



Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec



Wet air oxidation of paracetamol over precious metal/Ti mesh monolith catalyst

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ARTICLE INFO

Article history:

Received 26 September 2016
Received in revised form 2 November 2016
Accepted 7 November 2016
Available online xxx

Keywords:

Wet oxidation
Paracetamol
Monolith catalysts
Precious metal/Ti

ABSTRACT

The catalytic wet oxidation of paracetamol (PAR) was tested with Pt, Ru, Ir containing Ti monoliths measuring COD, TOC and TN conversion and compared with that of the non-catalytic reaction. The decrease of PAR concentration during reaction was followed by UV–vis spectrometry also. The catalysts were characterized by XPS, PGAA, TPR and SEM-EDX. The monometallic Pt and Ru/Ti catalysts were the most active, even below 150 °C. RuO₂/Ti had the highest specific activity. After 100 h reaction time the Pt loss was 23%, while the RuO₂/Ti kept its Ru content. The RuO₂/TiO₂ composite formation explains the highest activity and stability.

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Introduction

The presence of non-steroidal anti-inflammatory drugs (e.g. ibuprofen, ketoprofen, paracetamol, etc.) in natural water has been reported in several cases [1–3]. The contamination of natural waters with pharmaceuticals ensues from the production of these chemicals and their excretion into domestic wastewater. Beside the intensification of biological wastewater treatment with special bacteria and microorganisms [4,5], other possible solutions to decrease the amount of pharmaceutical contaminants are the advanced oxidation processes (AOPs) [6,7].

Paracetamol (PAR) is a frequently used analgesic drug, which often escapes from the conventional WWTPs (Wastewater Treatment Plant) and it can be detected in lakes and rivers. [3] Various advanced oxidation processes have been used to minimize its concentration with its effective decomposition. These methods are applicable mostly at the end of the WWTP lines before the treated water flows into the recipient natural waters [8–11]. This solution has a huge limitation in the case of high PAR concentration. Therefore a more complex, highly concentrated process

wastewater can be treated less efficiently with AOP, which generates OH• under mild conditions [11].

Wet (air) oxidation (WAO) or catalytic wet (air) oxidation (CWAO) is a non-selective oxidation method for treating liquid wastes from different industrial processes. It has been studied extensively for the degradation of organic compounds at high concentration [12–16]. Precious metals, such as Pt or Ru have proved to be active catalysts in CWAO. They are in most cases resistant to leaching, but are sensitive to poisons (halogen-, sulfur-, etc. containing compounds). Other reasons for the loss of their activity can be the so-called over-oxidation under CWAO conditions and formation of carbon containing deposits [17–21]. From the viewpoint of technological application, the stability of a catalyst is a decisive parameter. If the activity is going to decrease after a few hours on stream the scaling up process would not be worth doing.

Wet (air) oxidation (WAO), and especially CWAO of PAR on different catalysts was not yet studied in detail [22]. PAR is categorized as a micro-pollutant, treated often by AOPs. On the other hand, in the pharmaceutical companies' effluents the concentration of PAR could be very high. An example is the wastewater of Eastman Fine Chemicals (Newcastle, UK) that contains, among other pollutants, PAR with a COD close to 70,000–80,000 mg/l. The PAR in this case could be successfully treated by wet oxidation on an industrial scale (265 °C, 110 bar, 2.5 h residence

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<http://dx.doi.org/10.1016/j.jiec.2016.11.005>

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time, COD conversion >99%) [15,16]. The present research focuses on the degradation of PAR by means of CWAOW in order to eliminate this compound from the wastewater before it is fed to the WWTP.

The primary aim of this research is finding an appropriate catalyst, which can be a promising candidate in the practical applications, where the scaling up of the oxidation process requires a commercially available and robust catalytic system. The good stability could even compensate for a somewhat lower activity. In the catalytic wet oxidation of pharmaceutical process wastewaters, the Ti mesh (a precious metal covered monolith catalyst) proved to be active and relatively stable (during circa 100 h on stream) [23–25]. The commercially available Ti meshes developed for electrochemical processes are covered with Pt, Pt–Ir, Ru, Ru–Ir, and Ir. Although the preparation methods and precious metal contents are optimized for the electrode applications, in previous investigations they proved active and stable enough in the wet oxidation of different wastewaters [23,24]. The advantages of such monolith catalysts are obvious in comparison with the powder-form supported catalysts. The second purpose of this research work was the comparison of the Ti meshes coated by different precious metals, this time in wet oxidation of PAR. PAR contains phenolic and amino functional groups, aromatic moiety, and therefore is suitable for determining both activity and stability of the catalysts. With respect to the latter property, the nitrogen containing substrates potentially can accelerate the leaching of the precious metals [26,27].

