



Wet Air Oxidation of Organic Acids and Phenol for Odour Control Processes

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The treatment of odorous pollutants by catalytic wet air oxidation (CWAO) was investigated for model water solutions of different organic acids, such as acetic, succinic and p-hydroxybenzoic acids, and phenol.

CWAO reactions of phenol and acetic acid runs were carried out in a continuous micropilot trickle-bed reactor for about 300 h. Experiments were performed with carbon-supported catalysts PZ-65 (0.6 % Ru+5 % CeO₂/ Sibunit), PZ-68 (0.6 % Ru + 8 % CeO₂/ Sibunit) and carbon material Sibunit-4 at 180 °C for phenol oxidation and at 200 °C for acetic acid oxidation at 50 bar air total pressure. The treated solution was periodically analyzed, collected and submitted to a recycling run. Total organic carbon content (TOC), inorganic carbon content (IC) and concentrations of separate organic substances C_i were analyzed by means of a TOC-meter and an HPLC.

The CWAO of succinic and p-hydroxybenzoic acids have been investigated in a batch reactor at 140 °C and 50 bar air total pressure.

All catalysts were rather active in oxidation of phenol and the activity was found very stable in all cases. No deactivation was observed. After several sets of recycling of treated solutions on catalyst PZ-68, the oxidation activity measured on a fresh phenol solution was found similar to the initial activity. CWAO experiments with acetic acid have shown that Sibunit catalyst did not exhibit catalytic activity up to temperature of 225 °C, whereas the promoted Ru-CeO₂/Sibunit catalysts exhibited high activity at 200 °C; however, their activity decreased significantly as a function of time on stream after 100 h.

Transmission electron microscopic (TEM) investigations of (Ru+CeO₂)/Sibunit catalysts have shown that 1nm-large Ru-particles are associated with 5 nm-large CeO₂ particles supported on the carbon surface. This association is probably very beneficial to the activity of the catalyst.

The results of study have demonstrated that CWAO over Ru-carbon supported catalysts may a suitable technique for degradation of diluted aqueous solutions of organic acids and odour control processes. The mineralization is complete, and a leaching of the metal by the water-organic solutions is most insignificant.

1. Introduction

Wastewaters of many industrial plants are powerful source of odorous organic compounds (Dobrynkin et. al., 2010). Odorous compounds, including organic acids, ketones, sulfides, mercaptans and other noxious compounds are typical representatives released from wastewater treatment facilities, and they

represent strong danger to the environment and populated areas. Short chain volatile organic acids are malodorous compounds and can be easily formed from degradation of different organic compounds, e.g. phenol, aniline, ethers, and corresponding alcohols (Roberts and Hutson, 1999; Boxall, 2009). Although effective odour removal can be achieved by sorption of individual chemicals onto suitable porous adsorbent in some cases, this seems to be inefficient for adsorption of odorous contaminants from water solutions of complex composition (Freitas et. al., 2007). Various odour abatement technologies (biological, chemical, physical, thermal treatments and liquid oxidation) have been developed and applied to treat such substances directly in medium of wastewater in order to minimize emissions of odorous pollutants in environment. Among them catalytic wet air oxidation (CWAO) over heterogeneous catalysts is attracting more interest. CWAO allows to eliminate the odorous molecules and to convert them into environmentally friendly odorless products (e.g. CO₂, N₂, H₂O). CWAO is one of the most economical advanced oxidation process used to treat various high concentrated toxic and non-biodegradable contaminants. The process CWAO is particularly cost effective for treatment of industrial wastewaters with medium chemical oxygen demand (10 g O₂ L⁻¹ <COD<150 g O₂ L⁻¹, Oliviero et. al., 2000; Mikulová et. al., 2007). However for this technology special catalysts are required. Heterogeneous Ru/carbon catalysts are developed intensively for deep oxidation of organic pollutants because their exclusive high activity and good stability despite the fact of high cost of the noble metal.

Our previous studies (Dobrynkin et. al., 2005; Dobrynkin et. al., 2010) conducted with use of the perfect-mixing metal batch reactor have allowed us to evaluate the efficiency of wide set Ru/carbon catalysts, and to determine the initial levels of activity and selectivity of catalysts in WAO of variety substances during short-term experiments (some cycles of tests - totally within 3-12 hours). In contrast of other catalytic systems with high ruthenium content (3-5 % Ru) we have been demonstrated a possibility of the creation of effective ruthenium catalysts Ru-CeO₂/Sibunit and Ru-ZrO₂-CeO₂/Sibunit with a low ruthenium content (~0.6 % Ru) for the deep cleaning of the polluted waters at the moderate temperatures and the odor prevention.

