CATALYTIC ACTIVITY OF Ni-NANOCLASTER DENDRITIC AGGREGATES INSIDE OF NANOPOROUS CARBON

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Introduction

Fractal route to structure analysis of disordered nanosized and nanostructured media is widely used elsewhere [1,2]. In this work we applied this approach to analyze the structure peculiarities of nickel nanoclusters that are formed in carbon nanopores. Obtained data was correlated with catalytic activity of synthesized materials in two different reactions.

Experimental

Nanostructured high porous carbon material for catalyst support (TC) was prepared by template synthesis [3]. Nickel was deposited on carbon support by method [4] from nickel dimethylglyoxime alcoholic solution of different concentrations with subsequent reduction to metallic state in flowing hydrogen gas at temperature 250-300°C. Small-angle X-ray scattering (SAXS) experiments were performed using a Kratky camera. The FFSAXS package [5] was used to smooth out the SAXS curves and to correct them for parasitic scattering. The global unified equation of Beaucage [6] has been used to fit the measured SAXS intensity curves. The nitrogen adsorption-desorption isotherms were measured by Sorptometer "KELVIN-1042" (Costech Microanalytical). The pore size distributions were calculated using BJH method.

Catalytic activity test in reaction of cathodic reduction of hydrated protons at temperatures 45-90°C and atmospheric pressure was carried out in electrochemical equipment [7]. Hydrocracking of isopropyl benzene at temperatures 270°C and pressure 4.0 MPa was carried out in membrane reactor [8]. Tested catalysts were deposited in form of thin layer on the surface of proton conducting membrane at cathode side.

Results and Discussion

Pore size distribution of TC with deposited Ni nanoclusters is showed in Fig. 1. Parameters of pore structure are presented in Table 1. Fig. 1 shows that effective pore diameter of initial TC decreases on about 1.6 nm after nickel deposition. So, an effective Ni nanoclusters size is about 0.8 nm. As a deposited Ni content increases, a pore diameter of TC weakly decreases and a width of pores size distribution some spreads (Table 1).

SAXS curve of initial TC (curve 1, Fig. 2) has 3 rectilinear regions that correspond to 3 levels of fractal aggregation. The 1st region corresponds to the primary pores. The 2nd region corresponds to mass fractal aggregates of pores with mean diameter about 30 nm (Table 1, Fig. 3). The 3rd level aggregates diameter exceed the upper bound of the camera resolution (more than 500 nm).

SAXS curve 2 (Fig. 2) of catalyst system with 1.25% Ni has only two 2 rectilinear regions but their slopes are similar to ones in curve 1 (Fig. 2) of initial TC support.

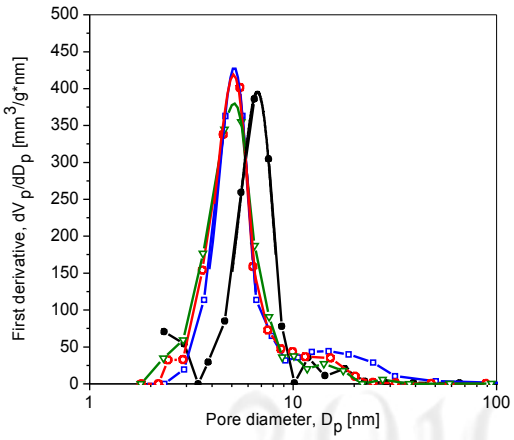

Fig. 1 Pore size distribution of TC with deposited Ni: 1 – initial TC; 2 – 1.25% Ni on TC; 3 – 2.5% Ni on TC; 4 –5.0% Ni on TC.

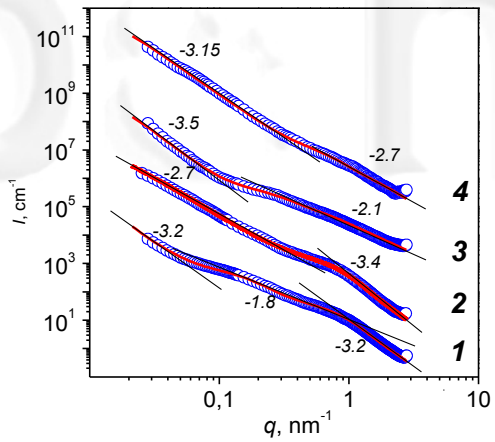

Fig. 2 Normalized SAXS curves in log(I) – log(q) scale: **1** – initial TC; **2** – 1.25% Ni on TC; **3** – 2.5% Ni on TC; **4** –5.0% Ni on TC

X-ray scattering intensity of Ni nanoclusters is about an order greater than of initial TC. So the curves 2-4 in Fig. 2 represent X-ray scattering mainly by Ni nanoclusters. The size of primary particles at low Ni content is close to such for matrix pores (Table 1). It means that Ni clusters deposited on inner surface of pores. The size of mass fractal aggregates of 2nd level is beyond of registration region.

