

Ni/C/SiO₂ NANOSTRUCTURED COMPOSITES SYNTHESIZED BY CARBONIZATION OF CARBOXYMETHYL CELLULOSE.

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Abstract

Ni/C/SiO₂ porous composites were synthesized by one-pot approach by carbonization of sodium carboxymethyl cellulose/SiO₂ xerogels containing NiCl₂. Synthesized composites are mesoporous materials (average pore size 11.8 -15.1 nm) with the surface area 72.1-91.1 m²/g. Ni nanoparticles of 30-90 nm in diameter are evenly distributed within the volume of composites. The hydrogen sorption capacity at -196 °C and 20 bar measured for as-synthesized samples was 0,32 wt%.

1 Introduction

Porous nanostructured carbon materials are of increasing demand for energy conversion and storage, catalysis, separation and adsorption technologies, biotechnology applications etc. [1, 2].

Using porous templates for carbonization of organic compounds is very prospective approach for the synthesis of various carbon materials with well controlled morphology and properties [1-3]. Pyrolysis and carbonization of precursor occurs directly in the template pores that act as “nanoreactors” influencing morphology and properties of formed carbon.

The main drawbacks of template approach is high cost of templates and use of aggressive reagents (e.g. concentrated alkaline and hydrofluoric acid solutions) for template removal [3].

Taking into account that inorganic templates usually have good mechanical and thermal stability, the possible way to produce value-added materials and to simultaneously reduce expenses and environmental impact of template synthesis of carbon nanostructures is combining the inorganic template with carbon synthesized in its pores into composites displaying improved working characteristics [3].

Structure and properties of synthesized carbon are determined not only by the template used but also by chemical properties of precursor: way to introduce it into the template, use of catalyst and carbonization conditions [1, 4-5].

Sustainable production of carbon nanomaterials could not be performed without using permanently available precursors. Among the best candidates for this purpose, cellulose is one that best suite, not only because it is the most abundant bio-polymer but also because of large variety of well characterized cellulose derivatives with wide range of properties [6]. This allows different ways to introduce cellulose and its derivatives to templates.

The aim of our work was one-pot synthesis of Ni/Carbon/SiO₂ composites by the carbonization of Ni(II) salt/sodium carboxymethyl cellulose/fumed SiO₂ xerogels and study their hydrogen sorption properties.

2 Experimental

2.1 Synthesis of porous precursor-containing xerogels

Fumed silica with specific surface area of 97 m²/g (Alfa Aesar) was used as a structure-forming agent for the gel preparation.

Water solutions of sodium carboxymethyl cellulose (CMC, M_w~90 000, Aldrich) with concentration of 2.0 g/100ml and 3.0 g/100 ml were used as dispersion media for the preparations of gels (C2, Ni/C2 and C3, Ni/C3 correspondently). A 0.2 M water solutions of NiCl₂ (prepared from NiCl₂·6H₂O, ACS grade, Alfa Aesar) were added to gels.

Fumed silica was mixed with CMC solutions and treated in ultrasonic bath during 10 minutes. After sonication, NiCl₂ solutions (Ni/C2, Ni/C3) or water (C2, C3) were added to dispersions. Prepared composites were kept several weeks in tightly closed polypropylene containers for ageing; then formed gels were dried in air at temperature 18-20 °C until constant weight was reached. The composition of xerogels is shown in the table 1.

name	m SiO ₂ [g]	m CMC [g]	m NiCl ₂ ·6H ₂ O [g]
C2	1	0.10	-
C3	1	0.15	-
Ni/C2	1	0.10	0.08
Ni/C3	1	0.15	0.12

Table 1. Composition of precursor containing xerogels used for carbonization.

2.2 Synthesis of porous carbon/SiO₂ composites

The carbonization of porous precursor-containing xerogels was carried out in a quartz tube furnace Tempress in N₂ flow (1 l/minute) by heating up to 750 °C (heating rate was 5 °C/min). Samples were kept at the highest temperature for 30 minutes before cooling down. Before each heating treatment the furnace was purged with N₂ for 5 minutes.