Nevertheless, owing to technical features of the reactor, the catalyst in tests of this kind is subjected force to mechanical effects and crushed. Therefore, the additional long tests of the catalyst are necessary for objective further valuations of developed catalysts. Besides, the results of tests in a continuous micropilot trickle-bed reactor are very useful for the scaling of the process. Among the possible methods of long-term tests of a reactionary medium effect on the catalyst the continuous methods of a measurement of catalytic activity are most simple and convenient (Boreskov, 2003). The experimental technique is well-described for differ cases of heterogeneous catalytic reactions in three-phase systems. In view of the aforesaid the trickle-bed reactors (TBR) are most suitable for laboratory and pilot tests of solid catalysts. The various aspects of TBR applications for CWAO have been reviewed in details by Gianetto and Specchia (1992) and Ranade (2011). As it is well established in literature most of organic components (including phenol and higher aromatic hydrocarbons) from industrial wastewaters are oxidized to CO₂ via intermediate formation of organic acids of short chain (acetic, formic, succinic etc). Besides, phenol and acetic acid are intermediate products in oxidation of various compounds of higher molecular weight; therefore phenol and organic acids were selected as convenient model systems for catalytic wet air oxidation of odorous wastewaters.

2. Experimental and analytical

The catalysts (Ru+CeO₂)/C were prepared by successive supporting CeO₂ and Ru on graphite-like carbon Sibunit-4 as has been described elsewhere (Dobrynkin et. al., 2010).

Catalysts PZ-65 (0.6 % Ru+5 % CeO₂/ Sibunit), PZ-68 (0.6 % Ru+8 % CeO₂/ Sibunit), and Sibunit-4 were tested in 2 reactions: 1) phenol oxidation and 2) acetic acid oxidation. Experiments were performed in TBR (Hastelloy C22, length of 0.15 m, ID of 10 mm). The detailed description of the reactor and the test procedure used in this study has been given by Béziat et al. (1999). Reactions runs carried out for about 300 h, periodically the treated solution was collected, analyzed, and submitted to another WAO run for recycling it. Catalysts (1.0 g): PZ-65 (0.6 % Ru +5 % CeO₂/Sibunit), PZ-68 (0.6 % Ru+8 % CeO₂/ Sibunit), Sibunit-4); solutions: PhOH/H₂O, CH₃COOH/H₂O (C_{0,SOLUTION} of 1.00 g/L); experiments were performed at 180 °C for phenol oxidation and at 200 °C for acetic acid oxidation, 5.0 NL/h of V_{air} , 0.06 L/h of V_{liq}, 50 bar of air total pressure. The layer of catalyst was

located in isothermal zone of the reactor, and the glass balls ($D = 2.0$ mm) were used as a top and bottom inert beds.

Catalysts PZ-45 (0.4 % Ru + 5 % CeO₂/ Sibunit) and PZ-64 (0.6 % Ru + 4 % CeO₂/ Sibunit) were tested in two reactions:

1) Oxidation of succinic acid was performed at 190 °C, 50 bar air total pressure using 150 mL of an aqueous solution containing 5 g/L of succinic acid ($[\text{succinic acid}]_0 = 42.4$ mmol/L, $[\text{TOC}]_0 = 2,035$ mg/L) in the presence of 500 mg of catalyst. Intermediate compounds identified are acrylic acid, acetic acid and in some cases fumaric acid at the beginning of the reaction.

2) Oxidation of p-hydroxybenzoic acid was performed at 140 °C, 50 bar air total pressure using 150 mL of water containing 10 mmol/L of the pollutant ($[\text{TOC}]_0 = 840$ mg/L) and 500 mg of catalyst. Intermediates detected are hydroquinone, phenol, maleic acid.

Wet air oxidation experiments with succinic and p-hydroxybenzoic acid were performed in a Hastelloy C22 reactor of 300 mL volume, fitted with a magnetic stirrer. The other details of operating procedure have been described in (Perkas et. al., 2005). High performance liquid chromatography (HPLC) was used for determination of intermediate compounds by comparing them with external standards of the supposed compounds. Quantification was based on the comparison of chromatograms with those of external standards that were prepared with known concentrations of the identified compounds. Liquid samples (5 mL) were periodically withdrawn and analyzed by HPLC (Car-H column, 0.005 M H₂SO₄ mobile phase, UV detector) to analyze the concentration of the pollutant and to follow the formation of the intermediates and the final products. The TOC (total organic carbon) and IC (inorganic carbon) content were determined with a Shimadzu 5050 TOC analyzer.

