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**INFLUENCE OF MANGANESE
AND MANGANESE-COPPER CATALYSTS SYNTHESIS
ON DECOMPOSITION OF HYDROGEN PEROXIDE
AND PHENOL OXIDATION**

**WPLYW METOD SYNTEZY KATALIZATORÓW MANGANOWYCH
I MANGANOWO-MIEDZIOWYCH NA ROZKŁAD
NADTLENKU WODORU I UTLENIANIE FENOLU**

Abstract: Characterisation of performance of manganese and manganese-copper oxide catalysts obtained by different methods of synthesis is presented. The specific surface area and catalytic activity were determined in decomposition of hydrogen peroxide and phenol oxidation. The catalytic performance of the catalysts studied was different in the two reactions.

Keywords: catalyst synthesis, hydrogen peroxide decomposition, phenol oxidation

Effective removal of organic compounds from industrial waste is still an important problem from the point of view of the environment protection. Catalytic oxidation of organic compounds in water solutions requires proper catalysts and oxidising agents. Usually the oxidising agents of organic compounds are molecular oxygen, ozone or hydrogen peroxide. The most often used catalysts are those that can be active at mild temperature and under atmospheric pressure. The catalysts used should decompose organic compounds to carbon dioxide and water or other environmentally friendly products. Moreover, the catalysts used in water solutions should have hydrophobic surface. Usually they are oxides of ignoble metals [1]. In the earlier published paper [2] the types of catalysts used in phenol oxidation were listed. The problems related to removal of phenol has been recently discussed in [3, 4]. Phenol is one of the organic compounds usually present in the industrial organic waste that are harmful to people and animals, in particular to microorganisms. This compound disturbs the processes of

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self-purification of water and in concentrations high enough it totally inhibits photosynthesis [1].

In our study phenol was removed from water environment by catalytic oxidation with hydrogen peroxide. The catalysts were synthetic oxides of manganese and manganese-copper obtained by four synthetic pathways: as a result of Mn^{2+} ions oxidation with KMnO_4 or by oxidation with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, by reduction of Mn^{7+} ions with hydrochloric acid and by thermal decomposition of nitrates(V).

Experimental

Synthesis of the catalysts

Synthesis of the manganese and manganese-copper catalysts was performed along the four pathways described below.

Series I. Sample 1 was obtained by oxidation of Mn^{2+} ions by KMnO_4 . Boiling solutions of KMnO_4 and $\text{Mn}(\text{NO}_3)_2$ were mixed and the mixture was maintained at boiling for 15 minutes. Sample 2 was obtained by oxidation of Mn^{2+} ions in the presence of Cu^{2+} by KMnO_4 . Crystalline KMnO_4 was added to a mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ solutions at the molar ratio of 2:3; the mixture was kept at 95 °C for 15 minutes. Sample 3 was obtained by addition of a mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ solutions at the molar ratio 2:3 to a solution of KMnO_4 , the mixture was kept at 95 °C for 15 minutes. Sample 4 was obtained by addition of a mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{OH})_2$ solutions at the molar ratio 2:3 to a solution of KMnO_4 ; the mixture was kept at 95 °C for 15 minutes.

Series II. Sample 5 was obtained by reduction of Mn^{7+} ions by hydrochloric acid. To a solution of KMnO_4 heated to 80 °C, small portions of chloric acid were added (1:1). The addition was stopped when liberation of chlorine was no longer observed. Sample 6 was obtained as above, but later the mixture was washed with nitric(V) acid at 90 °C for two hours. Sample 7 was obtained as above, but in the presence of KMnO_4 solution, $\text{Cu}(\text{OH})_2$ was precipitated and then the mixture was heated to 80 °C and small portions of hydrochloric acid (1:1) were added to it. After elimination of chlorine, washing and drying, the sample was washed with 3 M HNO_3 at 90 °C for 2 hours.