2.3 Investigation of porous carbon/SiO₂ composites

Morphology of synthesized composites was investigated with **Scanning Electron Microscopy (SEM)**. To perform SEM, native (uncoated) samples were placed on sample holders with double-sided conductive glue tape. The acceleration voltage was chosen to be in the range of 1.5 to 10 kV.

Structure of composites was examined with **X-Ray Diffraction (XRD)**. XRD was carried out with Philips X'Pert Materials Research Diffractometer (MRD). Radiation was generated with an X-ray tube with Cu anode (K α radiation, $\lambda=1.54184$ Å) at 45 kV and 40 mA. An X-Ray lens (glass poly-capillary optics) with Ni filter was used as incident optics (the primary beam area was 1.2×0.7 mm²), and a parallel beam collimator was used as diffracted optics. The 2 θ range was 15-80°, and the resolution was 0.05° with 40 seconds averaging time per step.

X-ray Photoelectron Spectroscopy (XPS) was carried out with the Quantum 2000 scanning ESCA microprobe from Physical Electronics in order to investigate chemical structure of composite surface. An Al K α (1486.6 eV) X-ray source was used and the beam size was 100 μm . The analyzed area was approximately 500 \times 500 μm^2 .

Specific surface area and pore size distribution of synthesized composites was determined from low-temperature nitrogen sorption/desorption with the TriStar 3000 Surface Area and Pore Size Analyzer, Micromeritics. Pore size distribution was determined according to desorption isotherm. Outgassing of samples before measurements was performed in vacuum at 200 $^{\circ}\text{C}$ during 3 hours.

Hydrogen sorption isotherms of carbonized Ni/C3 composite were recorded in an intelligent gravimetric analyzer (IGA, Hiden) at temperature -196 $^{\circ}\text{C}$ and pressure range 0-20 Bar; sample was outgassed at 120 $^{\circ}\text{C}$ during several hours prior measurement. Measurements were repeated two times with the same sample.

3 Results and discussion

Silica nanoparticles in water form stable spatial structures gels [7]. Using solutions of polymers as dispersion media leads to the formation of complex polymer/silica gels that transform into porous xerogels after drying [4-5, 7-8].

Carbonization of CMC/SiO₂ xerogels results in porous composites consisting of silica backbone covered with nanostructured carbon layer (fig.1). According to SEM size of primary carbon coated silica particles is <50 nm.

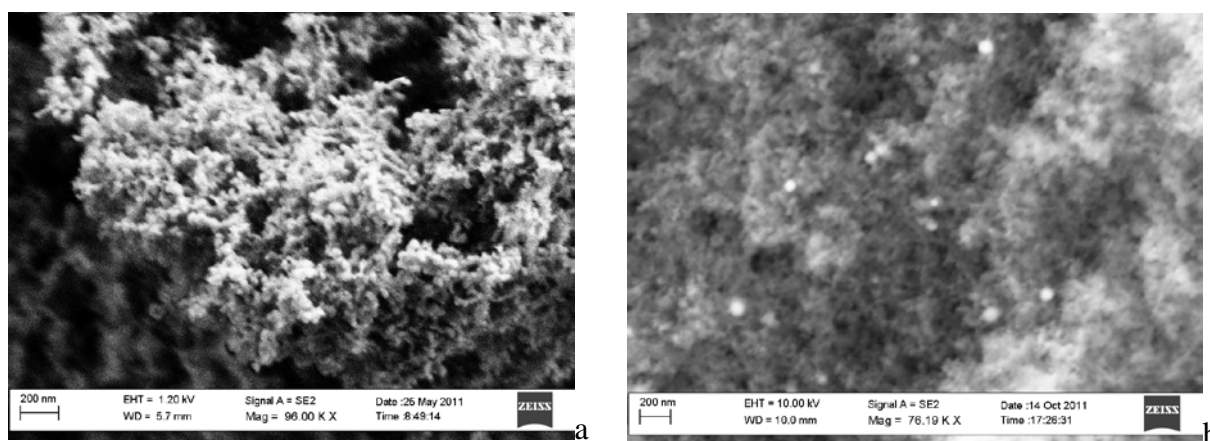


Figure 1. SEM image of porous C/SiO₂ composite synthesized by the carbonization of C3 (a) and Ni/C3 (b) xerogels.

