

EFFICIENT REMOVAL OF EMERGING POLLUTANTS FROM WASTEWATER BY MEANS OF CATALYTIC OXIDATION

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ABSTRACT

In this study, the performance of various Ru/TiO₂ catalysts to promote oxidation of aqueous solutions of formic acid, acetic acid, phenol and bisphenol A was investigated in a continuous-flow trickle-bed reactor. Oxidation experiments were carried out at T=328-523 K and total pressures up to 50 bar. Complete oxidation of formic acid was obtained at mild operating conditions (383 K), and no catalyst deactivation occurred that could be attributed to the dissolution of active ingredient material. Liquid-phase oxidation of recalcitrant acetic acid was found to be structure sensitive; the highest catalyst activity was obtained, when Ru phase on the catalyst surface prevailed in zero-valent oxidation state. The employed Ru/TiO₂ catalysts enable complete removal of phenol and bisphenol A as well as more than 99 % removal of TOC at temperatures above 483 K; at these conditions, no carbonaceous deposits were accumulated on the catalyst surface. In the presence of a Ru/TiO₂ catalyst in the trickle-bed reactor, the toxicity to *Daphnia magna* and *Vibrio fischeri* of the oxidized materials was greatly reduced compared with that of the starting solutions.

Keywords: catalytic wet-air oxidation, heterogeneous catalysis, ruthenium catalysts, trickle-bed reactor, wastewater treatment.

INTRODUCTION

Considering the need for environmental protection, one of the promising options for removal of toxic and non-biodegradable organic compounds from industrial wastewaters is destruction of these contaminants by catalytic wet air oxidation (CWAO) [1]. In the CWAO process, the organic pollutants are oxidized by activated O₂ species in the presence of a solid catalyst, usually at temperatures of 403-523 K and pressures of 10-50 bar, into biodegradable intermediate products or mineralized into CO₂, water and associated inorganic salts. The CWAO of various organic compounds has been studied over metal oxides, mixed metal oxide systems and noble metal catalysts [2]. Titania and zirconia supported Ru catalysts have received much attention recently, because they exhibited high activity and chemical resistance in CWAO of different model pollutants [3-5] and industrial wastewaters [6,7].

Acetic acid is a refractory intermediate typically produced in the oxidation route of various organic oxygenated compounds including phenol [8]. During the wet-air oxidation of phenol in a continuous-flow bubble-column reactor packed with a pelletized Ru/ZrO₂-TiO₂ catalyst, maleic acid, acetic acid and formic acid were identified as the main reaction intermediates [9]. Supported Ru catalysts exhibit good activity for CWAO of acetic acid to CO₂ [3,10].

In this work, Ru/TiO₂ catalysts were prepared by incipient-wetness impregnation method and tested for CWAO of formic acid, acetic acid and phenol in a continuous-flow trickle-bed reactor operating in a wide range of reaction conditions. CWAO of formic acid was investigated in this study, because little information regarding the oxidation of this compound is available. CWAO of phenol was carried out to investigate a potential of employed catalysts for effective removal of the parent molecule and intermediates from the liquid phase, without a noticeable accumulation of carbonaceous species on the catalyst

surface. Bisphenol A is an organic pollutant, commonly used in the production of polycarbonate plastics and epoxy resins. The acute toxicity to *Daphnia magna* and *Vibrio fischeri* of feed and treated solutions, given as global efficiencies of Ru/TiO₂ catalysts for degradation and detoxification of model pollutants in water, are reported.

EXPERIMENTAL

The catalysts containing 1.5 and 3.0 wt. % of Ru were prepared by incipient-wetness impregnation of TiO₂ extrudates (Degussa-Hüls, Aerolyst type, d_p: 1.4 mm) with an aqueous solution of RuCl₃. The obtained precursors were dried and reduced for 1 h in H₂ atmosphere at 573 K. Textural properties of synthesized catalysts are listed in Table 1.

CWAO of aqueous solutions of formic acid, acetic acid, phenol (feed concentration up to 2.0 g/l) and bisphenol A by using pure O₂ or air was carried out in a computer-controlled continuous-flow trickle-bed reactor system (PID Eng&Tech, model MA-Ref). The reactor made of SS operated in the low-interaction trickle-flow regime at T=328-523 K and P_{tot}=10-50 bar; the residence time of the liquid phase in the catalytic bed (3.0 g) was in the range from 0.12 to 0.33 min. Representative liquid-phase samples, continuously collected from the reactor unit, were analyzed by means of HPLC and total organic carbon (TOC) analyses.

Table 1. Textural and physicochemical properties of catalysts.

