



# DIVISÃO DE CATÁLISE

# 4<sup>o</sup> encontro



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## CATALYTIC WET AIR OXIDATION OF BUTYRIC ACID

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Air oxidation is a useful process for reducing the total organic carbon (TOC) of waste waters and depending on the nature of the stream it can be used as the only process, or as pre-/post-treatment. Traditionally in wet air oxidation (WAO) organic pollutants are oxidized to CO<sub>2</sub> and H<sub>2</sub>O with an oxidizing source (air or O<sub>2</sub>) under conditions of high pressure (70-130 bar) and temperatures (200-300°C). As such conditions severely affect the process economics, there is a strong effort on the research and development of stable heterogeneous catalysts in order to bring down pressure and temperature to milder values – catalytic wet air oxidation (CWAO). Carbon supported noble metal catalysts have been proved to be very active systems for this process.

In this paper we used butyric acid as a model compound, and investigated the influence of support oxidation and impregnation method on the activity of the catalysts. A kinetic study based on the initial butyric acid consumption rates was also performed and parameters such as the activation energy and the reaction orders, were determined with respect to substrate and catalyst concentration and oxygen pressure.

Four iridium catalysts (5 wt %) were prepared by impregnation with aqueous solutions of (NH<sub>4</sub>)<sub>3</sub>IrCl<sub>6</sub>. Norit ROX 0.8 active carbon HCl washed was used as support with and without HNO<sub>3</sub> oxidation. Two different impregnation methods were used: (1) the solution was poured over the support in a single step, using the appropriate concentration to obtain 5 wt % metal load, and (2) two solutions were used in successive steps in order to obtain the same load.

Catalytic wet air oxidation studies were performed in a 160 ml stainless steel high pressure reactor with a glass liner to prevent severe corrosion problems, heated by an electronically controlled heating mantle. Samples were withdrawn periodically by a sampling valve and analyzed on a gas phase chromatograph equipped with a flame ionization detector. The oxidation reactions with 5 g/L butyric acid solutions were performed at 200°C and 6.9 bar oxygen pressure with 11.4 g/L catalyst load. Initial

butyric acid consumption rates ( $r_i$ ) under these conditions are presented in Table 1, as well as the textural characterization of the catalysts used in each run.

Table 1 – Catalyst characterization and initial butyric acid consumption rates ( $r_i$ ) (T=200°C, P<sub>O<sub>2</sub></sub>=6.9 bar, C<sub>ButOOH</sub>=5 g/L, C<sub>Catalyst</sub>=11.5 g/L)

Catalyst	S <sub>BET</sub> (m <sup>2</sup> /g)	S <sub>Meso</sub> (m <sup>2</sup> /g)	W <sub>o</sub> (cm <sup>3</sup> /g)	D <sub>M</sub> (%)	r <sub>i</sub> (mmol·h <sup>-1</sup> ·g <sub>Ir</sub> <sup>-1</sup> )
Ir/C-1	1023	112	0.392	8.8	5.8
Ir/C(Ox)-1	1024	108	0.396	13.7	5.8
Ir/C-2	992	104	0.385	11.6	29.8
Ir/C(Ox)-2	1025	113	0.394	27.4	18.1

We can conclude that iridium catalysts supported on the HNO<sub>3</sub> oxidized supports (with a predominance of surface carboxylic acid groups) are less active compared to those supported on the untreated carbon. As far as the impregnation method is concerned, catalysts prepared with the successive incipient impregnation method are much more active than the ones prepared with the direct incipient impregnation method.

The kinetic parameters for the butyric acid oxidation reaction were determined by varying reaction temperature, substrate and catalyst concentrations and oxygen pressure. The kinetic law was developed and can be expressed as :

$$r_i = 1.8 \times 10^5 e^{-\frac{50377}{RT}} [\text{ButOOH}] P_{O_2}^{0.43} [\text{Ir}]^{-0.63} \quad (1)$$

Catalytic wet air oxidation reaction kinetics for model compounds are useful for the interpretation and prediction of the behaviour of real waste water industrial streams and for the design industrial CWAO units with the maximum efficiency at lower cost.

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