Analytically measured values were: content of total organic carbon - TOC, inorganic carbon - IC, (mg/L), concentrations of separate organic substances C_i (mg/L). Selectivity and conversion were used as calculated values: $S_{\text{CO}_2} = (\text{TOC}_0 - \text{TOC}_i) / \text{TOC}_0 = \Delta \text{TOC} / \text{TOC}_0$, $X = (C_0 - C_i) / C_0 = \Delta C / C_0$. The initial reaction rates were calculated from the curves, giving the concentration of corresponding substance or the TOC as a function of time at low conversion.

Active component concentrations were determined by X-ray fluorescent technique using a VRA-20 instrument with a W anode in the X-ray tube. Transmission electron microscopic (TEM) micrographs were recorded on a Hitachi H-600 transmission electron microscope and used for determination of dimensions and distribution of nanoparticles.

3. Results and Discussion

Figures 1 and 2 show the experimental data for phenol and acetic acid oxidation in the presence of catalysts Sibunit-4, PZ65 and PZ68. The blank CWAO experiments performed on the carbon support indicate clearly the self-activity of Sibunits in any cases. This phenomenon has been pointed and the nature of Sibunit catalytic activity has been investigated by various methods by authors of present paper early (Batygina et. al., 2003, Dobrynkin et. al., 2005; Dobrynkin et. al., 2010). Data of the chromatographic analysis of the reaction mixture show the identical complicated composition of the components for phenol oxidation in all cases. Intermediate compounds identified are maleic, acetic and fumaric acids, hydroquinone plus catechol at the beginning of the reaction.

As it was determined, all catalysts are rather active and are stable in oxidation of phenol. For each of them the observable regularities of activity and selectivity in deep oxidation, and also the composition of products are identical. The Sibunit catalyst did not exhibit catalytic activity in acetic acid oxidation up to temperature of 225 °C, whereas the promoted Ru-CeO₂/Sibunit catalysts exhibited high activity at 200 °C (conversion values of acetic acid over Sibunit are roughly 1-3 % at 200-220 °C to be compared with 20-40 % on PZ-65 (0.6 % Ru + 5 % CeO₂/ Sibunit) and PZ-68 (0.6 % Ru + 8 % CeO₂/ Sibunit) catalysts at 200 °C for instance). However, their activity decreased significantly as a function of time on stream after 100 h. Atomic absorptive analysis showed the absence of Ru leaching within the detection limits of ICP (< 0.5 ppm Ru), moreover the content of the supported metal (Ru) and promoter (CeO₂) have exceeded the initial values for the catalyst samples used in acetic acid oxidation, that indicates considerable modification of the surface of carbon as a result of interaction of Sibunit with CH₃COOH and oxygen. TEM investigations of (Ru+CeO₂)/Sibunit catalysts have shown that 1 nm-large Ru-

particles are associated with 5 nm-large CeO_2 particles supported on the carbon surface. This association is probably very beneficial to the activity of the catalyst.