XRD studies showed that carbon synthesized by carbonization of CMC at 750 $^{\circ}\text{C}$ in silica template is amorphous (fig.2).

Carbonization of NiCl₂ containing CMC/SiO₂ composites leads to formation of Ni/C/SiO₂ composites (fig. 2) where Ni is presented mainly as particles with diameter of 30-90 nm (fig 1b). According to XRD, Ni is presented in the face centered cubic phase (fig. 2).

Besides crystalline phase of Ni Ni/C2 and Ni/C3, composites contain NaCl. There are two possible ways of NaCl formation: 1. –through the reaction between CMC and NiCl₂ resulting in Ni salt of carboxymethyl cellulose and NaCl occurring during gel preparation and ageing; 2. – during CMC pyrolysis and NiCl₂ decomposition.

In our opinion the second way is more probable since we did not observe any visible precipitation of insoluble Ni salt of carboxymethyl cellulose in the non-heated mixture of pure NiCl₂ and CMC solutions even after several months. Our observations are consistent with [9], where heating was applied to carry out the reaction between CMC and Ni salts.

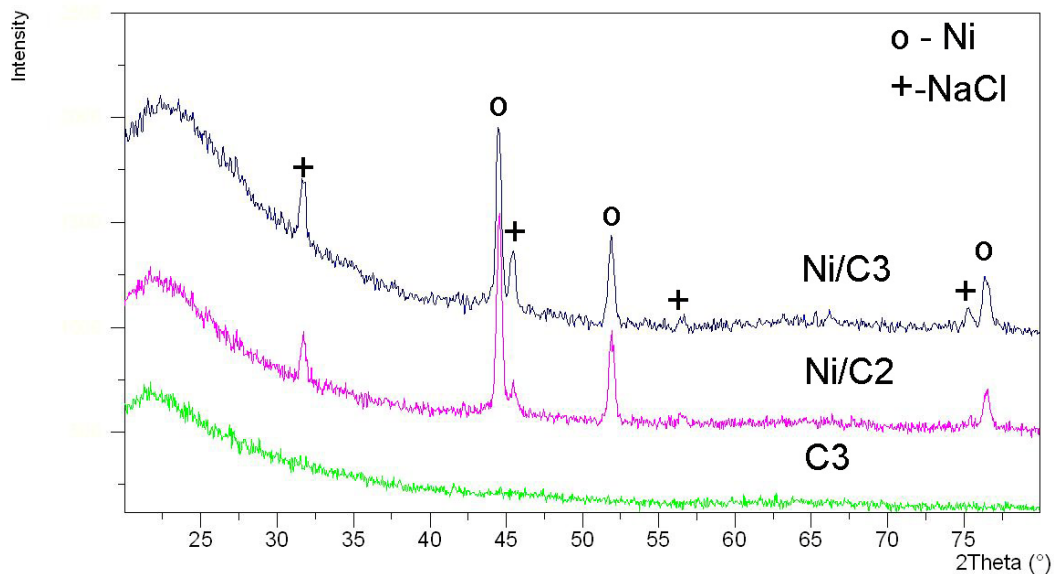


Figure 2. XRD patterns of carbonized C/SiO₂ composites.

C1s XPS spectra of C/SiO₂ composites are asymmetric and broadened (fig.3); they have been deconvoluted to several individual components that could be assigned to the presence of C-C (284.0 eV), C-O (286.0 eV), C=O (287.5 eV), COO (288.8 eV) [4].

