

Studies on the Phenol Wet Peroxide Oxidation in the Presence of Solid Catalysts

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Abstract

The comparative study of Fe-, Mn- and Cu-oxide catalysts supported on α -Al₂O₃, TiO₂, CeO₂ and pure graphite-like porous carbon Sibunit in the catalytic wet peroxide oxidation by hydrogen peroxide in a stirred batch reactor at 90 °C was performed. The Fe-containing samples supported on α -Al₂O₃ are sufficiently active and most stable and selective in respect to the CO₂ evolution. Cu-containing catalysts are most active, Fe-containing catalysts appear to be much more stable and ecologically benign. The pure Sibunit has shown an appreciable activity and highest selectivity in respect to CO₂. Hydroquinone and pyrocatechol have been found in the liquid phase as intermediates of the oxidation. Kinetics of the change of the phenol, hydrogen peroxide as well as intermediates concentration has been recorded. The oxidation of phenol over Sibunit is assumed to occur via a mechanism, which is different from that for the oxide catalysts.

INTRODUCTION

Aqueous effluents of chemical, petrochemical, pharmaceutical, *etc.* industries contain toxic organic pollutants usually in concentration, which are too high to be treated via their biological oxidation. Catalytic wet oxidation (CWO) employing air (CWAO), ozone or hydrogen peroxide (CWPO) appears to be more efficient and economical, because it allows to reduce significantly the temperature and pressure of the treatment in comparison with non catalytic wet oxidation.

Homogeneous catalysts such as transition metal cations and complexes (Fe and Cu are usually used) are known to be efficient catalysts in the CWAO and CWPO processes [1–3]. However, the heterogeneous catalysts allow simplification the catalyst separation and regeneration. There are two groups of heterogeneous catalysts used usually in CWO. The first group consists of pure and mixed oxides of transition metals (usually Cu, Fe, Mn, Co) or their oxides supported on oxide carriers [1, 3–11]. These catalysts are sufficiently efficient, but

have an essential imperfection, since; the active component can usually leach from the catalysts under the reaction conditions. The second group is noble metals supported on either oxides or carbon [4, 12–17]. In contrast to the oxide catalysts, these catalyst are usually stable, but appear to be much more expensive.

This work is aimed to compare the activity and stability of a wide range of transition metal oxide catalysts as well as pure graphite like carbon Sibunit in the model reaction of the phenol wet oxidation with the hydrogen peroxide.

EXPERIMENTAL

Catalysts preparation

Fe-, Mn- and Cu-containing catalysts were prepared via supporting on such carriers as α -Al₂O₃ (BET surface area 3 m²/g), TiO₂ (BET surface area 9.6 m²/g), CeO₂ (BET surface area 5 m²/g) which are resistant to solving in aggressive aqueous solutions. The catalysts were

synthesized via the precipitation of either nitrate or chloride of the active metal by sodium hydroxide in the presence of an aqueous suspension of the carrier at vigorous stirring. Then the catalysts were washed, dried and calcinated at 260 °C for the Cu- and Mn-containing, or at 500 °C for the Fe-containing samples. The Fe- and Mn-containing catalysts contain 2 % mass while the Cu-containing catalysts contains 1 % mass of the active metal. The catalyst $\text{MnO}_2/\text{CeO}_2$ was prepared via coprecipitation of $\text{Ce}(\text{NO}_3)_3$ and MnCl_2 as described in [10]. This catalyst contains 70 % mol. of Ce and 30 % mol. of Mn. The commercial catalysts Fe-containing catalyst IC-12-74 and commercial sample Sibunit were crushed to powder, and grading fraction with size less than 0.2 mm was used.

Catalysts testing

The catalysts stability tests and screening of the catalyst performance were carried out in the reaction of phenol oxidation by hydrogen peroxide.

The phenol oxidation was carried out in a well-stirred glass batch reactor with a reflux condenser at atmospheric pressure and temperature 90 °C. The initial concentrations of phenol and hydrogen peroxide were 0.01 and 0.1 mol/l, respectively. 1 ml of solution was periodically withdrawn from the reactor for chemical analysis.