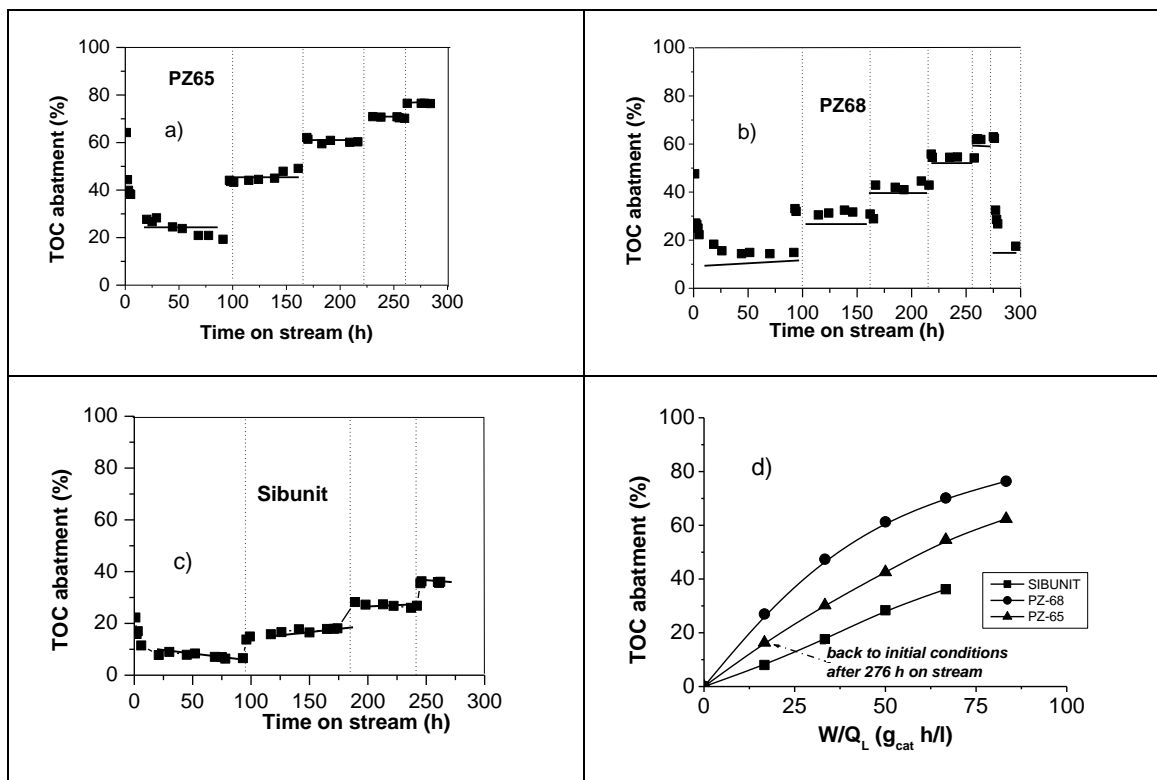


Figure 1: TOC abatement of phenol over (a) PZ-65 (0.6 % Ru+5 % CeO_2 / Sibunit), (b) PZ-68 (0.6 % Ru + 8 % CeO_2 / Sibunit) and (c) Sibunit-4 catalysts ($T = 180^\circ\text{C}$); (d) TOC abatement of phenol versus the ratio between catalyst weight (W) and liquid flow rate (Q_L)

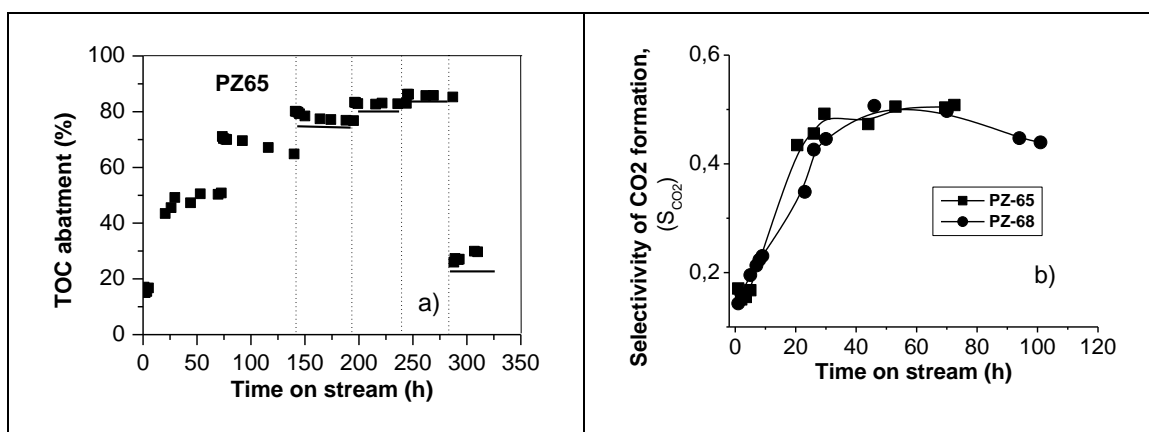


Figure 2: (a) TOC abatement for PZ-65 and (b) selectivity of CO_2 formation in oxidation of acetic acid over PZ-65 (0.6 % Ru + 5 % CeO_2 / Sibunit) and PZ-68 (0.6 % Ru + 8 % CeO_2 / Sibunit) catalysts ($T=200^\circ\text{C}$)

