

DECOMPOSITION OF HYDROGEN PEROXIDE ON NICKEL-SILVER TWO-COMPONENT CATALYSTS

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The catalytic and physico-chemical properties of low-temperature nickel-silver catalysts with nickel oxide concentrations up to 43.8% (*m/m*) are examined *via* decomposition of hydrogen peroxide in aqueous solution. The mixed catalysts prepared at 250°C are composed of partly decomposed silver carbonate or oxide and nickel carbonate or hydroxide decomposed to a low degree only and exhibiting a very defective crystal structure. The activity of these catalysts is determined by the surface concentration of silver ions, which is affected by the nickel component present. The latter also contributes to the thermal stability of the catalytic centres of the silver component, *viz.* the Ag⁺ ions. The concentration of these ions varies with the temperature of the catalyst treatment, the activity varies qualitatively in the same manner, and the system approaches the Ag-NiO composition. The catalytic centres are very susceptible to poisoning by chloride ions. A previous exposition of the catalyst to a gamma dose of 10 kGy from a ⁶⁰Co source has no measurable effect on the physico-chemical properties of the system.

The decomposition of hydrogen peroxide on silver catalysts, with or without modifiers, has received considerable interest; still, the mechanism of the process has not been elucidated completely. The complexity of this problem is documented, for instance, by the fact that the reaction order varies within the interval of 1–2 in dependence on the various parameters of the system such as the pH, initial peroxide concentration, *etc.*¹ The reaction course is complicated by the partial dissolution of silver^{1,2} and its partial surface oxidation^{1,3}, resulting in variations in the catalyst activity during the reaction. This indicates that the catalyst activity is markedly affected by the oxygen present on its surface⁴. Chemisorbed oxygen on the surface of a silver catalyst influences significantly the concentration of acceptor-type catalytic centres, which are believed^{4,5} to be decisive for the hydrogen peroxide decomposition.

The study of the kinetics of decomposition of hydrogen peroxide on a silver catalyst and the preparation of an efficient silver contact are of practical importance since silver catalysts are used for the preparation of cathodes for oxygen-hydrogen fuel cells on which oxygen is reduced, the catalyst accelerating the hydrogen peroxide decomposition and thereby the total rate of the electrochemical reduction⁶.

The objectives of the present work were to examine how the activity of silver catalysts is affected by nickel compounds, which are used, mostly in the form of nickel oxide, as components in fuel cell electrode catalysts; to establish the effect of the catalyst preparation temperature on the activity; and to seek whether

the catalyst activity can be modified by ionizing radiation similarly as for other two-component systems involving nickel oxide⁷.

EXPERIMENTAL

The silver–nickel mixed catalyst specimens were prepared by precipitation with potassium carbonate in solutions containing nitrates of the two metals in different proportions (all compounds were of reagent grade purity). After repeated washing with hot water and filtration, the precipitates were dried at room temperature in darkness for 12 h and then at 50°C for 5 h. The dry products were calcinated in air in an electric furnace at 250°C. The samples were washed with hot water until a negative reaction to phenolphthalein, dried, and ground in a ball mill. Screened fractions of grain size below 60 µm were used. Some of the samples were thermally treated at temperatures from 200 to 500°C. In the final contacts, silver and nickel were determined by titration with potassium rhodanide and with Chelaton 3, respectively. In addition to total silver, silver ions in the catalyst surface layer present in Ag₂O were also determined with regard to the fact that silver oxide is to a degree soluble in water:



In the presence of potassium iodide added to the aqueous suspension of the catalyst, equilibria (B) and (A) shift forward and silver oxide dissolves completely. The amount of silver ions in the catalyst can be determined by titrating the unreacted iodide with silver titrant solution. The surface concentration of the chemisorbed oxygen was determined in all samples by iodometric titration after Weller⁸. The specific surface area was measured *via* low-temperature adsorption of nitrogen from a 1 : 3 nitrogen–hydrogen mixture; titanium dioxide whose specific surface had been measured by the BET method served as the standard. The microstructure of the samples was examined by X-ray diffraction (Cu anode) on a TUR M 62 instrument equipped with a goniometer. Immediately prior to the testing, portions of the catalysts were exposed to a 10 kGy dose of ⁶⁰Co gamma radiation in air at room temperature. The kinetics of the test reaction was investigated by measuring the rate of oxygen evolution from the reaction system at constant temperature and pressure. An aqueous solution containing hydrogen peroxide in a concentration of 0.12 mol l⁻¹ was used for the measurements at four different temperatures, *viz.* 15, 20, 25, and 30°C. With the amounts of catalyst used, 5–10 mg, the total error lay in the range of ±20%. Under these conditions the reaction was proved to proceed in the kinetic region.