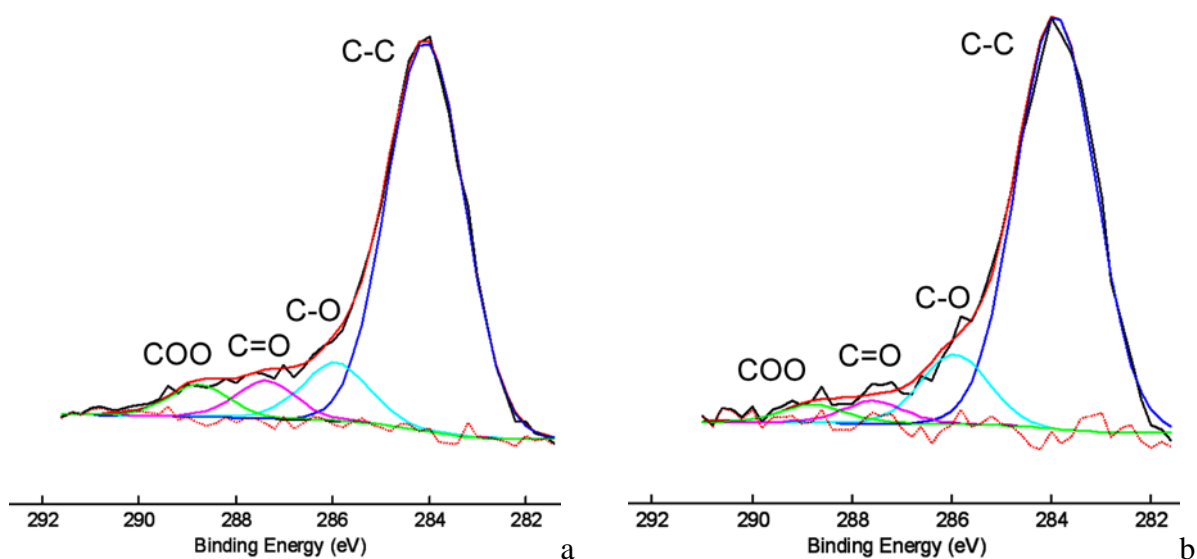


Figure 3. C1s spectra of carbonized C/SiO₂ composites: C3 (a), Ni/C3 (b)

Content of COO and C=O bonds in C/SiO₂ composites with Ni is significantly lower compared to samples synthesized without NiCl₂ (table 2). This could be caused by catalytic action of Ni nanoparticles formed *in situ*.

composite	Area [%]			
	C-C	C-O	C=O	COO
C2	61.9	21.0	9.9	7.2
Ni/C2	79.5	13.4	2.9	4.2
C3	77.4	10.8	6.3	5.5
Ni/C3	81.5	11.8	3.7	3.0

Table 2. Area, % of individual components of C1s spectra of C/SiO₂ composites..

According to the data from low-temperature nitrogen adsorption synthesized C/SiO₂ nanocomposites are mainly mesoporous materials with specific surface area lower than specific surface area of starting fumed SiO₂ (table 4). Large decrease of external surface area is compensated to some extent by the evolution of microporosity.

As could be seen from table 3 change of composites structural properties with their content do not have linear behavior. Ni/C/SiO₂ composites display both higher surface area and higher average pore size compared to C/SiO₂ composite. Both micropore area and external surface area contribute to increase of BET surface area in Ni/C/SiO₂ composites. Results obtained could be explained with complex influence of NiCl₂ and/or Ni formed during heat treatment. Increase of microporous area is caused most likely by carbon layer which is formed, with higher yield, in the presence of Ni catalyst. Higher external surface area of Ni/C/SiO₂ composites is caused by addition of Ni nanoparticles surface area to the total surface area. Increase in the average pore size in Ni/C/SiO₂ composites could be explained by the influence of NiCl₂ on the structure of initially formed wet gels; crystals of NiCl₂·6H₂O did not let gels shrink to the same extent as pure CMC/SiO₂ gels.

composite	BET surface area [m ² /g]	Micropore area [m ² /g]	External surface area [m ² /g]	Average pore size [nm]
Starting SiO ₂	96	n/a	96	n/a
C3	72.1	14.5	57.6	11.8
Ni/C2	91.1	17.3	73.8	15.1
Ni/C3	88.7	15.8	72.9	13.7

Table 3. Structural characteristics of C/SiO₂ composites.

