

Catalytic wet air oxidation of stearic acid on cerium oxide supported noble metal catalysts

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Abstract

Catalytic wet air oxidation (CWAO) of stearic acid was carried out in a batch reactor over noble metals (Ru, Pd, Pt, Ir) catalysts supported on ceria. The influence of reaction conditions such as temperature, oxygen pressure and stearic acid concentration were investigated. The reaction occurs via a complex mechanism. The molecule of stearic acid can be oxidized by successive carboxy-decarboxylation ($R_n\text{-COOH} + \text{O}_2 \rightarrow R_{n-1}\text{-COOH} + \text{CO}_2$) yielding essentially CO_2 (route A). It may also be oxidized after C–C bond rupture within the alkyl chain, which gives rise to significant amounts of acetic acid besides CO_2 (route B). Pt/CeO₂ is a very active catalyst in the conversion of stearic acid and extremely selective to carbon dioxide (route A), while the mechanism via C–C bond splitting is much more marked on Ru/CeO₂. The catalyst characterization indicates that both noble metal and CeO₂ particles remain stable during the reaction.

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1. Introduction

Nowadays, advanced oxidation processes like wet air oxidation (WAO) emerge and find promising applications in industrial and urban wastewater detoxification. It concerns typically effluents with medium chemical oxygen demand (COD) from 5 to 150 g(O₂) L⁻¹ and finds its greater application for treating toxic or non-biodegradable pollutants. The process consists in oxidizing the pollutants under oxygen or air pressure (0.5–20 MPa) at elevated temperature (120–360 °C) [1,2]. Wet air oxidation is able to oxidize C_xH_yN_z organic compounds into CO₂, low molecular weight carboxylic acids, NH₃, NO₃⁻ and molecular nitrogen. Halogen and sulfur are converted into inorganic halides and sulfates [2]. The degree of oxidation is mainly a function

of pollutant stability, reaction temperature, oxygen partial pressure and residence time.

Different WAO processes are commercialized and WAO units are generally used for the treatment of sewage sludges in order to improve significantly sterility, filterability, and dewatering properties [3]. WAO has been used successfully to treat a wide range of industrial wastewaters. Studies of WAO on industrial wastewaters have been reported for high concentrated chemical wastewaters obtained from a petrochemical company [4], printing and dyeing [5,6]. But WAO is an expensive process because of the required severe conditions. So an alternative to reduce the costs is the use of suitable catalysts able to promote the WAO under milder operating conditions and shorter residence times. Catalysts can also lead to a higher oxidation rate of organic compounds. Consequently, during the last decade catalytic wet air oxidation (CWAO) over various homogeneous and heterogeneous catalysts has received a particular attention. Homogeneous catalysts (copper and iron salts) [1,7–9] have

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been proved to be powerful oxidation catalysts for organic pollutants. However, CWAO processes based on these catalysts induce a separation step such as precipitation to remove or recover the catalysts ions from the treated effluent. To overcome this drawback, attempts at developing stable active heterogeneous catalysts has been made. Several noble metals (Pt, Ru, Rh, Ir, Pd. . .) [8] and transition metal oxides (Cu, Fe, Co, Mn. . .) have been tested [10]. In the case of heterogeneous oxide transition metals, a partial leaching of metal ions has been observed during the reaction and a recovery step is necessary. Noble metals, stable in severe reaction conditions, were then investigated with a great attention. These catalysts have been proved their efficiencies in the treatment of a wide range of pollutants like carboxylic acids [1,9,11,12], phenol [13], nitrogen compounds [14,15].

This study deals with the CWAO of fatty acids in aqueous media by supported noble metal catalysts. Due to their low solubility, fatty acids form part of refractory products for the conventional biological treatment of food industry effluents. However, some processes such as incineration or agricultural valorization allow their elimination [16], but the large amount of fatty wastes to be removed, combined with a gradual increase in the severity of the environmental assessment, impose to develop new processes with higher efficiency. The literature on CWAO and WAO of fatty wastewaters is very scarce. Pech and Debellefontaine [16] have studied the oxidation of fatty wastes with hydrogen peroxide at elevated temperature. More recently, Sève and Antonini [17] have investigated the WAO of fatty wastewaters and have noticed that a high air pressure (5 MPa) and a temperature of 240 °C, were necessary to remove significantly saturated fatty acids, which are more refractory than the unsaturated ones.

