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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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impurities. A BET surface area of 1053 m^2/g was calculated from the nitrogen adsorption isotherm obtained with an automatic analyzer (Coulter OMNISORP 100 CX), after the catalysts had been outgassed at 350 °C under vacuum. A more detailed characterization of these catalysts is given in previous publications.[27,28]

Prior to each reaction, the catalyst was heat treated in a helium flow at 400 °C for 2 h, reduced under hydrogen diluted with helium (12.5% v/v) at 350 °C for 3 h, and flushed at 350 °C for 30 min under helium to remove physisorbed hydrogen.

Thermogravimetric experiments were conducted on a Mettler TA4000/TG 50 system under an oxidizing atmosphere. X-ray photoelectron spectroscopy (XPS) analysis was performed on an Escalab 200-A-VG scientific spectrometer, operated with monochromatized Mg Kα X-ray radiation (hv = 1253.6 eV) under a residual vacuum of 10^{-15} bar. Temperature-programmed reduction (TPR) studies were carried out in a U-shaped quartz reactor coupled with a mass spectrometer detector. The amounts of metal within the catalyst before and after reaction were determined by burning away the carbon support and measuring the weight of the remaining metal.

Oxidation Procedure. Catalytic wet air oxidation studies were performed batchwise using a 316 stainless steel high-pressure reactor with acapacity of 160 mL (model 4564, Parr Instrument Company, Moline, IL) coated with a glass liner to prevent severe corrosion problems. The reactor also includes a stirrer, gas supply system, and temperature controller. In a typical run, the reactor was loaded with 70 mL of 5 g/L butyric acid solution (prepared from concentrated butyric acid, 99%, Riedel-de-Haën) and 0.8 g of catalyst. Before pressurization with air, the reactor was flushed with nitrogen for 15 min and heated to the reaction temperature under continuous stirring (500 rpm). Time zero was defined when the preset pressure was attained. Standard operating conditions were 200 °C and 6.9 bar of oxygen partial pressure.

Periodically, a sample (1 mL) was withdrawn from the reactor and the product distribution analyzed by gas chromatography on a capillary column (DBWAXetr, 0.32-mm i.d., 1 μL of film). The corresponding analytical conditions were optimized and presented elsewhere.[26]

The absence of external and internal diffusion limitations was verified by running experiments with different stirring speeds and particle size diameters, respectively.

Results and Discussion

Reaction Tests. Butyric acid oxidation was first investigated (i) without catalyst and (ii) with the support without metal, and it was found that, at 200 °C and 6.9 bar of oxygen partial pressure, the butyric acid conversions after 8 h of reaction were 3.1 and 5.1%, respectively. For the same standard conditions but in the presence of the Ir/C catalyst with a metal load of 5%, the conversion was 63%, and it rose to 78% in the presence of the Pt/C catalyst with a metal load of 1%. To a good approximation, the conversion curves followed the behavior described in previous works[26,27] under similar standard conditions. The conversions obtained with the Pt/C and Ir/C catalysts are far higher than those obtained with the bare support, confirming the catalytic effect. By determining the metallic contents of the catalysts before and after the reaction, it was concluded that almost no metal leaching occurred with

Table 1. Metal Contents of the Catalysts before and after Reaction

catalyst	% M/C before reaction	% M/C after reaction
Pt/C	1.7 ± 0.2	1.5 ± 0.2
Ir/C	5.5 ± 0.6	5.1 ± 0.5

these catalytic systems (Table 1). Noble metals are thermodynamically stable in the zerovalent state in a very broad range of conditions and specifically at the conditions employed in this work, thus leading to the absence of leaching.

The explanation anticipated for the difference in activity observed between the Pt/C and Ir/C catalysts is based on the reduction potentials of the respective metals. As iridium has a lower reduction potential than platinum, its surface has a higher propensity for oxygen adsorption.[34,35] Oxygen will compete with butyric acid for adsorption at the metal active sites. Compared with the platinum catalyst, the iridium catalyst will have fewer active sites available for butyric acid adsorption, the first step in the butyric acid oxidation reaction mechanism, and thus, it will exhibit lower activity.

