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CWAO of Butyric Acid Solutions: Catalyst Deactivation Analysis

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Carbon-supported platinum and iridium catalysts were prepared for catalytic wet air oxidation (CWAO) applications. These catalysts were tested in the CWAO of butyric acid aqueous solutions at 200 °C and 6.9 bar of oxygen partial pressure, and significant conversions above 70% were obtained depending on the catalyst used. The long-term deactivation resistance of the Pt/C catalyst is higher than that of the Ir/C catalyst. The deactivation observed with the Ir/C catalyst was attributed to the overoxidation of the surface of iridium by molecular oxygen. A deactivation study of the catalysts was conducted using N_2 adsorption, thermogravimetric analysis, temperature-programmed reduction, and X-ray photoelectron spectroscopy. A kinetic model describing the observed deactivation phenomena in the Ir/C catalyst is proposed and tested using the experimental data obtained in the CWAO of the systems studied.

Introduction

Awareness of the vital importance of water resources for the growth of developed economies has led to the enforcement of increasingly stringent environmental regulations, forcing chemical, petrochemical, and pharmaceutical industries to treat more efficiently the liquid effluents generated in their processes before discharging them into river courses. Several treatment technologies are available that can be used depending on the nature and volume of the effluent. Incineration is certainly the most efficient destruction method, but because of the high energetic costs involved and, above all, the release of noxious compounds into the atmosphere, incineration is suitable only as an end-of-pipe treatment or when the chemical oxygen demand (COD) of the effluents is higher than 300 g/L. Biological treatment is an inexpensive and simple method, but the toxicity of the effluent makes this treatment ineffective for organic concentrations above 70−200 mg/L.[1] Potential technologies for COD removal between these two extremes include physicochemical treatment methods, air-based oxidation, and chemical oxidation. From the point of view of energy efficiency, wet air oxidation (WAO) and catalytic wet air oxidation (CWAO) are suitable for wastewaters with COD loads within the given limits.[2] Herbicide removal,[3] oxidative treatment of pulp and paper mill effluents,[4] pretreatment of waters from alkaloid plants (typically high-strength industrial wastewater with COD around 27 g/L),[5] treatment of printing and dyeing wastewaters from the textile industry,[6−8] and treatment of H-acid manufacturing process effluents[9] are recent examples of applications of this technology.

WAO is a treatment by which the organic species present in industrial effluents are mineralized to carbon dioxide and water using air or oxygen at relatively high temperatures and pressures (200−350 °C, 70−230 bar), conditions that severely affect the economics of this technology.[2,10,11] By using a suitable catalyst, the operating conditions needed for the noncatalytic process can be lowered to more amenable values (120−220 °C, 5−50 bar) without loss of degradation efficiency and with consequent economic advantages.[12−14] Homogeneous catalysts are very efficient for the process,[15−19] but their use implies the need for an additional separation step in the process for the removal of the toxic ions from the solution. As heterogeneous catalysts are easily removed, their development and optimization has been the subject of several works in recent decades.[20−25] These studies mainly aimed at determining initial activities and kinetic parameters without much attention being given to catalyst deactivation. In previous works, we have shown that carbon-supported platinum and iridium catalysts are very efficient in the CWAO of butyric acid solutions. Butyric acid is a low-molecular-weight organic compound that is very refractory to oxidation;[26−28] it is a good model system because it occurs in most of the degradation pathways of more complex organic compounds and it is a precursor of acetic acid, a typical end product of this type of oxidations. As expected, the conditions used in this process are quite favorable to the occurrence of various catalyst deactivation phenomena, such as poisoning, sintering, metal leaching into solution, and coke formation.[24,29−33]

In the present work, the deactivation of such catalysts is studied to determine their industrial applicability. Several experimental techniques are used in an effort to understand the deactivation mechanism, such as N_2 adsorption, thermogravimetric analysis, temperature-programmed reduction, and X-ray photoelectron spectroscopy. Starting from a previously developed kinetic model,[28] the deactivation of the catalyst is now introduced, and a new consistent kinetic model is proposed.

Materials and Methods

Catalyst Preparation and Characterization. Carbon-supported platinum (~1% Pt) and iridium (~5% Ir) catalysts were prepared by incipient wetness impregnation using H_2PtCl_6 (Aldrich) and $(NH_4)IrCl_6$ (Alfa-Aesar), respectively, as metallic precursors. Hydrogen chemisorption measurements gave a metal dispersion of at least 0.25 for both catalysts. The support material used was the activated carbon Norit ROX 0.8 in pellet form (cylinders with a diameter of 800 μm and a length of 4−4.5 mm), washed with HCl to eliminate mineral

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