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Catalytic wet air oxidation of butyric acid solutions using carbon-supported iridium catalysts

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Abstract

Aqueous solutions of butyric acid were treated by catalytic wet air oxidation using carbon-supported iridium catalysts in a stirred reactor. Under the operating conditions of 6.9 bar of oxygen partial pressure and 200 °C of temperature, conversions up to 52.9% after 2 h were obtained depending on the type of catalyst used. The effects of butyric acid initial concentration, loading of catalyst, oxygen partial pressure and temperature were investigated and the empirical rate law for acid conversion is presented. Oxidation intermediates such as propionic and acetic acid were identified. The heterogeneous catalyzed free-radical oxidation of butyric acid is discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic wet air oxidation; Butyric acid; Carbon-supported iridium catalysts

1. Introduction

The search for new advanced cleanup catalytic technologies imparted a recrudescent interest to catalytic wet air oxidation (CWAO) in recent years [1,2]. At present, more than 90 plants using CWAO are operative worldwide, mainly for treatment of waste streams from petrochemical, chemical, pharmaceutical [3] and textile industries [4,5]. CWAO can be used either for complete oxidative degradation, or as pre-treatment for biological degradation of downstream wastewaters [6]. 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 (BA) 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 (non-CWAO) [7]. These demanding conditions prompted us to develop heterogeneous catalysts, more efficient at milder conditions.

This paper represents to our knowledge, the first detailed application of carbon-supported iridium catalysts to the CWAO of organic pollutants in wastewaters. Except for a short mention in a study involving ceria-supported iridium catalysts [8], there is no mention in the literature to the application of this metal. In the present study the exploratory preparation and characterization of catalysts by the incipient wetness impregnation method is described and their performance is compared to a commercial catalyst.

2. Experimental

2.1. Catalyst preparation

Activated carbon pellets (Norit ROX 0.8) were used as support material to prepare the iridium catalysts.

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Prior to any use, the support was washed to remove any impurities, first with HCl 2 N under reflux for 12 h, then with water until the pH of the rinsing waters reached a value of 6, and finally was dried overnight at 110 °C. Textural characterization of the support was made by analysis of the N_2 adsorption isotherm at −196 °C which gave a BET surface area (S_{BET}) of 1053 $m^2\,g^{-1}$ with a micropore volume (V_{micro}) of 0.405 $cm^3\,g^{-1}$ and a mesopore surface area (S_{meso}) of 113 $m^2\,g^{-1}$.

The iridium catalysts (5 wt.%) used in the exploratory experiments were prepared by incipient wetness impregnation using aqueous solutions of $(NH_4)_3IrCl_6$ according to two different procedures. In the first procedure, the precursor solution was poured down onto the support in a single step, using the appropriate concentration to obtain 5 wt.% metal load (Ir/C-1). In the second procedure, two solutions were used in successive steps in order to obtain the same load (5 wt.%, Ir/C-2). After each impregnation step, the catalysts were dried overnight at 110 °C. Prior to reaction, the catalyst was heated in helium at 400 °C for 2 h. Reduction was then carried out in a stream (25 $cm^3\,min^{-1}$) of helium diluted hydrogen (10% v/v) at 350 °C for 3 h. In order to evaluate the effect of temperature on the reduction of the metal, one of the catalysts was reduced at higher temperature (450 °C). Finally, the catalyst was flushed with helium at 350 °C for 30 min.

The amount of iridium on the catalysts before and after reaction was measured by a gravimetric combustion method described elsewhere [9]. The metal particle size was estimated from H_2 chemisorption experiments using an automatic Coulter Omnisorp 100 CX.

A powdered commercial catalyst (Ir/C-α, 5 wt.%, Alfa-Aeasar, EWG-Nr.: 231-095-9) of a single lot (4/1283) was used in the CWAO kinetic studies of BA and the results obtained were used as comparison standard for the prepared catalysts.

