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Influence of the Polymer Matrix on the Development and Aging of Nickel(II)- and Cobalt(II)-Containing Catalysts in the Liquid-Phase Oxidation of the Sulfide Anion with Dioxygen

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Abstract—The development and aging effects for Ni(II)- and Co(II)-containing catalysts involved in the oxidation of the sulfide ion with dioxygen depend on the nature of the active metal ion and on whether or not the support (polyacrylamide hydrogel) is present. The development time depends on the sulfide phase formation conditions and is note correlated with the catalytic properties of nickel an cobalt sulfides. Increasing the extent of cross-linking of the gel from 1 to 10% does not produce any significant effect on the activity and stability of the catalyst.

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An example of interaction between a catalyst and a reaction medium is a phase transition in the catalyst during a chemical reaction. Such a phase transition can either increase or decrease the catalytic activity [1–4], thus causing catalyst development or aging [5, 6]. These changes can be due to both the reorganization of the phase itself (amorphous-to-crystalline transition, recrystallization, change in the extent of dispersion of the phase, etc.) and changes in the composition and structure of the active sites of the catalyst.

For metallopolymer catalysts, there are other possible factors in development and aging because the immobilization of active sites on a polymer support exerts a strong effect on the activity and performance stability of the catalyst [7]. For example, whether or not the catalyst will develop during Na_2S oxidation with dioxygen depends on the nature of the functional group of the ion exchanger coordinated to the metal ion. Studies of Ni(II)-containing catalysts based on hydrolyzed and unhydrolyzed polyacrylamide hydrogel (PAAH) demonstrated that the development and aging of the catalyst in sodium sulfide oxidation are governed by the cell size of the three-dimensional polymer network of the support [9, 10]. The cell size was deduced to vary from the finding that the hydrolyzed metal-free catalyst has a three times higher swelling capacity than the original polymer, without determining the extent of cross-linking of the hydrolyzed gel.

This study concerns the effects of sulfide phase formation conditions (the presence or absence of a support and the extent of cross-linking of the support) and of the nature of the metal ion on the development and aging of Ni(II)- and Cu(II)-containing catalysts in the oxidation of the sulfide anion with dioxygen.

EXPERIMENTAL

PAAH was obtained by the free-radical polymerization of acrylamide (AA) and *N*,*N*'-methylene-bisacrylamide (B) according to a procedure described in [9]. The reaction initiator was ammonium persulfate (AP), and the promoter of the initiator was *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMED). The reactants were combined in the following order: 4 ml of a solution of B (*m*, g) was added to 12 ml of a solution of AA (*n*, g); next, 1.4 ml of 0.043 M AP and 1.4 ml of 0.043 M TMED were added. The reaction mixture was adjusted to 20 ml by adding water and was left standing for 18–20 h at room temperature. The extent of cross-linking of the gel (s) was controlled by varying the proportion of the cross-linking agent (B) in the mixture of the monomers (AA and B):

$$s = 100 \times n/(n + m), \%$$

where $n + m$, the total amount of the monomers, is 1 g.

The resulting gels were palletized by forcing through a sieve with an opening diameter of 1 mm. The pellets were washed with water and were dried with a series of water–acetone mixtures in which the proportion of acetone was gradually increased from 50 to 100%. The product was filtered and held in air until constant weight.

The swelling capacity (q) of PAAH was determined gravimetrically. A sample of the dry polymer was held in an excess of water for at least 2 h to reach the equilibrium swelling. The resulting gel was separated by fil-

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† Deceased.

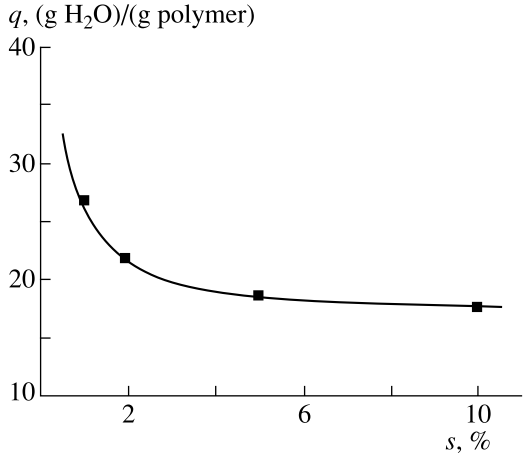

Fig. 1. Swelling capacity (q) of PAAH in water as a function of the extent of cross-linking (s).