Products yields were determined in percents from the theoretical yield.

Analysis procedures

The concentrations of phenol and the products of its oxidation like hydroquinone and pyrocatechol were detected by HPLC with a Milichrom-4 chromatograph (Russia) equipped with an UV detector. The column 2×78 mm with sorbent Nucleosil 100 C-18 5 and eluent 10 % MeOH + 0.05 M NH_4Ac + H_2O were used. Products yields were determined in percents from the theoretical yield.

The concentration of hydrogen peroxide was determined by UV-Vis spectroscopy (spectrophotometer Simadzu UV-300) via the reaction

with Ti. The metal leaches were detected with an atomic absorptive analyzer.

RESULTS AND DISCUSSION

Screening of the catalyst performance in the wet peroxide oxidation of phenol in a stirred batch reactor

The conversion of phenol and hydrogen peroxide after 30 min and 3 h of the reaction and the total organic carbon (TOC) abatement after 3 h are shown in Table 1. The Table 1 presents also the amount of active metals found in the liquid solution after the reaction as well as its final pH.

A blank experiment (No. 1) showed that phenol can be oxidized with hydrogen peroxide at 90 °C without a catalyst, but its conversion after 3 h was only 44 %, and the TOC abatement 12 %. The solution after the reaction has a dark brown color. The rate of the phenol oxidation and selectivity with respect to the CO_2 evolution is noticeably higher in the presence of the catalysts.

At first, we compared activity, selectivity, in respect to CO_2 evolution, and stability from active component leaching for the supported Fe, Mn, Cu-containing oxide catalysts. The nature of the carrier affects essentially the resistance of the active component to leaching under the reaction conditions. The catalyst stability decreases in the order: $\text{CeO}_2 > \text{Al}_2\text{O}_3 > \text{TiO}_2$.

The samples containing CeO_2 (see Table 1, No. 2, 6, 8) turns out to be much more stable. However this observation seems to be connected with the lower pH of the final solution observed in these cases.

The stability of the catalysts supported on same carrier decreases in line: $\text{Fe} > \text{Mn} > \text{Cu}$. The nature of the support affects essentially the catalytic activity of the samples. The sequence of the activity found is following: $\text{Al}_2\text{O}_3 > \text{TiO}_2 > \text{CeO}_2$, the samples supported on CeO_2 (Table 1, No. 2, 6, 8) being not active in the reaction of phenol oxidation. It is well known that the catalysts based on CeO_2 are very active in CWAO [4, 8, 10, 11]. However, the sample $\text{MnO}_2/\text{CeO}_2$ prepared as written in [10] appears to be poorly active in the phenol

TABLE 1

Behavior of tested catalysts in the phenol oxidation by hydrogen peroxide

No.	Catalyst	Phenol conversion, %		H ₂ O ₂ conversion, %		TOC abatement, % (3 h)	Active metal leaching, %	Final pH
		0.5 h	3 h	0.5 h	3 h			
1	None	5	44	15	33	12	—	3.7
2	2 % Fe/CeO ₂	0	0	100	100	0	0.3	4.0
3	2 % Fe/ α -Al ₂ O ₃	46	100	15	100	26	21	2.9
	Second run ^a	17	90	95	100	10	4 ^d	2.9
4	1 % Cu/ α -Al ₂ O ₃	100	100	100	100	48	65	3.0
	Second run ^a	98	100	68	100	55	6 ^d	2.8
5	1 % Cu/TiO ₂	100	100	100	100	39	80	3.0
	Second run ^a	68	97	27	85	35	1.8 ^d	2.9
6	1 % Cu/CeO ₂	5	6	100	100	0	27	4.0
7	2 % Mn/ α -Al ₂ O ₃	41	81	31	59	14	60	3.5
	Second run ^a	26	88	10	62	8	2.4 ^d	3.1
8	2 % Mn/CeO ₂	0	0	100	100	0	39	5.1
9	MnO ₂ /CeO ₂ ^b	14	35	100	100	41	6	5.5
	Second run ^a	10	24	100	100	21	5 ^d	5.7
10	IC-12-74 ^c	13	98	40	100	56	5	2.9
	Second run ^a	99	100	100	100	62	11 ^d	3.6
11	Sibunit	50	86	21	76	50	—	2.7
	Second run ^a	22	77	22	89	60	—	2.9

^aThe catalyst was separated from the solution, washed, dried and then used for the oxidation of the fresh phenol solution.