The cause for metal deactivation in oxidation reactions is the poisoning of the metallic surface by oxygen, accompanied sometimes by the irreversible adsorption of reaction products.[36] Oxygen tends to partially cover the metal by chemisorption, forming strong M−O (or M−OH) bonds.[37] In the case of Pt/C catalysts, the formation of PtO$_2$ was also suggested and was confirmed by hydrogen titration experiments.[37] Both mechanisms of deactivation are reversible, allowing for catalyst partial reactivation by exposure to a nitrogen stream.[38] Surface coverage by oxygen depends on the relative affinity of the metal for oxygen, but in the presence of an organic substrate, competition has to be taken into account.

In previous works,[27,28] we have concluded that, after initial adsorption of butyric acid onto the substrate, oxidation proceeds by hydrogen abstraction at the metal surface assisted by chemisorbed oxygen. The dynamic balance of the competitive adsorption between oxygen and the substrate controls the initial reaction rate and the reaction progress. The balance favors higher oxygen coverages as the concentration of the substrate in solution decreases, thus lowering the reaction rate. Total or partial catalyst deactivation is interpreted in terms of the overoxidation of the metallic surface,[38−41] a high oxidation activity being obtained when the competitive adsorption between oxygen and the organic substrate at the metallic surface is equilibrated.

Some results from the literature reveal the existence of strongly adsorbed reaction products that block partially the surface, producing a genuine deactivation, which, when combined with overoxidation, results in a much higher deactivation rate.[40,42]

A similar mechanism of oxygen deactivation can be considered in the case of the Ir/C catalyst. This will explain to some extent the poorer fit between the experimental results and the kinetic model developed in a previous work, where deactivation was not considered.[28] The model is now improved by introducing the appropriate deactivation effect.

To fully characterize this effect, a study on the long-term resistance to deactivation of both systems was undertaken. For that purpose, the catalysts were recovered by filtration from the solution after reaction, washed with water, dried, and reused in successive runs with fresh butyric acid solutions. The results obtained are presented in Figure 1.
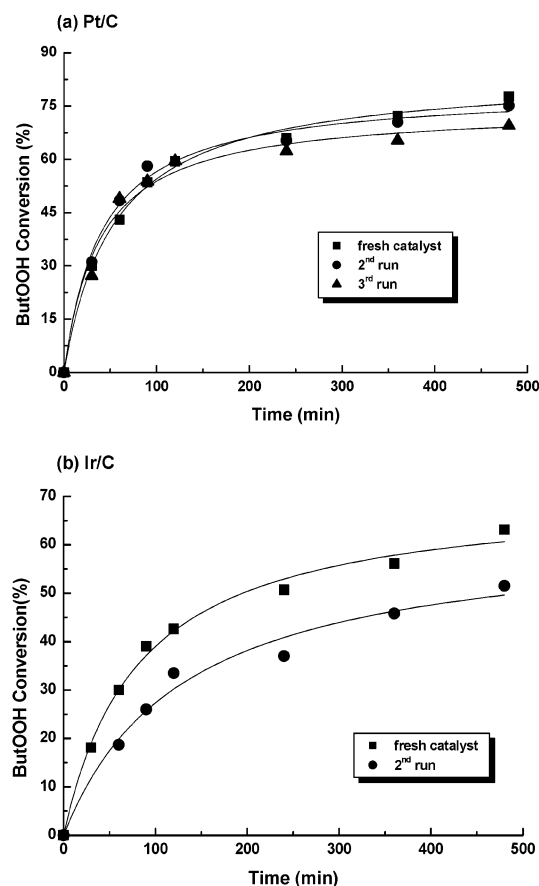
Figure 1. Conversion curves obtained in consecutive oxidation runs of fresh butyric acid solutions at 200 °C and 6.9 bar of oxygen partial pressure using (a) the Pt/C catalyst and (b) the Ir/C catalyst.

It can be observed that the Pt/C catalyst maintains nearly the same activity even in the third run, whereas the Ir/C catalyst already begins to lose activity in the second run. This deactivation can be explained in terms of the previously mentioned reduction potentials. The iridium catalyst is more prone to oxidation than the platinum catalyst. After the first oxidation run, the iridium surface gets covered with oxygen, thus affecting the catalyst activity in the second run. This observation was confirmed by performing XPS analysis on the catalyst before and after reaction, with a significant increase in the catalyst surface oxygen concentration being observed in the latter case. The same conclusion was reached by temperature-programmed reduction of the used catalyst under H_2 atmosphere, where a hydrogen consumption peak was observed at 80 °C, accompanied by the release of water molecules due to iridium surface oxygen titration.[28]

Other possible causes of deactivation, such as support stability and coke laydown, were also investigated.

