight losses are marked with subscripts 1 and 3, respectively. The second DSC peak is too weak.

Ni %	T_1 , °C	H_1 , J/g	T_3 , °C	H_3 , J/g
1	147,4	154,8	352.0	63,6
3	145,5	131,8	374,1	31.0
5	190,1	222,3	375,7	184,1
10	175,4	237,5	398,3	198.0
20	158,5	389,0	341,8	323,6
45	173,5	170.0	325,6	360.0

Similar peaks were observed in all DSC curves. Their temperatures and enthalpies depend on the concentration of Ni^{2+}, and on the scanning rate. Typical DSC and differential TG curves of 0.10 Ni/Si doped xerogel are shown in Fig. 2. The heating rate was 20 [K/min]. The derivative *dm/dT* of the TG curve is a measure of the rate of the weight loss. The temperature of the first DSC endothermic peak coincides with the temperature T_1 of the TG peak of weight losses. It is logical to suggest that the effect is caused by dehydration. In order to estimate the activation energy of this process samples with 5% Ni were scanned with heating rates varying between 3 and 40 K/min. The results are treated by the method of Qzawa (see [24–26]). Dependence of the logarithm of the heating rate $q = dT/dt$ against the reciprocal of the

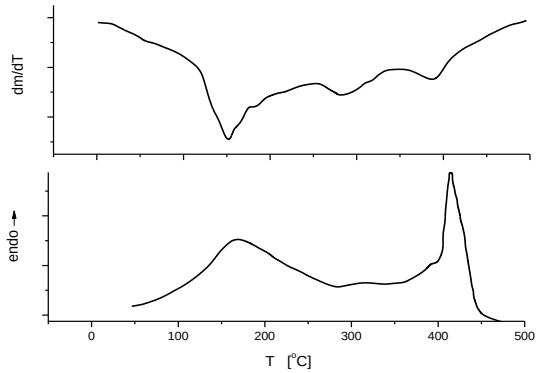

Fig. 1. Results of TG and DSC studies of the samples with 10 % Ni content at heating rates of 20 [K/min]. The top of the figure is the mass derivative as a function of temperature. The bottom presents the DSC scan.

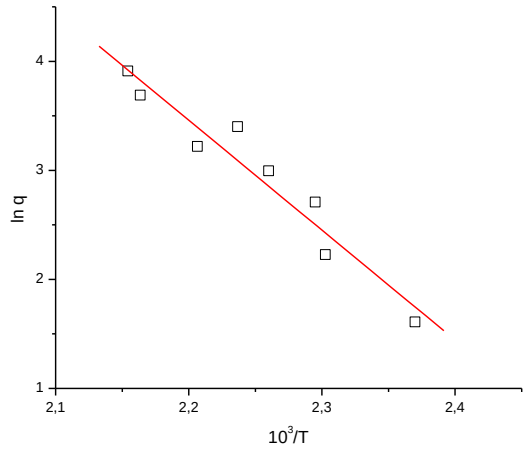

Fig.2. Arrhenius plot of the dependence of temperature of the reciprocal of the maximum of the first endothermic peak, T_{max} [K], on the heating rate, *q*.

maximum of temperature (in [K]) (Arrhenius coordinates) gives a straight line, the slope of which determines the corresponding activation energy, E_a. The dependence of the temperature of the maximum of the peak on the heating rate in Arrhenius coordinates leads to the value for $E_a = 80$ *[kJ/mo]l* (Fig. 2).

The heat treatment leads to two different processes - dehydration and chemical decomposition of the nitrate microcrystals. When heated to 500 ºC, samples change from transparent, light green, to opaque and black. It is known that after heating over 480 °C, nickel nitrate transforms to fully crystalline NiO [8]. Taking into account the results of the TG analysis, it follows that the high-temperature peak reflects the decomposition of dehydrated $Ni(NO_3)_2$. Unfortunately, the process is rather turbulent, resulting in noise in the high temperature peak. Therefore, in this case, analyses in Arrhenius coordinates were not reliable. The non-doped SiO_2 does not display such peak.

4. CONCLUSIONS

Nickel doped silica xerogels were prepared by sol–gel chemistry, including acid hydrolyzation, gelation and drying at 50ºC. From nickel contents about 5% and higher a microcrystalline phase of pure $Ni(NO_3)_2 \cdot 4H_2O$ co-existing with the amorphous SiO_2 gel was obtained. The TG analysis demonstrates presence of two volatile products at heating: water and nitrogen oxides. For the first time detailed DSC and TG analyses of Ni^{2+} doped xerogels is presented. The thermal properties of these gels depend strongly on the Ni content. The heating rate significantly affects the peaks registered by DSC and TG. Two different processes take place at heating: dehydration of xerogels and chemical decomposition of $Ni(NO_3)_2$.

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СВОЙСТВА НА НИКЕЛ (II) ДОТИРАНИ КСЕРОГЕЛИ

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(Резюме)

Силициеви ксерогели, легирани с различно съдържание на Ni^{2+} са подготвени с помощта на золгел метод, основан на киселинно катализиран хидролиз на тетраетилортосиликат (TEOS) и желиране при 50 ° C. Пробите са изследвани чрез диференциална сканираща калориметрия, DSC, термо гравиметрия, TG и рентгенова дифракция. Подробни термични анализи до 500 ° C показват силно влияние на съдържанието на Ni на кристализация поведението на легираните ксерогели. Остър ендотермен пик на дехидратация се наблюдава около 150 ° C. Активиращата енергия, свързани с този пик се оценява на E_A = 80 [кДж / мол]. Два допълнителни ендотермни пика са забелязани като те зависят както от съдържанието на Ni така и от скоростта на нагряване.