RESULTS

The data given in Table I give evidence that the catalysts contain, in addition to silver and nickel oxide, additional components whose concentration increases with the nickel oxide concentration (increase in the mass deficit *D*). The specific surface area increases in this direction up to a concentration of 35.8% NiO (sample No 10), followed by a rapid drop in this parameter. The amount of silver ions per unit amount of silver *a*_{Ag}, on the other hand, is independent of the catalyst composition and lies in the range of 35–50% except for sample containing 1.5% NiO where this amount

TABLE I

Composition of the catalysts, mass deficit D , specific surface area S , and relative amount of silver ions with respect to total silver a_{Ag}

Sample No	NiO % (m/m)	Ag % (m/m)	D %	S $m^2 g^{-1}$	a_{Ag} %
1	0.0	93.7	6.3	0.93	45.3
2	1.5	82.8	15.7	2.90	72.7
3	3.3	83.1	13.6	4.94	48.1
4	6.3	82.1	11.6	6.60	50.3
5	12.7	75.4	11.9	7.34	44.8
6	13.8	72.4	13.7	6.46	35.4
7	16.3	67.5	16.2	6.13	38.2
8	19.7	64.8	15.5	11.37	38.4
9	29.1	53.1	17.8	12.80	45.6
10	35.8	43.5	20.7	22.81	38.4
11	37.4	30.9	31.7	5.61	48.2
12	43.8	24.9	31.3	5.18	45.0

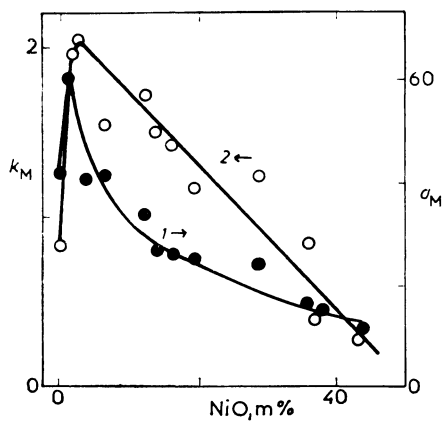


FIG. 1

Dependence of the amount of silver ions normalized with respect to the catalyst weight a_M (%) 1 and of the rate constant k_M ($l g^{-1} min^{-1}$) 2 on the composition of the contacts

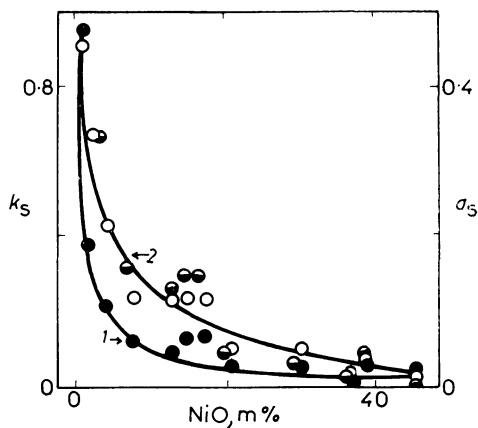


FIG. 2

Dependence of the amount of silver ions normalized with respect to the catalyst surface area a_S ($g m^{-2}$) 1 and of the rate constant k_S ($l m^{-2} min^{-1}$) 2 on the composition of nonirradiated (○) and gamma irradiated (●) contacts

is somewhat higher. The amount of silver ions per unit catalyst weight (a_M), however, is a markedly nonmonotonic function of composition with a pronounced maximum at 1.5% NiO (Fig. 1, curve 1), and the amount of silver ions per unit surface area (a_S) drops rapidly with increasing nickel oxide concentration particularly in the low-concentration region (Fig. 2, curve 1). No chemisorbed oxygen was detected iodometrically on any of the catalysts. The X-ray diffraction patterns displayed only the most intense selective reflections of silver metal or silver oxide and, in part, silver carbonate. All the reflections recorded were diffuse to a high extent.

