Catalytic Removal of Pharmaceutical Compounds in Water Medium under a H₂ stream over Various Metal Supported Catalysts: A Promising Process

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Abstract: To date, very few such prescriptive studies have been reported in the literature concerning the catalytic removal of pharmaceutical substances in wastewater using H₂ in the presence of O₂ for the in situ formation of H₂O₂, while the mechanism of the reaction have not been studied yet. Hydrogen Peroxide is a potent oxidizing agent used extensively in the Catalytic Wet Air Oxidation (CWAO) for the elimination of pharmaceuticals from waste water. In the present work an attempt has been made, to elucidate the actual effects of the in situ production of hydrogen peroxide on the catalytic wet air oxidation of pharmaceuticals. Therefore, the effects of the chemical composition of the support, the nature of the active phase (Pd, Pt, Rh etc), as well as the reaction conditions (feed gas composition) have been examined towards the reaction at hand. The results show that 1% Pt/Al₂O₃ and 1%Rh/Al₂O₃ are the most effective catalysts for the elimination of Paracetamol from the reaction medium using the reaction at hand, having a conversion of up to 70%. In addition to that, increasing the % proportion of H₂ to 95% and 100% relatively to the % of O₂, increased the conversion of Paracetamol to 90% in just 30 minutes, when using the 1% Rh/Al₂O₃ catalyst. The concentration of Paracetamol in the medium was determined at 0, 30, 60 and 120 minutes after the reaction using UV/vis spectrophotometry at 243 nm. Total Organic Carbon (TOC) values were also recorded, in order to determine the % of the Organic Carbon present in the medium, converted to Inorganic Carbon. At this point, Paracetamol and Caffeine were used in the catalytic experiments performed as both of them were readily available and are two of the most common pharmaceutical substances used worldwide. Other pharmaceutical substances (eg. Diclofenac Sodium and Tetracycline) will be used in various concentrations in the aforementioned catalytic reaction, in the near future. Moreover, the advanced methods of SEM-EDX, ICP-MS, SSITKA-DRIFTS will be used to determine the physicochemical properties of the catalysts, the effectiveness of the alumina-coating procedure, the effect of several experimental parameters, the nature of active species, and the steps in a sequencing reaction.

Keywords: oxidation; pharmaceuticals; catalytic removal; hydrogen peroxide.

INTRODUCTION

In the last decades, the consumption of pharmaceutical substances increased exponentially, with the environment to be especially burdened from their rejection. Human and veterinary drugs are rejected to the environment mainly as a result of manufacturing processes, improper disposal or metabolic excretion. In addition to that, the conventional technologies used for the treatment of organic pollutants do not completely remove the pharmaceutical residues from wastewater. Based on the literature (Hernando et al. 2006; Hernando et al. 2004; Makris and Snyder 2010; Ollers et al. 2001; Stackelberg et al. 2004), the amount of residues (ng/L to low μg/L) that remains even after going through wastewater treatment is still able to induce toxic effects. An alternative method is the catalytic wet air oxidation (CWAO) (Levec et al., 2007; Kyoung-Hun et al., 2011), which reduces the severity of reaction conditions compared to Wet Air Oxidation (WAO) and more easily decomposes even refractory substances. Heterogeneous catalysts are advantageous compared to homogeneous catalysts since they do not require an additional separation step to recover the metal ions from the effluent, which will increase the operation costs. Strong oxidizing agents like ozone, hydrogen peroxide and UV radiation which involve the generation of hydroxyl radical (OH) with high oxidative power can also be used in CWAO to further reduce the severity of reaction conditions. Methods involving ozone and UV radiation due to the specialized equipment needed are too expensive to be used widely. Hydrogen peroxide can be used as the radicals ·OH source due to its low cost. In addition, using hydrogen, in excess of oxygen/air, in the presence of a catalyst can lead to the in-situ production of hydrogen peroxide, which further reduces the cost of operation.
Only very few research studies have been reported to the literature (Kim et al. 2003; Lee et al. 2004) concerning the heterogeneous CWAO in excess of oxygen (air) and in the presence of hydrogen, while the mechanism of the reaction have not been studied yet. The scope of the present research is to develop a suitable, innovative catalytic system, which will show high reactivity and selectivity towards the CWAO of pharmaceutical substances in excess of oxygen and in the presence of hydrogen. For the first time ever the reactions of the in situ production of hydrogen peroxide and the catalytic wet oxidation of pharmaceuticals will be studied simultaneously, so as to find the best catalytic system for the oxidation of pharmaceuticals in water medium. In the present work an attempt has been made, to elucidate the actual effects of the in situ production of hydrogen peroxide on the catalytic wet air oxidation of pharmaceuticals. According to the limited literature (Kim et al. 2004; Lee et al. 2004) the introduction of small amount of hydrogen gas into air feed stream leads to an appreciable increase of the wet oxidation activity of the catalyst, making the operation costs significantly lower. Other advantages of the proposed catalytic system are the low cost of installation and maintenance, the transformation of pharmaceutical compounds to innocuous compounds, such as carbon dioxide and water, no bacterial contamination of the effluent and the environment occurs, and it can be used for the degradation of a wide spectrum of organic compounds in aqueous solutions since the method is not selective.