2.2. Oxidation procedure

CWAO of BA (99% Riedel-de-Haën) solutions were carried out in a 160 cm^3 stainless steel high-pressure reactor (Parr 4564) described in detail elsewhere [9]. In a typical experiment the reactor was loaded with 70 cm^3 of 5 $g\,dm^{-3}$ (57 $mmol\,dm^{-3}$) BA solution and 0.8 g of catalyst. Standard operating conditions were set to 8 h reaction time at 6.9 bar of oxygen partial pressure and 200 °C under continuous stirring (500 rpm). Samples were withdrawn periodically and analyzed by gas chromatography (capillary column DBWAXetr, 0.32 i.d., 1 μm film), with a flame ionization detector. Sample injection details are given elsewhere [9]. The initial reaction rates ($mmol_{BA}\,h^{-1}\,g_{Ir}^{-1}$) were calculated from the curves giving the concentration of BA as a function of time at low conversion [9]. The kinetic orders with respect to BA, to oxygen and to catalyst load were determined by varying the initial concentration of the organic substrate in the range 0.034–0.080 M, the oxygen partial pressure in the range 6.9–13.9 bar and the catalyst weight 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.

BA conversion without any catalyst was first investigated in order to test for the non-CWAO of the substrate. The results obtained under standard operation conditions gave a residual conversion of 3.1%. Another blank experiment using only the activated carbon (0.8 g) from the same batch that was used to prepare the catalysts, under the same standard conditions, gave a conversion of 5.1%, value that was kept as reference.

N-Methylaniline (98% Sigma-Aldrich) was used as free-radical inhibitor in heterogeneous catalyzed oxidation experiments.

3. Results and discussion

Using the incipient wetness impregnation method a series of carbon-supported metal catalysts was prepared in order to ascertain an activity pattern. At the standard conditions using the same load (0.57 $g_M\,dm^{-3}$) of 5 wt.% carbon-supported metal catalysts, the conversion of 57 $mmol\,dm^{-3}$ BA solution was found to increase in the order $Co \approx Ni < Cu \ll Ir < Pt$ (Fig. 1). For practical purposes, and considering the conversion obtained for carbon alone, Co- and Ni-supported catalysts can be considered inactive. The carbon-supported Pt catalyst is the most active (70.4% conversion after 2 h) and was already object of a preliminary report [9]. The second most active was the carbon-supported Ir catalyst, with an interesting value of 42.6% conversion after 2 h, which

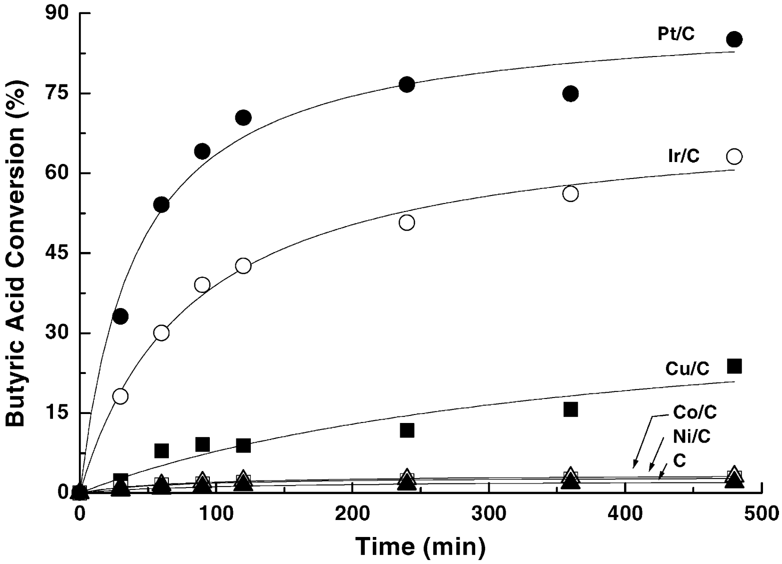

Fig. 1. Conversion (%) curves of the 57 mmol dm^{-3} BA solution carried out under air with a 6.9 bar partial pressure of O_2 at 200 °C, in the presence of several carbon-supported metal (5 wt.%) catalysts. The support (carbon) is given for reference.

prompted us to further investigate this system not so well reported in the literature.