Experimental

Catalyst characterization methods

Prompt gamma activation analysis (PGAA)

Prompt gamma activation analysis (PGAA) [28] was used for the determination of the precise amounts of metal content (especially for the precious ones, e.g. Ru, Ir, Pt, in the original state and after usage) of the monolith catalysts. The samples were tested as received, without destruction, which was important because of the high titanium content of the mesh. The exact procedure of the measurements as well as the data gathering and analysis were applied as it was described earlier [25]. The calculated precious metal contents were given in weight%.

Scanning electron microscopy (SEM)/(EDX)

The surface morphology of the catalysts was investigated by SEM (JEOL JSM 5600 LV). The magnification values were 500 \times , 1000 \times , 2500 \times and 5000 \times . The upper layer composition was given by data derived from Energy-dispersive X-ray spectra (EDX).

Temperature-programmed reduction (TPR)

The TPR measurement was used for the characterization (reducibility) of the fresh and used catalysts as well. TPR was carried out in a Micromeritics AutoChem II 2920 automated

catalyst characterization system. The linear temperature program started from room temperature and finished at 450 °C, with 10 °C/min heating rate in hydrogen (10%)-argon mixture with a flow rate of 50 cm³/min. After TPR measurements the samples were cooled in flowing Ar. The detection limit of the consumed hydrogen is \sim 10 μ l.

X-ray photoelectron spectroscopy (XPS)

The composition of the thin upper layer of each catalyst was characterized by X-ray photoelectron spectroscopy (XPS) measurements performed by a KRATOS XSAM 800 XPS machine equipped with an atmospheric reaction chamber. With an incident Al K α characteristic 1.486 KeV X-ray line, a 40 eV pass energy (energy steps 0.2 eV) and FAT mode were applied for recording the XPS lines of Ti 2p, O 1s, C 1s, Ru 3d, Pt 4f and Ir 4f. For charge compensation reference, the C 1s binding energy at 284.8 eV was used. The surface concentrations of the elements were calculated from the integral intensities of the XPS lines using sensitivity factors given by the manufacturer.

Wet oxidation (WO) and catalytic wet oxidation (CWO) experiments

Catalysts, catalytic oxidation process, determination of conversion in oxidation

Wet oxidation (non-catalytic) and catalytic wet oxidation (with five different catalysts) of a PAR solution were tested. The measurements are listed in Table 1. Titanium mesh, as a carrier material was applied in every case. This type of mesh is originally made for electrochemical application as an electrode material (supplied by Magneto Bv. [29]). Its use in wet oxidation is much easier than that of the powder form catalysts. One of the biggest advantages of this type of catalyst is at the end of the reaction there is no need filtration for removing the catalytically active compounds, and the continuous operation is easily carried out. The precious metal layers are prepared by impregnation with the solution of the corresponding metal salts, followed by calcination, resulting in mixed oxides and metallic species. The only exception is Pt, which is applied by electrolysis, giving a metallic surface layer [29].

For the catalytic reactions, 5 mmol PAR was dissolved in 1 dm³ distilled water ($c_0 \sim$ 756 mg/l, COD₀ = 1465 mg/l, TOC₀ = 492 mg/l, TN₀ = 61 mg/l, pH \sim 7). This model solution was oxidized in a \sim 30 ml stainless steel high pressure autoclave (Autoclave Engineers). The reaction parameters were the following: T = 130–170 °C, p_{O2} \sim 20 bar, t = 1–2 h and the stirrer speed was fixed at 750 rpm (within the kinetic regime).

The procedures at every run were the follows: a 25 ml sample was loaded into the autoclave, pressurized with oxygen to 5 bar and heated up to the desired temperature with a standard linear temperature program. The stirring was continuous during the given reaction time. The pressure was controlled to the desired value by adding oxygen during the experiments. At the end of each

Table 1

The tested catalyst samples and their precious metal content in weight% and mg, determined by PGAA (titanium mesh with PT: platinum containing surface layer, IR: iridium containing surface layer, RU: ruthenium containing surface layer, PTIR: platinum and iridium containing surface layer, RUIR: ruthenium and iridium containing surface layer).

	m _{catalyst} [g]	Pt [wt%] (\pm 0.04)	Ru [wt%] (\pm 0.04)	Ir [wt%] (\pm 0.04)	Σ precious metal [wt%] (\pm 0.04)	Σ precious metal in the tested sample [mg]
PT	1.689	1.14 (0.88) ^b	0	0.08 (0.09) ^b	1.22	20.7
IR	1.950	0	0	0.75	0.76	14.8
RU	1.930	0	0.41 (0.47) ^b	0	0.41	7.9
PTIR	1.829	0.53	0	0.12	0.65	11.9
RUIR ^a	2.172	0	0.19	0.37	0.56	12.1

^a The RUIR catalyst was characterized in a previous paper [25], some of those data are used for comparison in this paper also.

^b Metal content in wt% after >100 h usage.

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