It is worth mentioning that in the present paper the first promising results derived from the study of the conversion of paracetamol by the use of different reaction mixture (% vol H2 in air) over various monometallic 1 wt. % M (M=Pd, Pt and Rh) catalysts supported on γ-Al2O3 spheres are presented. In addition, toxicity and total organic carbon of the solution were tested before and after the reaction (95 vol. % H2/5 vol. % air and 5 vol. % H2/95 vol. % air). Acute toxicity tests can provide preliminary information on the toxic nature of a substance for which no other toxicological information is available.

EXPERIMENTAL

The catalysts were prepared via modified wet impregnation method in accordance to our previous work (Theologides et al. 2011). Catalytic experiments were conducted in a custom-built autoclave (batch) reactor (Autoclave Engineers, U.S.A., and PID Eng &Tech, Spain) equipped with a Mahoney-Robinson catalyst basket. Paracetamol was chosen as the xenobiotic substance at concentration of 10 mg/L in water medium at 25 °C and pressure of 1.2 atm. Samples were taken at 0, 30, 60 and 120 min and tested using Ultraviolet Spectrophotometry at 243 nm, Toxicity analyzer and Total Organic Carbon (TOC) Analyzer.

RESULTS AND DISCUSSION

Catalytic Studies

The remarkable effect of the presence of hydrogen in the reaction’s feed stream in the presence of a catalyst towards the conversion of paracetamol with oxygen was reported for first time in a batch mode system. The conversion of paracetamol was studied over three monometallic catalysts, 1 wt. in % Pd/γ-Al2O3 (a) and 1 wt. % Pt/γ-Al2O3 (b) and 1 wt. % Rh/γ-Al2O3 (c) using different reducing feed gas composition. In Figure 1, the different conversion profiles obtained with Paracetamol are compared using the examined catalysts and different Hydrogen concentrations. As shown in Figure 1a, no remarkable change in the conversion of Paracetamol was observed over 1 wt. % Pd/γ-Al2O3, whereas an almost complete (>96 vol. % H2) conversion of Paracetamol occurs in the case of the 1 wt. % Rh/γ-Al2O3 catalyst (Figure 1c). In addition to that, the catalysts 1 wt. % Pd/γ-Al2O3 and 1 wt. % Rh/γ-Al2O3 catalysts show higher Paracetamol conversion (up to 30% more) than when using the 1 wt. % Pt/γ-Al2O3 catalyst at low H2 concentrations (≤5 vol. % H2). The latter result is probably due to the in situ production of Hydrogen Peroxide, which is a source of ·OH radicals production. It appears that Pt/Al2O3 does not favor the in situ production of Hydrogen Peroxide, which is consistent with the literature, where Pd containing catalysts are used for the direct formation of Hydrogen Peroxide from H2 and O2 (Lunsford J.H, 2003; Landon P. et al., 2003).
The comparative results presented in Figure 1 indicate that the conversion of paracetamol is clearly affected by the active phase of the catalyst, especially when Rh was used. Consequently, 1% wt Rh/Al₂O₃ catalyst is clearly the most efficient catalyst for the conversion of Paracetamol, particularly at high concentration of H₂ in the gas stream. Therefore, the catalytic performance of 1 wt % Rh/γ-Al₂O₃ catalyst was examined further and in detail, using different feed gas compositions.