Gasification of carbon is known to occur under oxidizing conditions such as those used in catalytic wet air oxidation reactions, thus limiting the applicability of this support. With the aim of evaluating the stability of the support used for the catalysts prepared in this work at the given reaction conditions, support and catalyst gasification studies in an oxidizing atmosphere were undertaken (Figure 2).

In the absence of metals, carbon gasification is seen to occur at a high rate at elevated temperatures (>500 °C), very far from the temperatures employed in
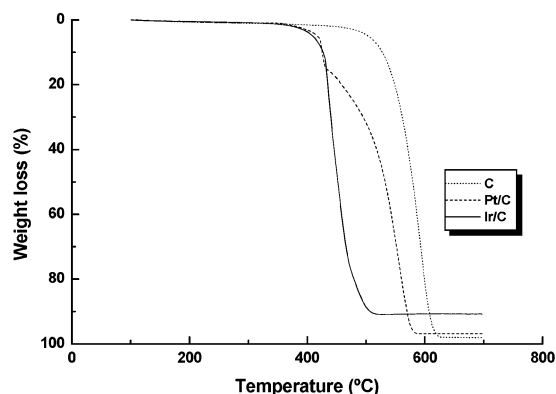

Figure 2. Temperature-programmed oxidations in air of the support Norit ROX 0.8 and of the prepared catalysts (heating rate = 20 °C/min).

Table 2. Hüttig and Tammann Temperatures

metal	T_f (°C)	T_H (°C)	T_T (°C)
platinum	1770	408	749
iridium	2450	635	1089

Table 3. Catalyst Textural Characterization before and after Reaction

catalyst	S_{BET} (m²/g)		S_{Meso} (m²/g)		V_{Micro} (cm³/g)	
	before	after	before	after	before	after
Pt/C	1064	992	125	113	0.409	0.391
Ir/C	1007	980	104	98	0.385	0.383

our work (200 °C). When the curves of the Pt/C and Ir/C catalysts are analyzed, one can see that the two metals do catalyze carbon gasification. The gasification reaction is appreciable above 410 °C. Once again, the required conditions for the occurrence of support gasification are much more severe than those used in our work, which guarantees the stability of the support during reaction. It is interesting to observe from Figure 2 that, although carbon gasification catalyzed by platinum occurs at a high rate at 410 °C, the catalyst activity decreases rapidly after the beginning of the reaction. Considering the temperatures involved, it is possible to anticipate the occurrence of either metal sintering or metal oxidation, leading to deactivation. The first hypothesis seems plausible, considering the Hüttig ($T_H \approx {}^1\!/_3 T_f$) and Tammann ($T_T \approx {}^1\!/_2 T_f$) temperatures (Table 2), where T_f represents the metal melting point, which gives an indication of the temperatures at which sintering starts to occur.[43] With the Ir/C catalyst, no deactivation in the gasification reaction was observed.

Several works have reported catalyst deactivation due to coke deposition on the catalyst surface,[24,44−46] blocking the pores. The Pt/C and Ir/C catalysts were texturally characterized before and after reaction by analysis of their N_2 adsorption isotherms. A slight loss in the catalysts specific surface areas and micropore volumes (Table 3) was observed after reaction, indicating the possibility of slight coke deposition.

In light of the above results, it was concluded that deactivation due to oxygen poisoning of the iridium surface in the Ir/C catalyst does occur, and a reaction−deactivation kinetic model for this process is proposed here.

Kinetic Modeling. The reaction scheme considered for the butyric acid oxidation reaction is presented in Scheme 1.