Ni/C3 sample was chosen to investigate hydrogen sorption properties. Low-temperature hydrogen sorption isotherm is presented at Fig.4.

Sample shows 0.32 wt% of reversible hydrogen uptake at 20 Bar and -196 °C. This result is repeatable.

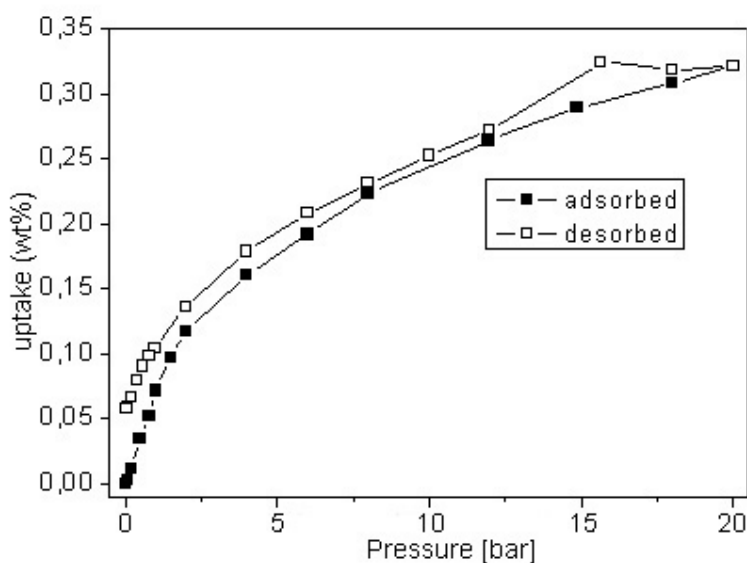


Figure 4. Hydrogen adsorption-desorption isotherm for sample Ni/C3 at -196 °C.

Comparison of results of hydrogen adsorption experiments reported elsewhere is quite difficult because of large range of conditions used and the various definitions of hydrogen adsorption [10-14]. Nevertheless analyzing hydrogen sorption properties of Ni/carbon composites studied in similar conditions, one could conclude that the hydrogen uptake in Ni/C3 is comparable or even higher than reported for composites with similar specific surface area [11].

According to [14] hydrogen sorption capacity of materials correlates to their porous structure and specific surface area. To estimate the general potential of Ni/C/SiO₂ composites synthesized by carbonization of CMC for hydrogen sorption applications we calculated the ratio of hydrogen uptake expressed in wt% to specific surface area of the Ni/C3 sample. This ratio is giving an approximate mass of hydrogen adsorbed at the surface of 1 m². The average value obtained for Ni/C3 material is 3,6×10⁻³ g/m². This value is 1.8 times higher than reported in [10] (2,0×10⁻³ g/m²) for similar materials, however it has been obtained for material with relatively low surface area. If the same ratio will be maintained for material with much higher specific surface area than our material with good hydrogen sorption performance could be synthesized. Taking into account that surface area of carbon composites could be significantly increased by choosing porous templates with higher surface area and by applying activation; CMC is potentially prospective precursor for production of hydrogen storage materials. and requires further investigations.

4. Conclusions

Ni/C/SiO₂ porous composites were synthesized by one-pot approach by carbonization of sodium carboxymethyl cellulose in silica template in the presence of NiCl₂. Synthesized composites are mesoporous materials with the surface area 72.1 – 91.1 m² containing Ni nanoparticles of 30-90 nm in diameter. At the moment the hydrogen sorption characteristics of the material obtained from sodium carboxymethyl cellulose far below performance of other materials, but it can be significantly improved by producing material with increased specific surface area. We are continuing intensive works in this direction since the amount of hydrogen stored per 1 squared meter of material is very promising.

Sodium carboxymethyl cellulose is potentially prospective precursor for synthesis of hydrogen storage materials.

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