Preliminary experiments revealed that conducted to a low degree of conversion only (10%) the reaction is one of the 1st order, and the catalyst activity can be characterized by the rate constant normalized with respect to either the catalyst weight (catalyst activity k_M) or surface area (specific catalyst activity k_S). In higher stages of the reaction, at higher reaction temperature, higher initial concentrations of hydrogen peroxide, or lower concentrations of catalyst, a change in the order of the reaction was observed in the sense of its slowing down. The catalyst samples were compared in terms of the above constants measured at 15°C (Figs 1 and 2, curves 2). The dependence of the rate constant k_M on composition agrees qualitatively with that of a_M (Fig. 1) with an expressive maximum at 3.3% NiO, and the dependence of the k_S constant is in qualitative accordance with that of a_S (Fig. 2) with a marked decrease in the specific catalyst activity with increasing nickel oxide content particularly in the region of its low concentrations.

The measurements at different temperatures showed that over the temperature region applied the Arrhenius relation is not fully satisfied; the apparent activation energy of the test reaction on the catalysts used thus could not be evaluated.

Chloride ions introduced into the solution in the form of sodium chloride inhibit the test reaction even in concentrations as low as 4.5 mmol l⁻¹ (Fig. 3).

Samples No 7 and 12, containing 16.3% and 43.8% (m/m) NiO, respectively, were subjected to heat treatment at temperatures from 200 to 500°C. The specific surface area decreased (except for sample No 7 treated at 250°C, where this parameter increased considerably), and the mass deficit as determined by chemical analysis decreased as well (Table II). The specific catalyst activity k_S and the specific amount of Ag⁺ ions a_S change with the heat treatment temperature in different ways for the two catalysts, for each of them, however, the parameters vary qualitatively in the same manner (Fig. 4). The X-ray diffraction examination for these samples showed that while the catalysts treated at 200 and 250°C still do exhibit the selective reflections of silver carbonate or oxide, those treated at 300°C or higher do not and the selective reflections of silver metal and nickel oxide only are observed.

The gamma irradiation leaves the physical properties of the catalysts unaltered; only for sample No 1 (silver catalyst) the surface became highly hydrophobic, so that its activity could not be measured. For the remaining irradiated samples the nature of the dependence of the specific catalytic activity on the nickel oxide concentration

is the same as for the unirradiated samples (Fig 2, curve 2). The observed quantitative changes in this parameter lie within the limit of the overall error of measurement, $\pm 20\%$.

TABLE II

Mass deficit D and specific surface area S for samples No 7 and 12 prepared at different temperatures

Temperature °C	Sample No 7		Sample No 12	
	D % (m/m)	S $\text{m}^2 \text{g}^{-1}$	D % (m/m)	S $\text{m}^2 \text{g}^{-1}$
200	19.0	1.52	—	—
250	16.2	9.27	31.3	4.27
300	9.2	7.15	19.3	0.83
350	7.8	3.87	19.4	0.40
400	5.1	1.79	9.2	0.37
500	—	—	2.7	0.31

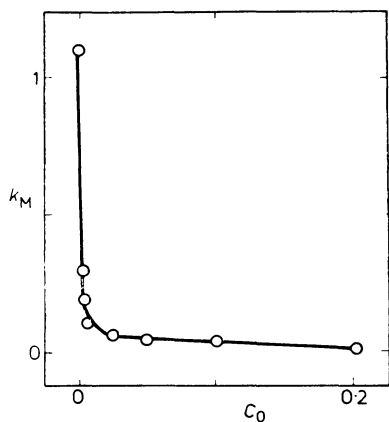


FIG. 3

Dependence of the rate constant k_M ($1 \text{ g}^{-1} \cdot \text{min}^{-1}$) at 15°C on the initial concentration of sodium chloride c_0 (mol l^{-1}) for sample No 2