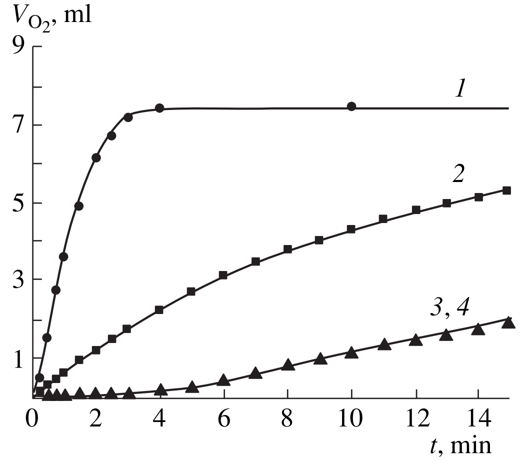

Fig. 2. Dioxygen uptake kinetics in Na_2S oxidation at 40°C in the presence of (*1*) $NiCl_2$, (*2*) $CoCl_2$, (*3*) PAAH ($s = 2\%$). (*4*) The same in the absence of a catalyst. $V_{Na_2S} = 5$ ml; $[Na_2S] = 0.1$ mol/l; $V_{MeCl_2} = 0.2$ ml; $[MeCl_2] = 0.01$ mol/l.

tration and weighed. The swelling capacity was calculated as

$$q = (m_s - m_0)/m_0,$$

where m_0 is the weight of the dry polymer and m_s is the weight of the swollen gel.

We synthesized PAAH samples with extents of cross-linking equal to 1, 2, 5, and 10 wt %. The swelling capacities of these samples were determined by averaging the results of at least three measurements. The swelling capacity of PAAH as a function of the extent of cross-linking is plotted in Fig. 1. Clearly, as the extent of cross-linking increases from 1 to 5%, the swelling capacity gradually decreases from 27 to 19 g H_2O per gram of polymer. Further raising the extent of cross-linking producers no significant effect on the swelling capacity of the polymer, which almost reaches its limit at $s = 10\%$. By contrast, at $s < 1\%$, q increases rapidly as s is decreased. However, it turned out that PAAH with such a low extent of cross-linking has mechanical properties unsuitable for a catalyst support.

Based on the swelling capacity data for PAAH with $s = 1$–10%, we determined the weight of the dry polymer that will be completely swollen on being impregnated with 0.2 ml of a 0.01 M metal chloride solution and will take up all of the solution. This technique enables one to prepare catalysts with a precisely known metal content (C_{Me}) of the polymer matrix (in this study, $C_{Me} = 2 \times 10^{-6}$ mol for all samples).

Catalytic activity was determined in a static system described in [10] under the following conditions: oxygen consumption was measured at atmospheric pressure with an accuracy of ±0.05 ml, O_2 was in excess, the reaction temperature was 40°C in all experiments, and the amount of the Na_2S solution (0.1 mol/l) was 5 ml.

The measured volumes were reduced to normal conditions using the formula

$$V_{O_2} = V_{meas}[273/(273 + t)](p_{atm} - p_{H_2O})/760,$$

where t is room temperature and p_{H_2O} is the water vapor pressure in the burette. From these data, we derived oxygen uptake (V_{O_2}) versus time (t) curves. By graphical differentiation of these curves, we determined current oxygen uptake rates (W).

We carried out at least three replica series of measurements for sodium sulfide oxidation in the presence of Ni(II)/PAAH, Co(II)/PAAH, $NiCl_2$, and $CoCl_2$. Furthermore, we demonstrated that the metal-free polymer matrix is catalytically inactive in the oxidation reaction. The data obtained are presented in Figs. 2–5.

RESULTS AND DISCUSSION

It follows from the data presented in Figs. 2–4 that the Ni(II)-containing catalysts are more active in Na_2S oxidation with dioxygen than the Co(II)-containing catalysts, irrespective of whether the gel support is employed. This result is in agreement with the order of the activities of transition metal ion catalysts established for the liquid-phase oxidation of the sulfide ion with dioxygen [11].

Note the S-like shape of the oxygen uptake curves, which indicates that the oxygen uptake rate passes through an extremum during the reaction in all catalytic systems. This is most clearly demonstrated in Fig. 5. The run of the curves reflects the changes in catalytic activity, which arise from the nonstationarity of the reaction system. Indeed, the catalytically active phase, which is cobalt or nickel sulfide, forms and evolves continuously as the oxidation of the sulfide ion with dioxygen proceeds. These processes may be accompanied by changes in the composition and structure of active sites. As a consequence, the oxygen uptake rate

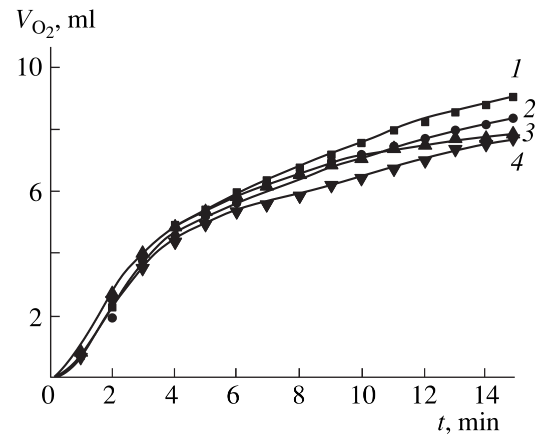

Fig. 3. Dioxygen uptake kinetics in Na_2S oxidation at 40°C in the presence of Ni(II)/PAAH with s = (*1*) 1, (*2*) 2, (*3*) 5, and (*4*) 10 wt %. V_{Na_2S} = 5 ml; $[Na_2S]$ = 0.1 mol/l; V_{NiCl_2} = 0.2 ml; $[NiCl_2]$ = 0.01 mol/l.