Figure 2 presents the paracetamol conversion profile obtained during 2h of reaction over 1 wt % Rh/γ-Al₂O₃ catalyst, when 95 vol.% H₂ in air, pure H₂ and pure O₂ are used in the feed gas. As shown in Figure 2, the conversion of Paracetamol at high H₂ concentrations was remarkably higher than when pure O₂ was used in the gas feed. More specifically, the conversion of Paracetamol when 95% H₂ and pure H₂ was used was above 95% in both cases, in just 30 minutes after the reaction, at which point it reached steady state. At 120 min after the reaction started, Paracetamol is completely converted and thus eliminated from the medium. Consequently, the use of high concentrations of H₂ in the gas stream using 1% wt. Rh/Al₂O₃ as a catalyst effectively eliminates Paracetamol from the water medium. The latter result clearly indicates that this process is extremely promising in elimination of xenobiotic substances from water medium, due to reduction instead of oxidation of the substance.
Moreover, to investigate the effectiveness of the reactions studied in this work, different Paracetamol concentrations were prepared and tested over the 1 wt. % Rh/γ-Al₂O₃ catalyst using 2 different gas feed concentrations (95% H₂/5% O₂ and 95% O₂/5% H₂) (Figure 3). As shown in Figure 3, the conversion of Paracetamol is greatly reduced with the increase of Paracetamol concentration when 5 vol. % H₂/95 vol. % air was used in the gas feed stream. This indicates that the reaction at hand is saturated above 10 mg/L, since Paracetamol is no longer converted and eliminated from the reaction solution at concentration above 10 ppm. In contrast to the above-mentioned results, in the case of 95 vol. % H₂/5 vol. % air reaction the conversion of Paracetamol remained at high levels (nearly 100%) regardless of the increase in concentration, indicating that the reaction mixture is not saturated with an increase in concentration of the pollutant. Therefore, the pollutant continues to be converted and eliminated even at concentrations of 500 ppm.
is expected. When 95% vol. H₂/5% vol. O₂ is used in the gas stream the toxicity decreases to negligible levels after the catalytic reaction, indicating that Paracetamol is eliminated from the water solution. This is extremely promising since it is shown that Paracetamol is eliminated even in high concentrations of the pollutant. On the contrary, when 5 vol. % H₂/95 vol. % was used in the gas feed stream (Figure 4b), the toxicity of the solution was kept at high levels for Paracetamol concentrations above 200 ppm, even though it decreases even at 500 ppm. This means that the catalytic reaction using 5 vol. % H₂/95 vol. % air in the gas feed stream can be used effectively for Paracetamol concentrations of up to 100 ppm.

Figure 4. Toxicity of the solution (before and after the reaction) as a function of Paracetamol concentration (mg/L) over 1 wt. % Rh/γ-Al₂O₃ by the use of different gas feed stream composition. Reaction conditions: Gas Feed Stream Composition= 95 vol. % H₂/5 vol. % air (a) and 5 vol. % H₂/95 vol. % air (b); Wcat= 4 g (dp=1.8mm); T= 25 °C; P= 1.2 atm.

The total organic carbon (TOC) of the solution was studied before and after 95 vol. % H₂/5 vol. % air (Figure 5a) and 5 vol. % H₂/95 vol. % air (Figure 5b) reactions for a range of Paracetamol concentrations (10-500 mg/L). As shown in Figures 5a and 5b, similar results were obtained for any reaction mixture. Figure 5 shows that the TOC values do not decrease considerably after the reaction takes places for both gas feed streams. This means that Paracetamol is converted in another organic substance (with the same number of organic carbons in its structure). The fact however, that for both gas feed streams, toxicity decreases after the reaction takes place indicate that Paracetamol is converted to a less toxic substance than Paracetamol that is extremely encouraging for the current catalytic procedures studied in this work.
CONCLUSION

Based on the results of the present research work, catalytic wet air oxidation using excess of H₂ appears a very promising technique for the complete removal of pharmaceutical residues from wastewater such as Paracetamol, especially when using monometallic Rh catalyst supported on γ-Al₂O₃ spheres. The later catalyst completely converts Paracetamol in 30 min of reaction, minimizing the cost of the process. In addition, TOC and toxicity analysis indicate that 1 wt. % Rh/γ-Al₂O₃ converts Paracetamol into less toxic derivatives with the same number of organic carbons in its structure. Future experiments will be conducted for further investigation and optimization of the method. Therefore, catalysts with other metal loadings and support oxides (TiO₂, CeO₂ and Fe₂O₃) will be tested. Moreover, several other pharmaceutical substances are going to be tested, in order to investigate the applicability of the method. The catalysts that will be found to be the most suitable for the oxidation of pharmaceutical substances will be further studied thoroughly using advanced techniques such as TPSR, SEM-EDX, SSITKA-DRIFTS. Mechanistic experiments are expected to provide significant information about the mechanism of the reaction.

REFERENCES