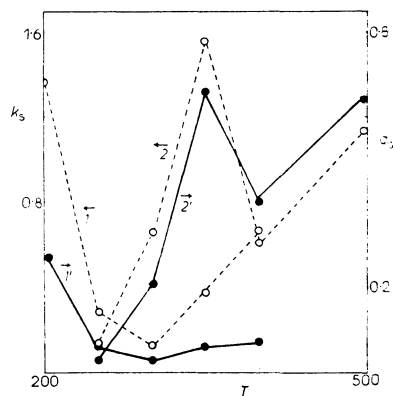


FIG. 4

Dependence of the specific catalyst activity k_S ($1 \text{ m}^{-2} \text{ min}^{-1}$) and of the amount of silver ions normalized with respect to the contact surface area a_S (g m^{-2}) on the temperature of heat treatment T ($^\circ\text{C}$) for samples No 7 1, 1' and 12 2, 2'

DISCUSSION

The fact that the system under study exhibits a considerable deficit in chemical analysis with respect to nickel oxide and silver metal (Table I) indicates that under the calcination conditions used the decomposition of the starting substrates was incomplete, probably on account of the comparatively low calcination temperature 250°C. Really, although silver carbonate starts to decompose at 200°C, complete decomposition only takes place at temperatures⁹ of 280–340°C. The product of this decomposition is silver oxide, which decomposes into silver metal¹⁰ at temperatures as high as 420°C. Similarly, although liberating water at temperatures of 100–210°C, basic nickel carbonate decomposes into nickel hydroxide only at temperatures¹¹ of 260–420°C, and nickel hydroxide in turn converts into nickel oxide in the temperature region¹² of 320–350°C. It follows that the catalytic system is a mixture of partially decomposed silver carbonate or oxide and partially decomposed nickel carbonate or hydroxide, both with a highly disturbed crystal structure. This is corroborated by the X-ray diffraction patterns of the catalysts exhibiting diffuse lines of silver, silver oxide, and silver carbonate. Since the decomposition temperatures of nickel compounds are higher than the corresponding temperatures for the silver compounds, the chemical analysis deficit increases with increasing nickel content of the samples (Table I). This is probably the reason why the specific surface area of the catalysts also increases in this direction; only for samples No 11 and 12, with the highest nickel oxide contents where the degree of decomposition of the precursors is very low, the specific surface area is relatively low (Table I). This concept is borne out by the parameters of the thermally treated samples (Table II), where the chemical analysis deficit diminishes with increasing temperature appreciably and the system composition approaches the silver–nickel oxide two-component catalyst, as confirmed by X-ray diffraction examinations. The associate decrease in the specific surface area is clearly due to the higher degree of ordering of the crystal structure and possibly also to sintering processes occurring on the surface of catalysts exposed to higher temperatures.

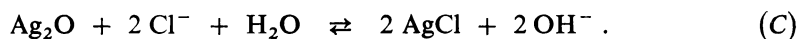
Since nickel oxide does not form in catalysts prepared at 250°C, overstoichiometric oxygen, which is typical for this oxide¹³, could not be detected on their surface.

Only about a half of the silver oxide decomposes into silver metal as evidenced by the a_{Ag} quantity lying in the 35–50% range (Table I). This decomposition is presumably initiated inside the catalyst grain and progresses towards its surface, as indicated by the dependence of a_s on the nickel concentration (Fig. 2, curve 1) which is monotonic in contrast to the analogous dependence of a_M (Fig. 1, curve 1), and also by the fact that lustrous silver metal particles were found inside the grains after dissolving off the catalyst surface layers.

The fact that the amount of silver ions per unit surface area (a_s) drops rapidly

with increasing nickel oxide concentration indicates that the nickel compounds even in low quantities induce reduction of silver oxide.