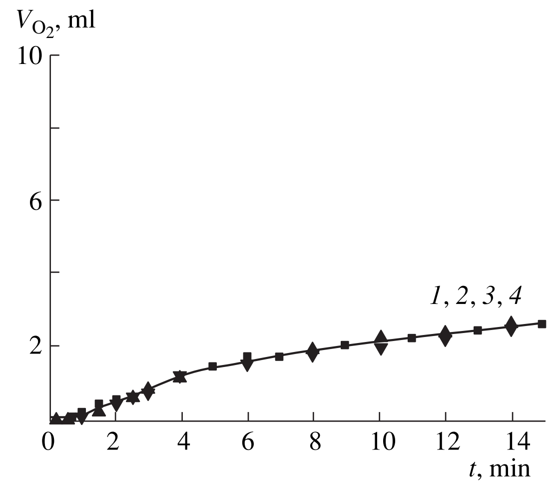

Fig. 4. Dioxygen uptake kinetics in Na_2S oxidation at 40°C in the presence of Co(II)/PAAH with s = (*1*) 1, (*2*) 2, (*3*) 5, and (*4*) 10 wt %. V_{Na_2S} = 5 ml; $[Na_2S]$ = 0.1 mol/l; V_{CoCl_2} = 0.2 ml; $[CoCl_2]$ = 0.01 mol/l.

in the catalytic system varies during the experiment. Regions of initial and maximum rates (W_0 and W_{max}) can be distinguished in the oxygen uptake curves. Furthermore, it is possible to determine the catalyst development time (τ).

It is demonstrated in Figs. 3 and 4 that increasing the extent of cross-linking of PAAH from 1 to 10% in the presence of Ni(II)/PAAH or Co(II)/PAAH causes no significant changes in the oxygen uptake rate over the initial 4–5 min of the experiment. Apparently, in the given range of s values, the activity of these catalysts is independent of s and is determined by the nature of the metal ion in the active phase. This finding indicates that there are no internal diffusion limitations in the polyacrylamide gels and correlates well with the weak dependence of the swelling capacity of PAAH on the extent of cross-linking.

The initial and maximum oxygen uptake rates in sulfide oxidation and the development time for the catalysts are listed in the table.

The activity of the unsupported nickel catalyst is higher than the activity of its cobalt counterpart by a factor of 4 at the beginning of the development period and by a factor of 7 at the maximum rate point. The value of W_{max} exceeds W_0 by a factor larger than 2 (by 116%) in the Ni(II)-containing system and only by 20% in the Co(II)-containing system. The maximum oxygen uptake rate is 3 times lower with Ni(II)/PAAH than with $NiCl_2$ and is 1.5 times lower with Co(II)/PAAH than with $CoCl_2$. The initial oxygen uptake rate in the Ni(II)/PAAH- and Co(II)/PAAH-containing systems is zero.

In an earlier study [10], although the development effect was observed only for the heterogenized catalyst, it was supposed that the unsupported catalyst is also capable of developing. In this study, by shortening the time interval of oxygen uptake measurements from 1 min to 15 s, we confirmed this supposition and were able to determine the development time for the unsupported catalysts. As is demonstrated by the data presented in Fig. 5 and in the table, this time is 30 s.

The results of replacing Ni(II) and Co(II) with Ni(II)/PAAH and Co(II)/PAAH, respectively, and the fact that the oxygen uptake rate is independent of the extent of cross-linking in the catalyst development period indicate that the polymer matrix reduces the reaction rate. This effect can be explained in terms of