Series III. Sample 8 was obtained by oxidation of Mn^{2+} ions by $(\text{NH}_4)_2\text{S}_2\text{O}_8$. A solution of MnSO_4 was heated to 90 °C and a solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 2M H_2SO_4 was dropwise added to the former one; the reaction lasted for 1 hour. Sample 9 was obtained by oxidation of Mn^{2+} ions by $(\text{NH}_4)_2\text{S}_2\text{O}_8$, after precipitation of $\text{Cu}(\text{OH})_2$ in the presence of oxidised sample. A mixture of MnSO_4 and $\text{Cu}(\text{OH})_2$ solutions was heated to 90 °C and to it small portions of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 2M H_2SO_4 were added; the reaction lasted for 1 hour. Samples 1–9 were filtered off, washed with water to pH = 7 and full decolouration. The precipitates were dried at 120 °C for 8 hours. $\text{Cu}(\text{OH})_2$ was precipitated with a solution of NH_4OH (1:3) from a water solution of $\text{Cu}(\text{NO}_3)_2$ at pH = 7.

Series IV. Sample **10** was obtained by thermal decomposition of fine powdered $\text{Mn}(\text{NO}_3)_2$ at 150 °C for 8 hours in the air atmosphere flown at the rate 30 cm^3/min . Sample **11** was obtained by thermal decomposition of powdered mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ (1:1) in the conditions described above.

Catalytic decomposition of H_2O_2

Catalytic decomposition of hydrogen peroxide was performed according to the procedure described in [2].

Catalytic decomposition of phenol

Catalytic oxidation of phenol of the initial concentration of 2500 ppm was performed with the use of H_2O_2 , according to the procedure described in [2].

Results and discussion

The performance of oxide catalysts with manganese ions or manganese and copper ions, obtained in different procedures, was studied in the reactions of decomposition of hydrogen peroxide and phenol.

Table 1 presents the labelling of samples and their specific surface area values. The surface areas of samples **1**, **5**, **6**, **8** from among the samples containing only Mn ions, are 44, 54, 59 and 252 m^2/g , respectively. Sample **10** obtained as a result of thermal decomposition of $\text{Mn}(\text{NO}_3)_2$ has very small specific surface area of 2 m^2/g .

Table 1

Sample labelling and their textural characterisation

Samples	Labelling	Type of oxide preparation	Specific surface area BET [m^2/g]
Series I Oxidation of Mn^{2+} by KMnO_4	1	Mn	44
	2	Cu-Mn	38
	3	Cu-Mn	118
	4	Cu-Mn	84
Series II Reduction of Mn^{7+} by HCl	5	Mn	54
	6	Mn	252
	7	Cu-Mn	70
Series III Oxidation of Mn^{2+} by $(\text{NH}_4)_2\text{S}_2\text{O}_8$	8	Mn	59
	9	Cu-Mn	92
Series IV Thermal decomposition	10	Mn	2
	11	Cu-Mn	30

According to decreasing values of the specific surface areas, the manganese oxide catalysts can be ordered as

$$6 \gg 8 \approx 5 > 1 \gg 10.$$

The most effective procedure giving the manganese oxide samples of the largest surface area was the reduction of KMnO_4 by hydrochloric acid (1:1) at 80 °C followed by leaching with 3 M nitric(V) acid at 90 °C.

From among the samples obtained by oxidation of $\text{Mn}(\text{NO}_3)_2$, (series I) sample 3 has a large specific surface area of 118 m^2/g , while sample 2 has the specific surface area over three times smaller. Sample 3 was obtained by oxidation of a mixture of water solutions of manganese(II) and copper(II) nitrates(V) by KMnO_4 , while sample 2 by oxidation of a mixture of manganese(II) and copper(II) nitrates(V) with crystalline KMnO_4 added upon boiling. Sample 4 (obtained by oxidation of a mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{OH})_2$ by KMnO_4 solution) has large specific surface area although by 30 % smaller than that of sample 3.

From among the samples from series II, sample 7, containing Mn and Cu ions, has the specific surface area over 3.5 times smaller than sample 6 containing only Mn ions.

From among the series III samples, sample 9 (obtained by oxidation of Mn ions in the presence of Cu ions by $(\text{NH}_4)_2\text{S}_2\text{O}_8$) has relatively large specific surface area but still over 20 % smaller than that of sample 3.

From among series IV samples, sample 11, obtained by thermal decomposition of a mixture of manganese(II) and copper(II) nitrates(V), has the smallest specific surface area of all samples considered. According to decreasing specific surface area, samples containing manganese and copper ions can be ordered as

$$3 > 9 > 4 > 7 \gg 2 \approx 11.$$

The above-discussed results prove that the reaction conditions and procedure influence the size of the specific surface area of the samples. The manganese-copper sample of the largest specific surface area was obtained by using a mixture of water solutions of manganese(II) and copper(II) nitrates(V) and KMnO_4 in solution. The manganese-copper sample of the smallest specific surface area was that obtained by thermal decomposition of a mixture of powdered manganese(II) and copper(II) nitrates(V).