The catalyst activity parameters k_M and k_S being dependent on the composition qualitatively in the same manner as the silver ion parameters a_M and a_S , respectively, warrant the assumption that the catalytic activity is in a direct relation to the surface concentration of Ag^+ ions. (In fact, the maxima for the dependences of k_M and a_M are mutually slightly shifted, which can be explained so that while the catalytic reaction takes place on the catalyst surface only, the Ag^+ ion concentration concerns both the surface and the sub-surface layers of the contacts.) This is borne out by the linear dependence of the specific activity k_S on the Ag^+ concentration normalized with respect to the catalyst surface area, a_S (Fig. 5). An additional evidence is provided by the suppression of the activity by chloride ions in the hydrogen peroxide solution. Chloride ions block probably the catalytic centres constituted by the Ag^+ ions, giving rise to silver chloride,



As a consequence of this reaction, the pH should increase, as was really observed. A similar poisoning effect of chloride on silver catalysts was observed by Bliznyakov and Lazarov¹⁴ for a catalyst prepared by decomposition of silver oxide at 400°C; prerequisite, however, was an increased alkalinity of the solution (pH 10), whereas at lower pH the dependence of the catalyst activity on the chloride concentration was nonmonotonic, with a pronounced maximum. This has been explained by the authors¹⁴ so that on the one hand, the chloride ions block the catalytic centres of the reaction while on the other hand, being adsorbed they activate other catalytic centres. In our case such a trend of the dependence was not observed, which indicates

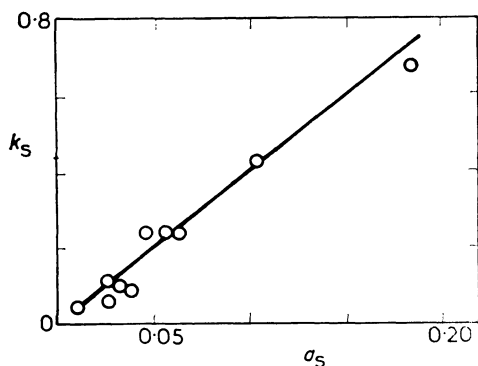


FIG. 5

Dependence of the specific catalyst activity k_S ($1 \text{ m}^{-2} \text{ min}^{-1}$) on the amount of silver ions normalized with respect to the catalyst surface area a_S (g m^{-2})

that the interaction of the catalytic centres of a silver catalyst with its environment depends on its preparation conditions.

Another important evidence for the tight relation between the catalyst activity and the Ag^+ ions is the qualitatively identical dependence of the k_s and a_s parameters on the heat treatment temperature. The fact that the observed changes in these parameters are not in a full quantitative agreement, particularly for sample No 7, shows that in addition to the variations in the Ag^+ ion content the heat treatment leads to other processes affecting the catalyst activity. In terms of the bivalent catalytic centres concept⁷, the Ag^+ ions constitute probably the minority centres⁵ which are in equilibrium with the majority centres of Ag^0 . The heat treatment can, for instance, induce changes in the charge interaction between these centres which is prerequisite for the catalytic effect.

It can be concluded that the activity of the catalysts under study is determined by the silver component solely, while the nickel component does not play a direct part. This is probably due to the fact that for nickel oxide to be catalytically active, Ni^{3+} ions would have to be present, and these were not detected in the catalysts prepared. The partly decomposed nickel carbonate or hydroxide thus only serves as the inactive support for the active moiety, although it affects the concentration of the catalytic silver centres (Fig. 2) and improves their thermal stability (Fig. 4).

The fact that the activity of the catalysts studied is determined by the surface concentration of the Ag^+ ions also offers an explanation for the retardation of the reaction observed in its higher stages, particularly at higher temperature, higher initial concentrations of hydrogen peroxide, or lower concentrations of catalyst: probably, the surface concentration of the Ag^+ ions decreases owing to the reduction of the silver oxide by hydrogen peroxide itself,



or owing to the slow dissolution of silver oxide in water according to Eqs (A) and (B).

The established insensitivity of the physical parameters to gamma radiation is probably due to the low dose applied (10 kGy). The catalyst activity remains virtually unchanged too, hence, the radiation does not alter the mechanism of the catalytic reaction. Moreover, the surface concentration of the silver ions, which are believed to be decisive for the catalyst activity, clearly does not change appreciably on the irradiation; since the initial concentration of Ag^+ ions in the catalytic system is rather high, a radiation oxidation of silver or reduction of silver ions could bring about only a small change in the relative concentration of the catalytic centres constituted by the Ag^+ ions, which would not show up in the total activity of the catalyst system.

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