Catalyst	Model pollutant	S _{BET} , m ² /g	V _{pore} , cm ³ /g	d _{pore} , Å	^b TC, µg/g
TiO ₂	-	51	0.364	282	228
	phenol	^a n.d.	n.d.	n.d.	104
Ru(1.5 wt. %)/TiO ₂	-	50	0.355	285	n.d.
	acetic acid	41	0.342	337	147
	phenol	44	0.347	314	197
Ru(3.0 wt. %)/TiO ₂	-	50	0.344	274	n.d.
	formic acid	54	0.345	255	^c 3494
	acetic acid	42	0.343	326	113
	phenol	43	0.340	316	100
	bisphenol A	47	0.340	273	67

^aNot determined. ^bTotal carbon content. ^cNo rinsing of catalyst sample with distilled water was performed after the completion of experiment.

The acute toxicity of feed and end-product solutions to *Vibrio fischeri* (freeze-dried bacteria NRRL-B-11177, Dr. Lange GmbH, Düsseldorf, Germany) and *Daphnia magna* (D. magna Straus 1820, Institut für Wasser, Boden und Lufthygiene des Umweltbundesamtes, Berlin, Germany) were determined by toxicity tests performed accordingly to the ISO standards [11,12].

RESULTS AND DISCUSSION

Fig. 1 shows the results of CWAO of HCOOH in the presence of various Ru/TiO₂ catalysts. It is seen that in both cases complete oxidation of model pollutant is obtained at mild operating conditions, and that no catalyst deactivation occurs that could be attributed to the dissolution of active ingredient material, as confirmed by means of ICP-MS analysis of aqueous-phase samples. It was found out by thorough TPR/TPO examination of fresh and spent catalyst samples that in parallel to HCOOH oxidation, oxidation of metallic Ru clusters on the catalyst surface to RuO₂ takes place in the given range of operating conditions. However, the nature of Ru active phase (being either in the metallic or oxidized state) has no influence on measured conversions of formic acid. It was further observed that besides

oxidation route thermal decomposition contributes significantly to the removal of formic acid; Ru/TiO₂ catalysts could be thus efficiently used for transformation of HCOOH to H₂ and CO₂.

On the contrary to the above, much higher temperatures are required to achieve significant extent of oxidation of acetic acid. Complete removal of this pollutant was obtained at T=503 K and above (Fig. 2). Furthermore, CWAO of acetic acid was found to be structure sensitive. The highest catalyst activity was measured at the beginning of oxidation run, when Ru phase on the catalyst surface prevailed in zero-valent state. Due to simultaneous oxidation of metallic Ru to RuO₂ during the reaction course (the extent of oxidation is a function of temperature and p(O₂)), non steady-state operation was observed and correspondingly lower conversion of acetic acid was measured in the reactor outlet (Fig. 2). This is in agreement with the results of another investigation [13].

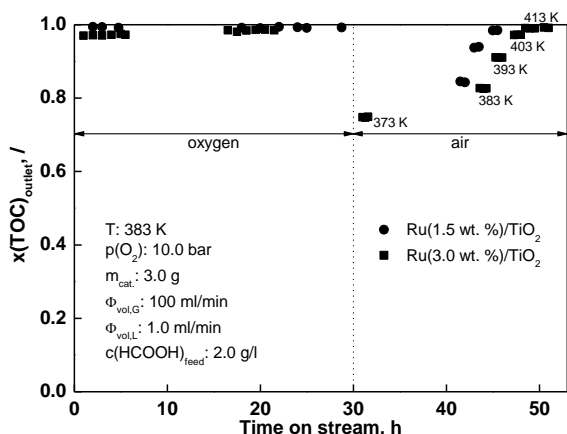


Figure 1. TOC conversion as a function of time on stream measured during HCOOH oxidation over various Ru/TiO₂ catalysts.

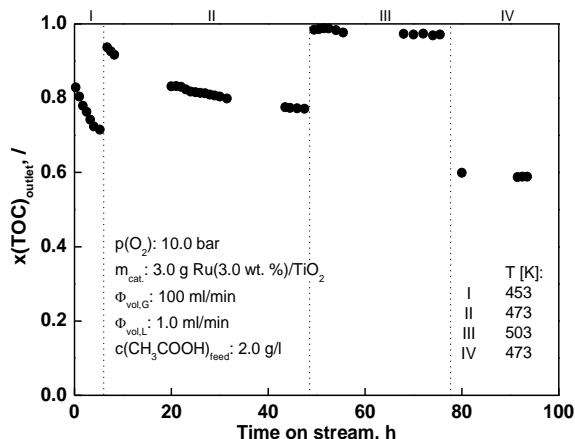


Figure 2. TOC conversion as a function of time on stream during the oxidation of acetic acid.