The performance of the Ir catalyst was found to be dependent on the method of preparation and pretreatment used. Two-step incipient wetness impregnation catalysts (Ir/C-2) are more active than those prepared by single step incipient wetness impregnation (Ir/C-1, Table 1). Increasing the reduction temperature from 350 (Ir/C-2(350)) to 450 °C (Ir/C-2(450)) does not increase the initial activity. The mean iridium particle size, estimated by chemisorption, was 4.4 nm in the case of Ir/C-2(350) and 6.9 nm for Ir/C-1(350). No significant changes of the metal particle size occurred during reaction, as the mean particle diameter of the Ir/C-2(350) measured after reaction was 4.6 nm. The catalysts are microporous but include significant mesoporosity. The calculated mean micropore diameter (using the Dubinin-Raduskevich method) was about 1 nm. Because this value is significantly smaller than the mean iridium particle diameter it is expected that the metal will be distributed outside the micropores, in the more active catalysts. Since there is no marked difference between all the prepared catalysts from the textural point of view, the activity must be correlated with the exposed metal area. The interesting fact is that the dimension of the metal particles

Table 1
Catalyst textural characterization and performance for oxidation of BA solutions (57 mmol dm^{-3}), under the given standard conditions

Catalyst[a]	S_{BET} ($m^2\,g^{-1}$)	S_{meso} ($m^2\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)	Initial rate ($mmol\,h^{-1}\,g_{Ir}{}^{-1}$)	Conversion after 2 h (%)
Ir/C-1(350)	1023	112	0.392	16.8 ± 0.7	28.0
Ir/C-2	994	109	0.383	23.0 ± 0.4	38.5
Ir/C-2(350)	1007	104	0.385	29.8 ± 1.3	42.6
Ir/C-2(450)	931	100	0.361	15.2 ± 1.3	24.1
Ir/C-α	1019	337	0.296	35.4 ± 0.3	52.9

[a] The number between brackets refers to the reduction temperature (°C) of the catalyst.

is proportional to the concentration of the impregnation solution: the higher the concentration of the precursor solution (as in the single step incipient wetness impregnation), the higher the rate of nucleation and growth of iridium particles over the support.

The initial rates of oxidation for degradation of BA under the standard conditions ranged from 15.2 to 29.8 mmol h^{-1} g_{Ir}^{-1} with the prepared catalysts, the commercial one giving a slightly better value (35.4 mmol h^{-1} g_{Ir}^{-1}).

3.1. Kinetics of BA oxidation

The BA 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. In Fig. 2, we can observe the composition of the reaction medium as a function of time under standard reaction conditions, using the commercial Ir/C-α catalyst. Similar curves were obtained using the prepared catalysts. After 8 h, 72.2% of BA conversion is obtained with 74.2% selectivity (calculated as the fraction of the acid converted into non-carboxylic acid products), the remaining 25.8% being intermediate refractory compounds such as acetic acid and propionic acid, which are further decomposed to the final products CO_2 and H_2O. Acetone was also detected as an unstable intermediate, which is readily converted to acetic acid. Possible intermediate products, such as oxalic acid or formic acid, would be readily oxidized into CO_2 under the present reaction conditions [10].

The metal load of the catalyst, determined before and after the CWAO reaction, confirmed that there was no leaching of iridium to the solution.

The degradation of BA followed pseudo-first-order kinetics ($-\mathrm{d}C_{BA}/\mathrm{d}t = k'C_{BA}$), and this dependency was also checked by running catalytic oxidation reactions with solutions containing different concentrations of BA (initial consumption rate analysis).

In order to investigate the effects of the different operation variables on the kinetics of the process, one operating variable was changed at a time, keeping the other fixed at the given standard conditions.

Measuring the initial specific consumption rates in the presence of different amounts of 5% Ir/C-α catalyst, shows that when the weight of catalyst per unit of volume is increased, there is a proportional decrease in the initial specific rate, with an order of −0.63 (Fig. 3). This value could reflect an external mass transfer control playing a role in the reaction [11,12], but under the

