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CATALYTIC WET AIR OXIDATION OF BUTYRIC ACID SOLUTIONS USING A CARBON SUPPORTED IRIDIUM CATALYST

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Introduction

The search for new advanced cleanup catalytic technologies imparted to catalytic wet air oxidation (CWAO) a recrudescent interest in recent years. At the present, more than 100 plants using CWAO are operative worldwide, mainly for treatment of streams from petrochemical, chemical, pharmaceutical and textile industries. CWAO can be used either for complete oxidative degradation, or as pre-treatment for biological degradation of downstream waste waters. On the other hand, it can also be used to act locally, on a specific pollutant upstream, aiming at recycling of waters and reduction of wastes. In this case, knowing the reaction mechanisms and reliable kinetics for the degradation of model compounds is of great importance. Butyric acid is known to oxidize at a significant rate under very severe conditions of pressure, temperature and residence times in the traditional non-catalytic wet air oxidation. These demanding conditions prompted us to develop heterogeneous catalysts, more efficient at milder conditions.

Experimental

The iridium catalyst (5 wt%) was prepared by incipient wetness impregnation with aqueous solutions of $(NH_4)_3IrCl_6$ according to two different procedures. Activated carbon Norit ROX 0.8 modified by different treatments was used as the catalyst support.

The amount of iridium on the catalysts before and after reaction was measured by a gravimetric combustion method. Metal dispersion was determined by oxygen titration with hydrogen. Scanning electron microscopy was used to characterize the morphology of iridium particles.

Catalytic wet air oxidation studies were performed in a 160 ml stainless steel high-pressure reactor coated with a glass liner to prevent severe corrosion problems, heated by an electronically controlled heating mantle and stirred with a magnetically driven stirrer. In each reaction the reactor was loaded with 70 ml of 5 g/l butyric acid solution and the catalyst. Standard operating conditions were set to 8 h reaction time at 6.9 bar of oxygen partial pressure and 200 °C. Samples were withdrawn periodically and analyzed by gas chromatography. The initial reaction rates (in $mmol_{acid} \, h^{-1} \, g_{Ir}^{-1}$) were calculated from the curves giving the concentration of butyric acid as a function of time at low conversion. The kinetic orders with respect to butyric acid, to oxygen and to catalyst load were determined by varying the initial butyric acid concentration in the range 0.034-0.080 M, the oxygen partial pressure in the range 6.9-13.9 bar and the catalyst load in the range 0.2-0.8 g, while the activation energy was obtained by varying the reaction temperature in the 180-220 °C range.

Results and discussion

The influence of support oxidation and impregnation method on the activity of the iridium catalyst was studied for the degradation of butyric acid under the standard conditions in terms of initial rates of oxidation. Values ranging from 5.8-29.8 mmol $h^{-1}g_{Ir}^{-1}$ were obtained. Catalysts prepared over non-oxidized supports were consistently more efficient in this process. Catalyst pre-treatments (reduction, oxidation and heating) were also investigated and the same upper limit value of 29.8 mmol $h^{-1}g_{Ir}^{-1}$ was obtained for the most efficient catalyst. The butyric acid degradation was followed over the reaction period and the results show the formation of more refractive low molecular acids such as propionic and acetic acid (Figure 1).
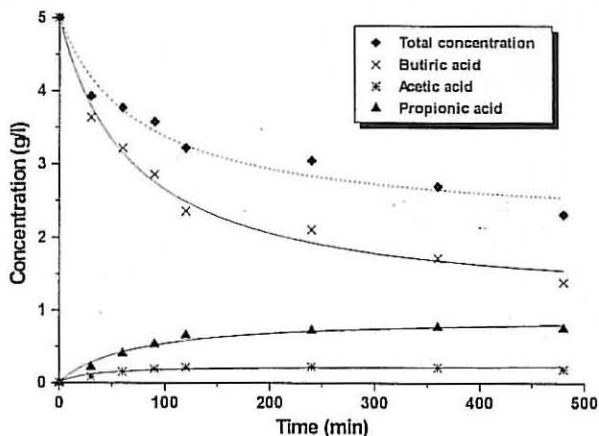

Figure 1 – Composition evolution obtained for an initial solution of butyric acid (5 g/l), under standard conditions (200°C, 6.9 bar P_{O2}). After 8h, 70% of butyric acid is converted with 70% selectivity to end products CO_2 and H_2O.

The activation energy for butyric acid conversion was found to be about half of the value found for the non-catalytic process. The empirical rate equation for the reaction of oxidative degradation was determined, and is in line with a heterogeneous mechanism, were the catalyzed abstraction of hydrogen from the substrate assisted by oxygen at the surface of the catalyst is the initiation step.

Acknowledgement