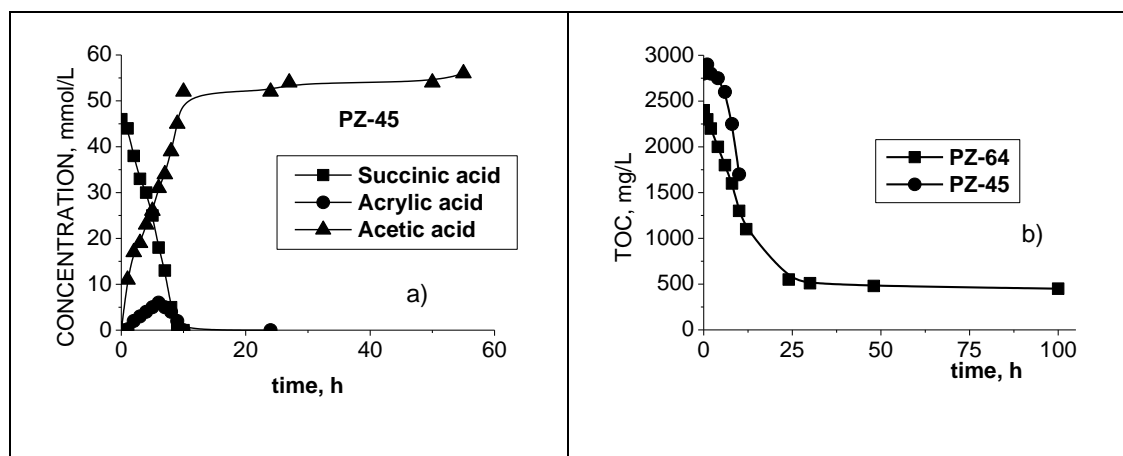


Figure 3: Oxidation of succinic acid in presence of PZ-45 and PZ-64: (a) evolution of the concentrations and (b) TOC content evolution as a function of time.

Figure 3a and b shows the concentration profile for succinic acid oxidation in the presence of catalysts PZ-45 and gives the TOC content during these oxidation reactions over catalysts PZ-45 and PZ-64. Fumaric acid is very easily oxidized so that at the end of the reaction there was only acetic acid left. As concerns the disappearance of succinic acid, initial reaction rates of 42 and 25 mol h⁻¹ mol_{Ru}⁻¹ were measured for PZ-45 and PZ-64, respectively. Under similar conditions our 3%Ru/ZrO₂ catalysts shows a reaction rate of 20 mol h⁻¹ mol_{Ru}⁻¹. PZ45 seems more active.

However, very surprising data were obtained for acetic acid concentration and for the TOC content in presence of catalyst PZ-45. The TOC content increased much at the beginning of the reaction up to 2,900 mg/L. At the same time, very high concentrations of acetic acid are detected by HPLC, much higher than ever observed with this reaction. Some adsorption of the phenolic compound was observed on the catalysts during oxidation of p-hydroxybenzoic acid, so that after heating under Ar the initial concentrations measured are lower than the concentrations introduced in the reactor. Reaction rates of oxidation of p-hydroxybenzoic acid over the reaction period (7h) are roughly 3.8 and 1.8 mol h⁻¹ mol_{Ru}⁻¹ to be compared with 1.3 mol h⁻¹ mol_{Ru}⁻¹ on 3%Ru/ZrO₂ for instance, reported in (Perkas et.al., 2005). As in the case of succinic acid, catalyst PZ-45 is more active than PZ-64.

The observation of the used catalyst by transmission electronic microscopy, after 300 h on stream at temperature 160 °C, did not show any change, either in the distribution of the ruthenium particles or in the particle size. Moreover, the analysis of the solution having passed six times over the catalyst revealed no dissolution of the catalyst within the detection limits (< 0.5 ppm Ru). These heterogeneous catalysts are thus very stable in the corrosive reaction mixtures employed. The activity decreased only for catalyst PZ-68 in acetic acid oxidation at temperature 200 °C by 15 % during 150 h on stream.

4. Conclusions

All catalysts were rather active in oxidation of phenol and the activity was found very stable in all cases. The activity for phenol conversion, the selectivity for deep oxidation (CO₂), and also the composition of products were identical. After several sets of recycling of treated solutions on catalyst PZ68, the oxidation activity measured on a fresh phenol solution was found similar to the initial activity. Wet air oxidation experiments were also carried out on acetic acid which is a pollutant very resistant to degradation by WAO. The Sibunit catalyst did not exhibit catalytic activity up to temperature of 225 °C, whereas the promoted Ru-CeO₂/Sibunit catalysts exhibited high activity at 200 °C; however, their activity decreased significantly as a function of time on stream after 100 h. Oxidation of succinic acid at 190 °C takes place with formation as intermediates of acrylic acid, acetic acid and in some cases fumaric acid at the beginning of the reaction. Initial reaction rates of 42 and 25 mol h⁻¹ mol_{Ru}⁻¹ were measured for PZ45 and PZ64, respectively. The described Ru-CeO₂/Sibunit catalysts for WAO process

allow to decrease the mineralization temperature for typical organic pollutants from 200–240 °C to 160 – 200 °C, and to reach high degrees of mineralization (99 - 99,5 %) at enough low temperatures; they contain only low amounts of Ru. The results obtained in this study have been demonstrated high activity and exclusive stability Ru-CeO₂/Sibunit catalysts during long-time tests and may be applied for practical use in odour control processes by CWAO technology.

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