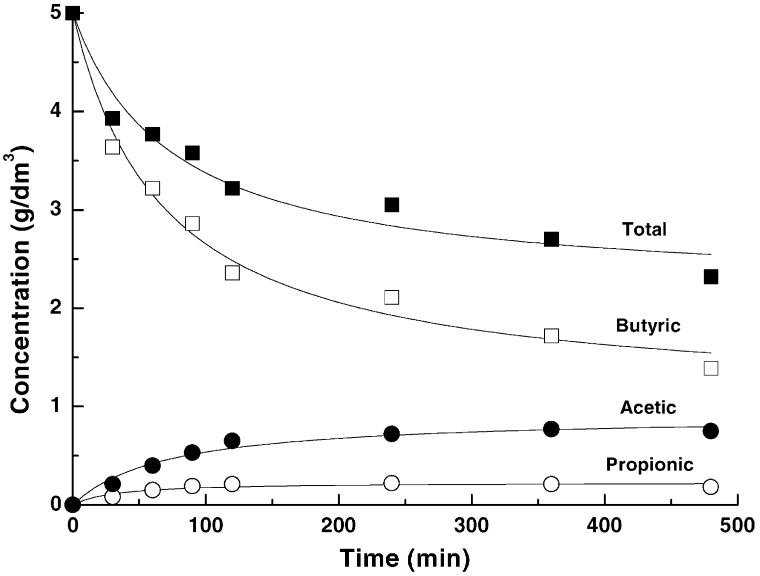

Fig. 2. Kinetics of BA (57 mmol dm^{-3} aqueous solution) disappearance, and propionic and acetic acid formation, under the standard conditions (200 °C, 6.9 bar P_{O_2}).

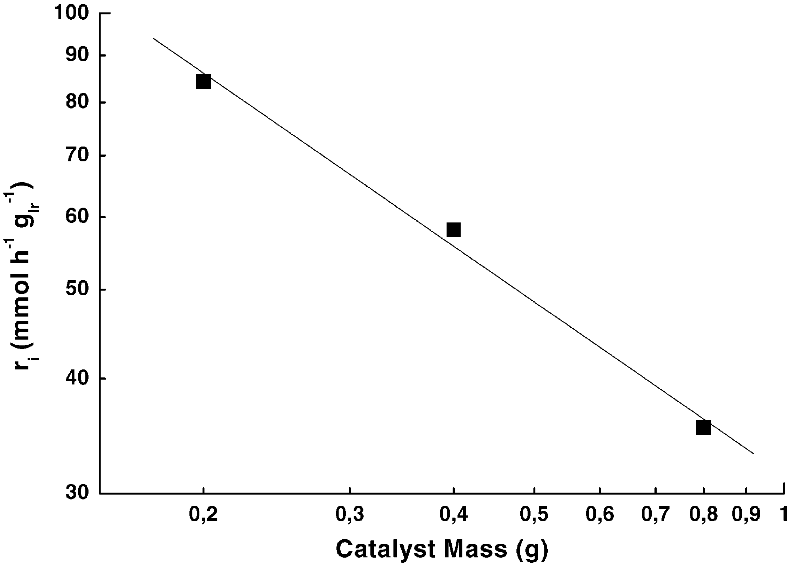

Fig. 3. Influence of the catalyst loading on the initial CWAO rate (r_i, mmol h^{-1} g_{Ir}^{-1}) of BA (57 mmol dm^{-3}).

standard conditions there was no dependency of the activity on stirring speed, going from 500 to 750 rpm. For the prepared catalysts, it was also verified that there is no internal diffusion control on the catalysts, because the activity of the catalyst also did not change with different diameter (200–800 μm) of the catalyst particles.

Another explanation for the unexpected effect of the catalyst loading is based on the heterogeneously catalyzed free-radical mechanism [13,14]. Oxygen assisted α- or β-hydrogen abstraction from BA takes place at the surface of the catalyst, the resulting radicals being released to solution where liquid-phase oxidation proceeds to end products. Adsorption of oxygen and BA molecules must occur at neighbor active sites on the iridium crystallites, since no significant conversion occurred in the presence of carbon alone. On the other hand, no oxygen assisted hydrogen abstraction takes place in the homogeneous phase since practically no conversion was obtained in the absence of catalyst. To account for a negative order it can be considered that higher concentration of catalyst per unit of volume increases the rate of the initiation step, which is the oxygen assisted radical formation from the hydrocarbon substrate on the adsorbed phase. Desorption of the radicals should be a fast step and leads to a high concentration of free-radicals in solution, which increases the rate of the free-radical termination step and consequently decreases the specific rate of the reaction.

In order to test the hypothesis of a liquid-phase hydrocarbon oxidation process, a free-radical inhibitor was introduced into the solution. *N*-Methylaniline was used, and as result almost no BA was converted during the reaction time, under the standard conditions.