^bThe catalysts was prepared as described in [10].

^cThe catalyst contains 4 % mass of Fe supported on γ -Al₂O₃.

^dAmount of the active metal in respect to the initial amount of this metal in catalyst the before the first use.

oxidation by hydrogen peroxide. This behavior seems to be connected with a competition of two reactions: the catalytic oxidation of phenol and its derivatives by hydrogen peroxide, and the disproportionation of hydrogen peroxide over the catalyst. The CeO₂ turns to be very active in the reaction of the disproportionation.

The catalytic activity of supported catalysts in respect to the phenol oxidation decreases in the order: Cu > Fe > Mn.

In all cases an essential amount of the active metal appeared to be leached into the solution (see Table 1). The leaching is particularly considerable for the Cu- and Mn-containing catalysts. Therefore, a contribution of homogeneous catalysis cannot be excluded in this case.

The most active samples were separated from the final suspension, then washed, dried, calcinated and then used for the oxidation of a

fresh portion of the phenol solution. The results of these experiments are shown in Table 1 (No. 3, 4, 5, 7). The quantity of the active metal leached from the catalysts at their repetitive use is particularly lower, the catalytic properties in respect to the phenol oxidation decreasing unessentially. The most active in this case proved to be the Cu-containing catalysts (No. 4, 5); the Fe-containing catalyst (No. 3) is less active, and the Mn-containing one (No. 7) is the least active.

Thus, taking into account that the solutions of copper cation are ecologically dangerous, the Fe-containing catalyst supported on α -Al₂O₃ may be considered as the most promising for practical application.

For the comparison we have tested a commercial catalyst IC-12-74 produced via impregnation of γ -Al₂O₃ with Fe. This catalyst contains 4 % mass of Fe (see Table 1, No. 10). The results received in the presence of this cata-

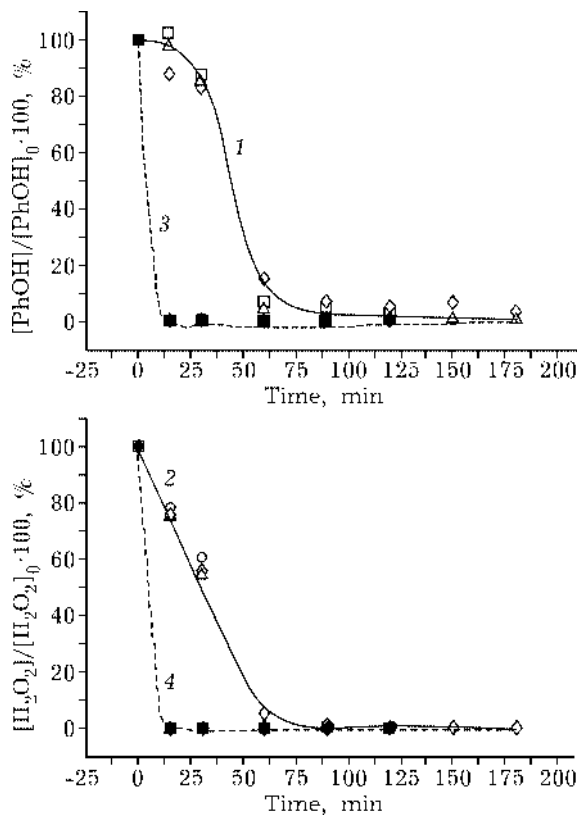


Fig. 1. Disappearance of phenol (1, 3) and H_2O_2 (2, 4) over IC-12-74 catalyst in respect to their initial concentrations (C_0). Solid lines – fresh catalysts; dotted lines – the catalyst was separated from suspension, washed, dried and repeatedly used for the oxidation of the fresh portion of phenol. Initial concentrations: $[\text{PhOH}] = 0.01\text{M}$; $[\text{H}_2\text{O}_2] = 0.1\text{M}$; $[\text{catalyst}] = 5 \text{ g/l}$; temperature 90°C .