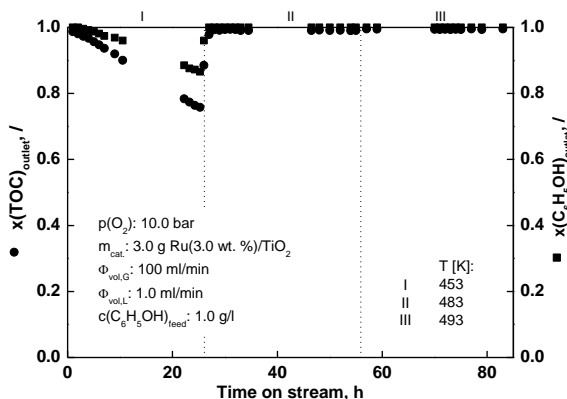


Figure 3. Phenol and TOC conversion as a function of time on stream.

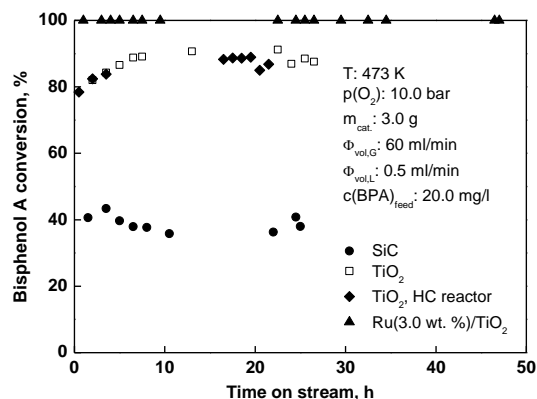


Figure 4. Bisphenol A conversion as a function of time on stream. Legend: HC = Hastelloy C276.

Figs. 3 and 4 illustrate that the employed Ru(3.0 wt. %)/TiO₂ catalyst enables complete removal of phenol and bisphenol A as well as TOC at temperatures above 483 K. At these conditions, no carbonaceous deposits were accumulated on the catalyst surface (Table 1). Apparent catalyst deactivation observed at T=453 K (Fig. 3, range I) is attributed to strong adsorption of partially oxidized intermediates (*i.e.* hydroquinones, benzoquinones) on the catalyst surface, which can be avoided by conducting the CWAO process at sufficiently high temperatures (above 473 K in this particular case). Due to low accumulation of intermediate acetic acid in the liquid phase, over-oxidation of Ru phase on the catalyst surface has negligible effect on oxidative phenol destruction.

CWAO using Ru/TiO₂ catalysts was very effective in removing the toxicity to *Daphnia magna* and *Vibrio fischeri* from the feed samples as toxicity significantly decreased in end products samples in comparison to the initial toxicity. Although lower toxicity was measured in the treated samples, it was evident that some compounds toxic to aquatic organisms still remain in the samples. The results clearly demonstrate that an application of analytical measurements and toxicity tests using aquatic organisms is of crucial importance for a reliable assessment of samples quality before discharging the effluents into aquatic environment.

Very recently, wet hydrogen peroxide catalytic oxidation of aqueous solutions of methylene blue was investigated in the presence of porous manganese functionalized silicates as superior Fenton-type nanocatalysts [14]. These solids facilitate deep oxidation of organic matter towards carbon dioxide, as they decompose 80 % of organic compound in 30 minutes under conditions of neutral pH and room temperature. This makes them highly promising catalysts for wastewater treatment by means of advanced oxidation processes.

CONCLUSION

Ru(1.5 wt. %)/TiO₂ and Ru(3.0 wt. %)/TiO₂ catalysts yielded complete removal of formic acid at T=383 K. Formation of partially oxidized Ru surface layer during the CWAO of formic acid seems not to affect the catalyst activity. Ru/TiO₂ promotes thermally induced decarboxylation of formic acid. The results of catalytic tests coupled with the physicochemical characterization of used catalysts after CWAO of acetic acid reveal that the decrease of catalytic activity is due to partial oxidation of metallic Ru particles to RuO₂. The amounts of RuO₂ and Ru⁰ depend on reaction temperature and concentration of liquid-dissolved O₂. Over 95 % TOC reduction could be achieved in the presence of Ru(3.0 wt. %)/TiO₂ catalyst at T=503 K, 10.0 bar of oxygen and residence time of 0.14 min. Ru/TiO₂ catalysts are active for total conversion of phenol and bisphenol A in aqueous solution at T≥483 K. The TOC abatement is greater than 99 %; the rest of carbon is found in the form of acetic acid. At lower reaction temperatures, adsorption of partially oxidized C-6 intermediates occurs, which results in apparent catalyst deactivation. This can be avoided by conducting the CWAO process at sufficiently high temperatures (close to 473 K), which facilitate desorption of intermediates and their transformation to CO₂.

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