Catalytic decomposition of hydrogen peroxide is characterised by the kinetic curves presented in Fig. 1. For the series of manganese catalysts their activity measured by the amount of liberated oxygen decreases as:

$$1 \approx 6 \approx 5 > 8 \gg 10.$$

The activities of samples 1, 5 and 6 were relatively high and similar, while that of sample 19 was the least active. The activity of sample 8 was relatively high, but lower than the activities of the manganese catalysts from series I and II. As follows from the results the catalytic activity of manganese catalysts in decomposition of H_2O_2 does not depend on the surface area because the activity of sample 6 of very large surface area was similar to those of samples 1 and 5, whose surface areas were 5–6 times smaller.

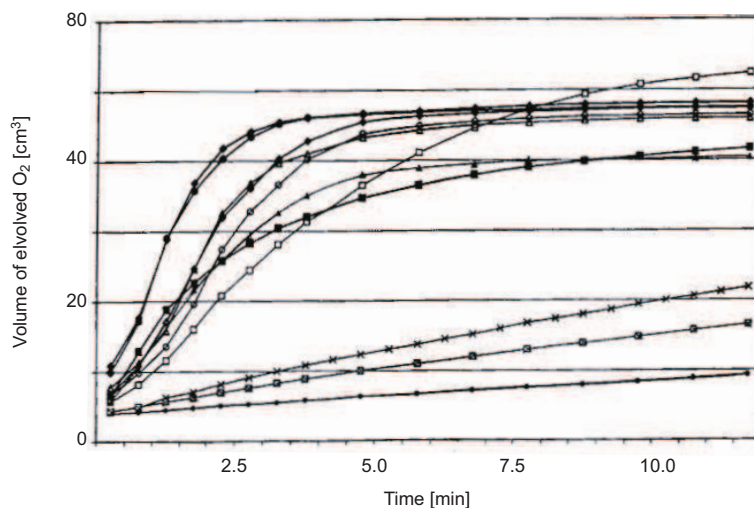


Fig. 1. Kinetic curves of catalytic decomposition of hydrogen peroxide: sample 1 – ◆, sample 2 – □, sample 3 – ▲, sample 4 – ×, sample 5 – Δ, sample 6 – ●, sample 7 – ◇, sample 8 – ■, sample 9 – ○, sample 10 – •, sample 11 – □

All manganese-copper catalysts, except for samples 4 and 11, show high activity in H_2O_2 decomposition. The highest was the activity of sample 2, according to decreasing activity in this reaction the manganese-copper catalysts can be ordered as:

$$2 > 7 \approx 9 > 3 \gg 4 > 11.$$

The catalytic activity of these catalysts in decomposition of H_2O_2 does not depend on their surface area. The catalyst of relatively small surface area (sample 2) proved much more active than the catalyst of 3 times greater surface area (sample 3). Moreover, the activity of the catalysts studied in this reaction was found practically independent of the method of the catalyst synthesis. It was shown that replacement of $\text{Cu}(\text{NO}_3)_2$ by $\text{Cu}(\text{OH})_2$ (samples 4 and 9) in the synthetic procedure gave catalysts of different activity. Sample 11 obtained by thermal decomposition of powdered mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ (1:1) is the least active in H_2O_2 decomposition, similarly as the manganese catalyst – sample 10 – obtained by thermal decomposition of fine powdered $\text{Mn}(\text{NO}_3)_2$.

