

Carbon supported platinum catalysts for catalytic wet air oxidation of refractory carboxylic acids

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Carbon supported platinum (1% wt) catalysts were prepared by the incipient wetness impregnation method and by organometallic chemical vapor deposition. Catalyst characterization was carried out by means of adsorption and thermogravimetric techniques, and by electron microscopy. The catalyst with higher metal dispersion was produced by incipient wetness impregnation. The catalysts were tested in the catalytic wet air oxidation (200 °C and 6.9 bar of oxygen partial pressure) of aqueous solutions containing low molecular weight (C₂ to C₄) carboxylic acids. Significant conversions (greater than 60% over 2 h) and 100% selectivity towards water and non-carboxylic acid products were observed for both systems. The initial reaction rate was used to compare the performance of the two catalytic materials and direct correspondence to the metal dispersion was found. No metal leaching was observed during reaction and no significant deactivation occurred in three successive catalytic oxidation runs. A kinetic model based on the Langmuir–Hinshelwood formulation was applied and the results were analyzed in terms of a heterogeneously catalyzed free radical mechanism.

KEY WORDS: catalytic wet air oxidation (CWAO); carbon supported platinum catalysts; incipient wetness impregnation; organometallic chemical vapor deposition (OMCVD)

1. Introduction

The unexpected persistence of toxic pollutants even at sublethal levels in the hydrosphere is raising concerns about sustainability in water quality. Catalytic oxidation methods for treatment of waters and wastewaters are at forefront of the discussion on strategic alternatives to be adopted in the near future. The choice of a given method is a function of several integrated variables such as the volume of water to treat, the nature and amount of the organic pollutant, and the adequacy of the method, among others. Small refractory molecules are often of great importance, not necessarily by their direct impact, but by the effects caused by their persistence. Methods that can deal efficiently with these low molecular weight organic compounds are required in many different and demanding instances. Among the existing alternatives, catalytic wet air oxidation (CWAO) is interesting for the treatment of industrial wastewaters due to its intrinsic efficiency in the reduction of chemical oxygen demanding species, by means of an oxidizing source under relatively mild conditions (125–220 °C, 5–50 bar) in the presence of an adequate catalyst. Recent examples of application include herbicide removal [1], pulp and paper mill effluent [2], printing and dyeing wastewaters from the textile industry [3], alkaloid factory wastewater [4], and wastewaters

from nuclear fuel processing plants [5]. Although, some very active homogeneous catalysts can be used, such as copper [6] and iron salts [7], they need to be separated from the treated effluent, which is a drawback for industrial applications. In order to avoid this problem, efficient heterogeneous catalysts have been reported such as Mn/Ce [8], Co/Bi [9] or supported copper oxides [10]. But unfortunately, under typical process conditions those catalysts are prone to lose metal through leaching [11], making them unattractive. Furthermore, the majority of metallic supported catalysts developed for CWAO show serious deactivation problems, including poisoning [12], fouling [13] and leaching [14]. In addition, the support material may suffer from stability problems, such as dissolution in the reaction medium or poor chemical resistance. As a result, in the last years a strong effort has been devoted to developing highly stable and active heterogeneous catalysts.

Supported metal catalysts using noble metals are able to attain high activities and great stability provided the right support is used. Activated carbon is a very suitable support in this respect, presenting a strong resistance in acidic media [15], allowing for the possibility of adjusting its porosity and chemical properties [16]. It is possible to prepare carbon supported platinum catalysts with very strong metal–support interactions [17] avoiding two of the catalyst major problems in CWAO, namely leaching and sintering. Although previous reports have considered Pt/C catalysts as fairly inactive

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