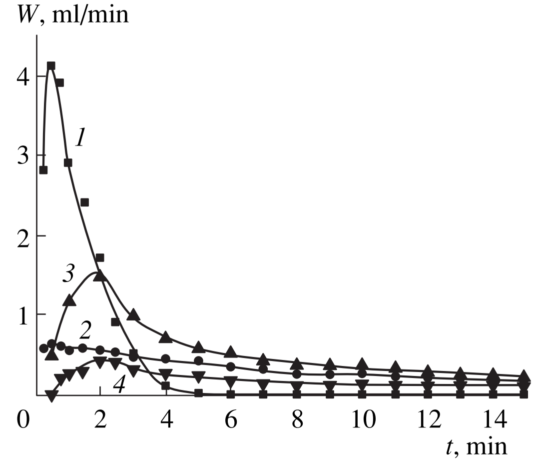

Fig. 5. Variation of the oxygen uptake rate in Na_2S oxidation at 40°C in the presence of (*1*) $NiCl_2$, (*2*) $CoCl_2$, (*3*) Ni(II)/PAAH, and (*4*) Co(II)/PAAH. V_{Na_2S} = 5 ml; $[Na_2S]$ = 0.1 mol/l; V_{MeCl_2} = 0.2 ml; $[MeCl_2]$ = 0.01 mol/l; s = 2%.

Effect of PAAH with $s = 2\%$ on the initial and maximum oxygen uptake rates (W_0 and W_{max}) and on the development time (τ) of the Ni(II)- and Co(II)-containing catalyst in Na_2S oxidation at 40°C

Catalyst	Oxygen uptake rate, ml/min		τ, s
	W_0	W_{max}	
Ni(II)	1.9	4.1	30
Ni(II)/PAAH	0	1.5	120
Co(II)	0.5	0.6	30
Co(II)/PAAH	0	0.4	120

active phase formation conditions [10]. For given active phase formation conditions, the catalyst development time τ is independent of the nature (catalytic activity) of the metal ion and is 30 s for both Ni(II) and Co(II) and 120 s for both Ni(II)/PAAH and Co(II)/PAAH. By contrast, the magnitude of the development effect, defined as the difference between W_{max} and W_0, depends on the nature of the nature of the metal ion: the nickel catalysts, which are more active, develop to a larger extent than the cobalt catalysts.

It is clear from the totality of data presented here that the evolution of a catalyst in the course of a model reaction does not end in the development of the catalyst understood as an increase in catalytic activity and caused by the formation and growth of active phase nuclei and by a change in the nature of the active sites. This is followed by changes resulting in gradual catalyst deactivation. The aging of catalysts is likely caused by the same process as their development. These processes are continuing physical and chemical reorganizations of the sulfide phase under the action of the reaction medium. The chemical changes in this phase are readily detectable: all the cobalt-containing catalysts after the reaction are brownish black, like cobalt sulfide; the nickel catalysts, which are black at the early stages of the reaction, discolor and acquire a gray color unnatural for nickel sulfide. It can, therefore, be assumed that the interaction between the nickel ion and the sulfide ion rapidly yields a highly active sulfide phase of variable composition and that this phase is oxidized simultaneously with the substrate to yield nickel sulfohydroxo species. If this is the case, the following sequence of transformations of the catalytic sites can take place during the reaction:

$$Ni^{2+} \longrightarrow NiS \longrightarrow Ni_xS_y \longrightarrow Ni_xS_yO_zH_k \longrightarrow Ni_xO_zH_k.$$

Indeed, the nickel ion reacts with the sulfide ion in the solution to yield α-NiS [12], which turns into $Ni_{1-x}S$ with a progressively increasing x value upon aging [13]. Nickel sulfide reacts with water and oxygen [14] to turn into NiOHS [13] or $(NiOH)_2S$ [12], and these compounds can undergo deeper oxidation.

The complete deactivation of the unsupported nickel catalyst is observed as early as the fifth minute of the run (Figs. 2, 5). The resulting nickel compounds do not catalyze the oxidation Na_2S and even slow down the background oxidation of the substrate. This is not observed with the supported nickel catalyst, and Ni(II)/PAAH and Co(II)/PAAH age in similar ways.

Thus, it follows from our data and the literature that the evolution of the nickel- and cobalt-containing catalysts in sodium sulfide oxidation with dioxygen is due to the formation and conversion of the polysulfides and hydroxosulfides of the active phase during this reaction. The following factors are essential here:

(1) the variability of the composition of the active phase (x, y, z, and k vary constantly, reaching the point of the complete absence of S, O, or H);

(2) the crystallization of an amorphous sulfide, yielding crystallites, and changes in the crystallite size;

(3) changes in the functional coverage of the crystallites.

CONCLUSIONS

The polymer matrix slows down the formation and reorganization of the sulfide phases of the nickel and cobalt catalysts and the crystallization of these phases by hampering the migration of metal ions between gel cells, but this is not correlated with the catalytic activity of the phases. Furthermore, the heterogenization of the catalysts reduces their catalytic activity and, at the same time, makes their performance more stable.

The extent of cross-linking of the polymer does not have any significant influence on the magnitudes of the catalyst development and aging effects.

The cobalt catalysts develop and age at a noticeably lower rate than the nickel catalysts. This correlates well with catalytic activity data: the less active the catalyst the lower its development and aging rates; the higher the development rate, the higher the aging rate.

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