The influence of the oxygen partial pressure was also studied by measuring the initial reaction rate, r_i, at different oxygen partial pressures (P_{O_2}) between 6.9 and 13.9 bar. For a given concentration of BA, equal to 57 mmol dm^{-3}, the plot of $\ln(r_i)$ as a function of $\ln(P_{O_2})$ gives a straight line from which a 0.61 reaction order can be calculated. This less than unity dependency was already found for both catalytic and non-CWAO processes [8,11] and may be indicative of a free-radical mechanism [15] on the assumption that oxygen is not strongly adsorbed on the catalyst, therefore it is available to complete the liquid-phase oxidation.

Finally, the influence of temperature was studied by running the reaction at three different temperature levels, 180, 200, and 220 °C, under the standard conditions (6.9 bar). From an Arrhenius-like plot of $\ln(r_i)$

as a function of 1/T, an apparent activation energy of 57.9 kJ mol^{-1} was estimated. This value is about half of the value reported [7] for the non-CWAO of BA (111.9 kJ mol^{-1}) under an oxygen partial pressure of 51.7 bar and is comparable to the value reported for the CWAO under the same conditions using a carbon-supported platinum catalyst [9].

From the results described above, the rate for CWAO of BA may be expressed as

$$r_{\mathrm{i}} = 3.2 \times 10^{5}\,\mathrm{e}^{-57900/RT} C_{\mathrm{BA}} P_{\mathrm{O_2}}^{0.61} C_{\mathrm{Ir}}^{-0.63} \qquad (1)$$

where the units of C_{BA} are in mol dm^{-3}, $P_{\mathrm{O_2}}$ in bars, and C_{Ir} in $\mathrm{g_{Ir}}$ dm^{-3}. The validity of this equation has to be limited to the used ranges of operating conditions, that are $34\,\mathrm{mmol\,dm^{-3}} < C_{\mathrm{BA}} < 80\,\mathrm{mmol\,dm^{-3}}$, $6.9\,\mathrm{bar} < P_{\mathrm{O_2}} < 13.9\,\mathrm{bar}$, $0.14\,\mathrm{g_{Ir}\,dm^{-3}} < C_{\mathrm{Ir}} < 0.57\,\mathrm{g_{Ir}\,dm^{-3}}$ and $180\,^{\circ}\mathrm{C} < t < 220\,^{\circ}\mathrm{C}$.

4. Conclusion

A heterogeneously catalyzed free-radical mechanism was evoked to justify the empirical rate law obtained. This explanation was supported by the kinetics of oxidation, which suggest that BA does not adsorb strongly on the iridium surface, and also by the results obtained using a free-radical inhibitor. The use of the Ir/C catalyst allowed for milder conditions of the degradation process and reduced number of intermediates, in comparison to the non-catalytic process.

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References

[1] V.S. Mishra, V.V. Mahajani, J.B. Joshi, Ind. Eng. Chem. Res. 34 (1995) 2.
[2] S. Imamura, Ind. Eng. Chem. Res. 38 (1999) 1743.
[3] F. Luck, Catal. Today 53 (1999) 81.
[4] K.R. Millington, JSDC 114 (1998) 286.
[5] G. Burkhard, Textilveredlung 22 (1987) 242.
[6] F.E. Hancock, Catal. Today 53 (1999) 3.
[7] P.E.L. Williams, P.L. Silveston, R.R. Hudgins, Can. J. Chem. Eng. 53 (1975) 354.
[8] J. Barbier Jr., F. Delanoë, F. Jabouille, D. Duprez, G. Blanchard, P. Isnard, J. Catal. 177 (1998) 378.
[9] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Appl. Catal. B 27 (2000) L217.
[10] P. Gallezot, N. Laurain, P. Isnard, Appl. Catal. B 9 (1996) L11.
[11] P. Gallezot, S. Chaumet, A. Perrard, P. Isnard, J. Catal. 168 (1997) 104.
[12] J.-C. Béziat, M. Besson, P. Gallezot, S. Durécu, J. Catal. 182 (1999) 129.
[13] A. Sadana, Ind. Eng. Chem. Process Des. Dev. 18 (1979) 50.
[14] H. Ohta, S. Goto, H. Teshima, Ind. Eng. Chem. Fundam. 19 (1980) 180.
[15] R.V. Shende, V.V. Mahajani, Ind. Eng. Chem. Res. 33 (1994) 3125.