lyst are very encouraging. The phenol conversion after three hours was approximately 100%, selectivity to CO_2 were 56 and 62% for the first and repeated uses, respectively. The quantity of iron leached from the catalyst was unessential; they were 5 and 11% for the first and repetitive uses, respectively. Moreover, an induction period was observed on the kinetics of the phenol and hydrogen peroxide consumption (Fig. 1, curves 1, 2). This induction period disappears at the repetitive use of the catalyst (see Fig. 1, curves 3, 4). This may be considered as an evidence for an activation of catalyst at the reaction conditions.

However, the most promising appear to be the results of testing pure porous graphite-like carbon Sibunit (see Table 1, No. 11). Pure activated carbon is widely applied for adsorption of toxic organics from polluted waters [4, 18, 19]. Furthermore, activated carbon as well

as graphite-like carbon are widely used as a good support for the noble metal catalysts [4, 12, 14, 15, 20]. However, we failed to find the published data on an appreciable catalytic activity of pure carbon in the WCO [12, 14, 15]. In our case, pure Sibunit has turned out to be very active in the phenol oxidation. It is less active than the Fe-containing catalysts, but its selectivity in respect to CO_2 is higher than the selectivity of all metal-oxide catalysts tested, except of IC-12-74 which has the same selectivity to CO_2 (ca. 50–60%).

Pure Sibunit turned out to be very active also in the reaction of hydrogen peroxide decomposition (Fig. 2, curve 1), the rate of the decomposition over Sibunit being noticeably higher in the absence of phenol (see Fig. 2, curve 2). This seems to be an evidence that on the Sibunit surface either the both reactions have the same intermediate (*e. g.*, an activated peroxide moiety) or two competitive adsorption processes proceed: that of phenol and of hydrogen peroxide. In the presence of phenol, a part of the Sibunit active sites are occupied, and the rate of the hydrogen peroxide disproportionation decreases.

Kinetic and mechanistic studies

HPLC was used to detect reaction intermediates in liquid phase. Hydroquinone and pyrocatechol were found as such intermediates.

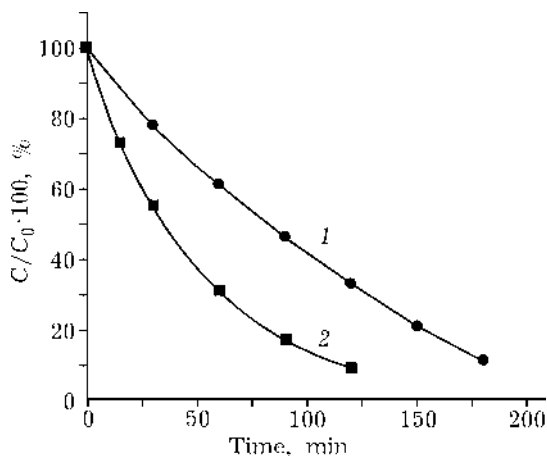


Fig. 2. Decomposition of H_2O_2 over Sibunit, in presence of phenol (1) and in the absence (2) of phenol. Initial concentrations: $[\text{PhOH}] = 0.01\text{M}$; $[\text{H}_2\text{O}_2] = 0.1\text{M}$; $[\text{catalyst}] = 5 \text{ g/l}$; temperature 90°C .