The performance of the catalysts studied in phenol oxidation is completely different. Fig. 2 presents the kinetic curves obtained for the catalysts in phenol oxidation. According to decreasing activity after 4 hours of the reaction, the catalysts can be ordered as:

$$6 > 10 > 8 > 5 > 1.$$

The most active is sample 6 obtained by reduction of Mn^{7+} ions and having the largest surface area. The next in the sequence is sample 10 of the smallest surface area,

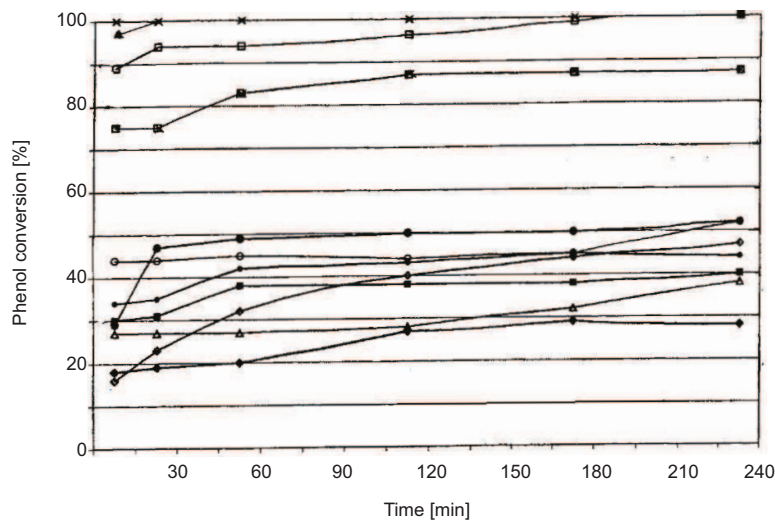


Fig. 2. Kinetic curves of catalytic oxidation of phenol: sample 1 – ◆, sample 2 – □, sample 3 – ▲, sample 4 – ×, sample 5 – Δ, sample 6 – ●, sample 7 – ◇, sample 8 – ■, sample 9 – ○, sample 10 – •, sample 11 – ◻

obtained by thermal decomposition of fine powdered $\text{Mn}(\text{NO}_3)_2$. Samples 8, 5, 1 have the surface areas in the range 44–59 m^2/g , and their ability to phenol oxidation is lower than that of sample 10 of the specific surface area of 2 m^2/g . No correlation between the sample activity and specific surface area was found. The results obtained for samples 5 and 6 show that the reduction of Mn^{7+} ions by hydrochloric acid is insufficient to give an active catalyst, the activity considerably increases after washing with nitric acid.

According to decreasing activity in phenol oxidation the manganese-copper catalysts are ordered as:

$$3 = 4 \geq 11 > 2 \gg 9 > 7.$$

Series I samples obtained by oxidation of Mn^{2+} by KMnO_4 show high activity in this reaction. The low activity of sample 2 from series I can be explained by lower reactivity of KMnO_4 in the crystalline form than that in the form of solution (samples 3 and 4). Surprisingly high was the activity of sample 11 obtained by thermal decomposition of powdered mixture of $\text{Mn}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ (1:1).

As follows from the results, irrespectively of the synthetic procedure applied, the catalysts obtained have the surface catalytic active centres of different number and strength. The centres are of different type in manganese and manganese-copper samples, however, their exact identification needs further studies.

Conclusions

Manganese and manganese-copper catalysts were obtained by four different methods of synthesis. The specific surface area of the samples varied from 2 to 252 m^2/g . In

decomposition of H_2O_2 the activity of the catalysts obtained was different; the lowest was that of the sample obtained by thermal decomposition of powdered mixture of $Mn(NO_3)_2$ and $Cu(NO_3)_2$ (1:1). In phenol oxidation the catalytic activity was the highest for the samples obtained by oxidation of Mn^{2+} by $KMnO_4$ and it was surprisingly high for the sample obtained by the thermal decomposition of powdered mixture of $Mn(NO_3)_2$ and $Cu(NO_3)_2$ (1:1).

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WPLYW METOD SYNTEZY KATALIZATORÓW MANGANOWYCH I MANGANOWO-MIEDZIOWYCH NA ROZKŁAD NADTLENU WODORU I UTLENIANIE FENOLU

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Abstrakt: Przedstawiono wyniki badań nad wykorzystaniem tlenkowych preparatów manganowych i manganowo-miedziowych otrzymanych różnymi metodami syntezy. Dla otrzymanych preparatów wyznaczono wielkość powierzchni właściwej oraz określono aktywność katalityczną w rozkładzie nadtlenu wodoru i utlenianiu fenolu. Wykazano zróżnicowaną aktywność katalityczną preparatów w obu wymienionych reakcjach.

Słowa kluczowe: katalizatory Mn i Mn-Cu, rozkład nadtlenu wodoru, utlenianie fenolu