The purpose of this work concerns specifically the catalytic wet air oxidation of stearic acid (C₁₈H₃₄O₂). This model molecule is the most common saturated fatty acid present in animal fats [18]. The reactions were carried out in a batch reactor on ceria-supported noble metal catalysts (Pt, Ru, Pd. . .). These catalysts, previously studied on CWAO of various organic compounds [11–15], were chosen for their high stability and activity during carboxylic acids oxidation [1,19,20]. Due to the strong adsorption of organic compounds at the catalyst surface, the oxidation rate is generally limited by the oxygen transfer from the liquid phase to the metal active sites. Cerium oxide, able to enhance this oxygen transfer [11,21,22], was chosen as the reference support of noble metals. The influence of reaction conditions on the catalyst behavior such as temperature, oxygen pressure and pollutant concentrations were investigated. The principal objective of this study, is to demonstrate the beneficial impact of the noble metal catalysts on the conversion but also on the mineralization of this very refractory compound. Particular attention is made on the carbon balance completion by analyzing precisely each reaction phase. For each experiment, catalyst characteriza-

tions such as XRD analysis, elementary analysis and dispersion measurements are performed on fresh and used catalysts.

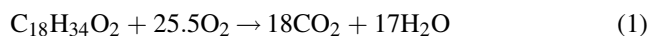
2. Materials and methods

2.1. Catalyst preparation

The support, which is under powder form, was a commercial Rhodia Rare Earth ceria HSA5 ($A_{\text{BET}} = 240 \text{ m}^2 \text{ g}^{-1}$), used without any further treatment. Different catalysts were prepared by impregnation and dry evaporation of the support with aqueous solution of metallic precursor salts (IrCl₃, Ru(NH₃)₆Cl₃, Pt(NH₃)₂(NO₂)₂, Pd(NO₃)₂). In every case, the metal loading was adjusted to 5% in weight. The slurry was then dried at 120 °C and the catalysts were activated by reduction under H₂ at 350 °C during 3 h before each run.

2.2. Oxidation reaction conditions

Catalytic wet air oxidation reactions were carried out in a 0.44 L Hastelloy C22 autoclave for 3 h (Fig. 1). The reaction temperature was in the range 160–230 °C. One sixty milliliter of aqueous solution, containing the stearic acid (under blank flake form) ($5 < \text{COD} < 40 \text{ g(O}_2\text{) L}^{-1}$ corresponding to $6 < [\text{stearic acid}] < 48 \text{ mmol L}^{-1}$) and 4 g L^{-1} of catalyst, were introduced in the reactor. After an initial purge of the autoclave under helium, the autoclave was heated up to the reaction temperature. The reaction starts after addition of the oxygen at pressure (0.1–2 MPa) maintained constant during the experiment. Due to the low solubility of O₂ in water, its concentration is limited ($5 < [\text{O}_2] < 100 \text{ mmol L}^{-1}$ at 200 °C [12]). The initial [O₂]/[stearic] molar ratio amounts to a value between 0.1 and 16. As total oxidation of stearic acid (Eq. (1)) requires [O₂]/[stearic] stoichiometric ratio of 25.5, stearic acid is always in excess.



2.3. Analysis

For each experiment, the reaction was monitored by the measurement of the effluent composition as a function of time. At appropriate intervals of time, liquid and gas aliquots were sampled and analyzed.

Gas phase was analyzed by a GC Intersmat IGC 120ML, equipped with a catharometer. A Porapak Q packed column (diam. = 0.6 mm, length = 0.5 m) was used to analyze CO₂. Hydrogen was chosen as carrier gas. Knowing the CO₂ partial pressure and by using specific calibration charts representing CO₂ in the gas phase versus CO₂ in the liquid phase it is possible to determine the total CO₂ content in the reactor. The charts elaborated in previous work [23] are obtained by oxidizing a known amount of formic acid (total

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