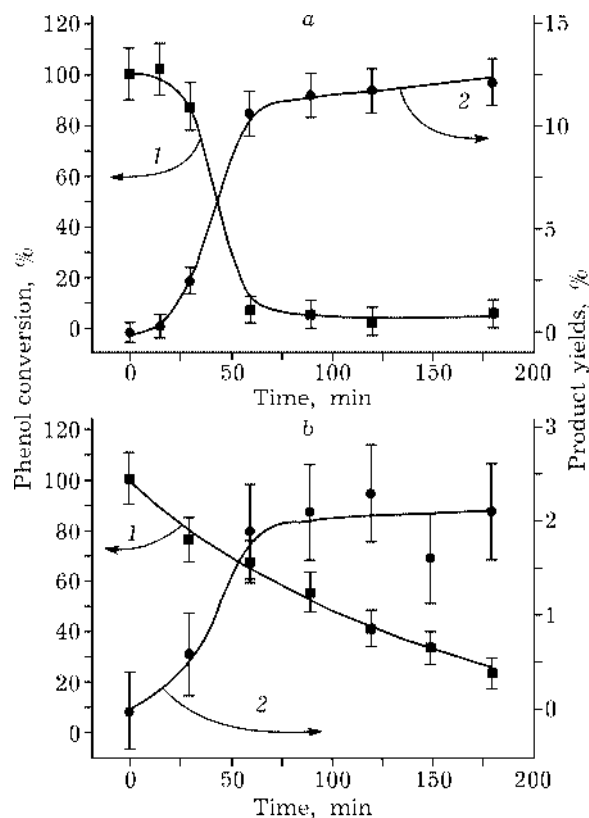


Fig. 3. Phenol conversion (1) and yields of dihydroxybenzenes (sum of hydroquinone and pirocatechol) (2) vs. time at the phenol oxidation with H_2O_2 over IC-12-74 (a) and pure Sibunit (b). Initial concentrations: $[\text{PhOH}] = 0.01\text{M}$; $[\text{H}_2\text{O}_2] = 0.1\text{M}$; $[\text{catalyst}] = 5 \text{ g/l}$; temperature 90°C . Accuracy of the dihydroxybenzenes concentration registration is ca. 10 %. Products yields were determined in percents from the theoretical yield.

We have studied the kinetics of the phenol and hydrogen peroxide consumption as well as the kinetics of the intermediates accumulation. Dihydroxybenzenes like hydroquinone and pyrocatechol were detected as the oxidation intermediates in all cases. However, the accumulation of these products is different for the oxide catalysts and for Sibunit.

In the case of the oxide catalysts, fast consumption of phenol and hydrogen peroxide has been recorded. Typical examples of the kinetics for phenol and dihydroxybenzenes disappearance are shown on Fig. 3, a. Noticeable amount of dihydroxybenzenes (their total yield sometime runs up to 30 %) was produced. If hydrogen peroxide was not spent after the phenol disappearance completely, then the concentration of dihydroxybenzenes disappears too. Moreover, the final solution in all cases with the oxide catalysts was colored from light to deep

brown. This may testify the production of some polymeric products, which are usually found at the phenol oxidation by Fenton-like reagents [2].

The rate of the phenol conversion in the presence of pure Sibunit was lower than in the presence of oxide catalysts, but the TOC abatement at the end of the reaction was higher. The total yields of hydroquinone and pyrocatechol didn't exceed 3 % (see Fig. 3, b), the uncolored solution being received finally.

The above results allow to assume that the oxidation of phenol over Sibunit occurs via a mechanism which is different from that for the oxide catalysts. Apparently, the deep phenol oxidation by hydrogen peroxide seems to proceed on the Sibunit surface without the release of the oxidation intermediates into the liquid phase.

CONCLUSION

The comparison of a large set of the Fe-, Cu- and Mn-containing catalysts supported on oxide carriers in the phenol oxidation by hydrogen peroxide in aqueous solution at 90°C shows that the Cu-containing catalysts are most active. However, the sufficient active metal leaches are found for all oxide catalysts. The stability of the catalysts from the leaching appears to be better at repeated used. Catalysts, which are based on Fe supported on $\alpha\text{-Al}_2\text{O}_3$, are sufficiently active, most selective in respect to the CO_2 evolution, stable and ecologically benign. Pure graphite-like carbon Sibunit has shown the appreciable activity and highest selectivity in respect to complete oxidation and CO_2 formation.

Hydroquinone and pyrocatechol appears to be the main intermediate products of the oxidation, which are evolved in the liquid phase. The studies on the kinetics of the phenol, hydrogen peroxide disappearance and the intermediates accumulation recorded evidence that the oxidation of phenol over Sibunit occurs via a mechanism, which is different from that for the oxide catalysts.

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