SAXS curve 3 (Fig. 2) of supported 2.5% Ni on TC is quite different nevertheless that it has also 2 rectilinear

regions. The size of primary particles (1st level, Table 1) enlarges and the slope of correspondent segment in the curve 3 (Fig. 2) fits to mass fractal aggregation. So, obtained dendritic structure of Ni nanoclusters appears on the inner surface of carbon pores. Dendrites of Ni nanoclusters sprout into neighboring pores enlarging the size of primary particles. The size of mass fractal aggregates of 2nd level is beyond of camera resolution.

SAXS curve 4 (Fig. 2) of supported 5% Ni on TC is similar to curve 3. But, because of compacting of Ni nanoclusters layer with increasing of metal content and converting one into condense metal layer the size of primary particles decreases, directed to the size of initial primary pores in TC.

Table 1. Structure of TC with deposited Ni

Fitting SAXS curves parameters						N_2 adsorption		
Sample	Fractal Aggr. level	Fractal Aggr. type [1]	**D**	**Rg,** nm	**ds,** nm	**Dp** nm	**Δ**	S_{BET} m^2/g
TC	1	S	2.8	2.2	5.7	6.7	2.9	1120
	2	M	1.8	11.0	28.4			
	3	S	2.8	> 200	> 500			
TC+ 1.25%Ni	1	S	2.6	2.3	5.9	5.1	2.2	990
	2	M	2.7	> 200	> 500			
TC+ 2.5% Ni	1	M	2.1	5.0	12.9	5.1	2.3	1060
	2	S	2.5	> 200	> 500			
TC+ 5.0% Ni	1	M	2.7	2.7	7.0	5.1	2.8	900
	2	S	2.8	> 200	> 500			

[1]Fractal aggregation type: **M** - mass fractal, **S** - surface fractal;
D – fractal dimension; **Rg**, - gyration radius;
ds = Rg·2.58, diameter of aggregates of appropriate level.
S_{BET} - BET surface area; **Dp** – pore diameter;
Δ - width of pore size distribution band at its half-height.

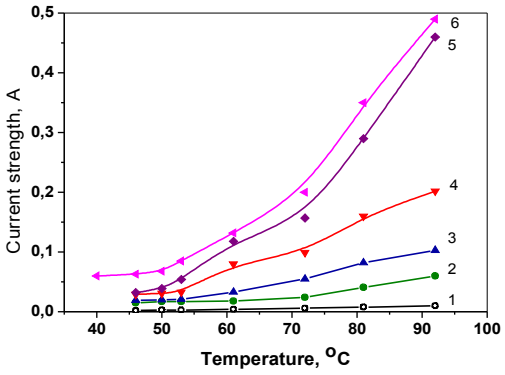

Fig. 4 Current strength with temperature for different cathodes (U=12V): 1 – initial TC; 2 – 5.0%Ni/TC; 3 – 1.25% Ni/TC; 4 – 2.5% Ni/TC; 5 – Raney nickel; 6 – Palladium black.

Catalytic activity of Ni-nanoclusters/TC in the processes of cathodic reduction of hydrated protons and hydrocracking of isopropyl benzene are presented in Fig. 4 and Fig. 5. The catalyst with dendritic structure of Ni nanoclusters (Ni content is 2.5%) shows maximum catalytic activity in both tested processes (curve 4, Fig.4 and curve 3, Fig.5).

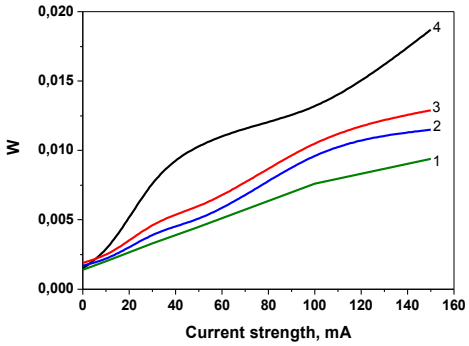

Fig. 5 Isopropyl benzene hydrocracking rate:
1 – 5.0%Ni/TC; 2 – 1.25%Ni/TC; 3 – 2.5%Ni/TC;
4 – industrial Al-Ni-Mo catalyst.

Conclusions

Structure peculiarities of templated nanoporous carbon material with nickel nanoclusters that formed in carbon pores were studied by SAXS and nitrogen adsorption methods. The catalytic activity of these materials in processes of cathodic reduction of hydrated protons and hydrocracking of alkylaromatic hydrocarbons was investigated. It was established that dendritic shape aggregates of Ni nanoclusters showed maximum specific catalytic activity in both catalytic processes. This investigation may be of interest for preliminary optimization of catalyst's performance.

References

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