Scheme 1. Reaction Scheme Proposed for the Butyric Acid Oxidation Reaction
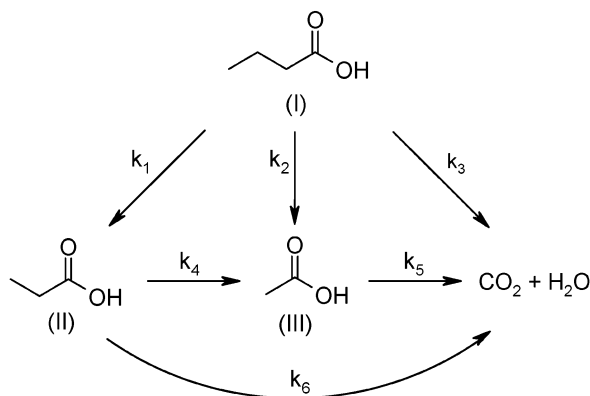
In this scheme, the oxidation of butyric acid (I) might proceed via the formation of propionic acid (II) or acetic acid (III) or directly through the formation of the end products, CO_2 and H_2O. Propionic acid can be degraded directly to the end products or via acetic acid. Acetic acid oxidation is considered to occur directly to the end products.

A Langmuir–Hinshelwood mechanism was assumed in the formulation of the mathematical model. The reaction was assumed to occur in the adsorbed phase between the organic substrates and dissociatively adsorbed oxygen, characterized by the adsorption constants K_{But}, K_{Prop}, K_{Ace}, and K_{O_2} and the independent reaction rate constants k_1-k_6. Competitive adsorption between the organic compounds and oxygen was also assumed to occur. Catalyst deactivation during the oxidation run was characterized by an empirical deactivation function α, defined as the fraction of nondeactivated active sites.[44,47] In this way, the butyric acid oxidation reaction can be described by the following set of differential equations

$$-\frac{d[But]}{dt}\frac{1}{W} = \frac{(k_1 + k_2 + k_3)K_{But}[But](K_{O_2}[O_2])^{1/2}\alpha}{(1 + K_{But}[But] + K_{Prop}[Prop] + K_{Ace}[Ace] + (K_{O_2}[O_2])^{1/2})^2} \quad (1)$$

$$\frac{d[Prop]}{dt}\frac{1}{W} = \frac{(k_1 K_{But}[But] - (k_4 + k_6)K_{Prop}[Prop])(K_{O_2}[O_2])^{1/2}\alpha}{(1 + K_{But}[But] + K_{Prop}[Prop] + K_{Ace}[Ace] + (K_{O_2}[O_2])^{1/2})^2} \quad (2)$$

$$\frac{d[Ace]}{dt}\frac{1}{W} = \frac{(k_2 K_{But}[But] + k_4 K_{Prop}[Prop] - k_5 K_{Ace}[Ace])(K_{O_2}[O_2])^{1/2}\alpha}{(1 + K_{But}[But] + K_{Prop}[Prop] + K_{Ace}[Ace] + (K_{O_2}[O_2])^{1/2})^2} \quad (3)$$

$$\alpha = e^{-kt} \quad (4)$$

where K_{But}, K_{Prop}, K_{Ace}, and K_{O_2} are the adsorption equilibrium constants of the various species (L·mmol^{-1}); k_1-k_6 are the kinetic rate constants of the reactions depicted in Scheme 1 (mmol·h^{-1}·g$_{Ir}^{-1}$); k is the first-order catalyst deactivation constant (h^{-1}); [But], [Prop],

[Ace], and [O$_2$] are the liquid-phase concentrations of the various species (mmol·L^{-1}); and W is the metal concentration (g$_{Ir}$·L^{-1}).
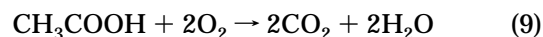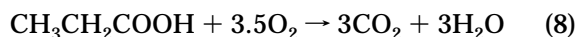
The following empirical equation (with T in °C and P_{O_2} in bar) was deduced for calculating the liquid-phase oxygen concentrations using literature data[45] within the range of oxygen partial pressures studied and for the temperatures used (180, 200, and 220 °C)

$$[O_2] = (0.0116T - 0.964)P_{O_2} \quad (5)$$

Assuming ideal behavior in the gas phase, a relationship between the oxygen concentration in the liquid phase and the oxygen concentration in the gas phase is obtained as

$$[O_2] = (0.0116T - 0.964)RT[O_2]_g \quad (6)$$

On the other hand, the gas-phase oxygen partial pressure decreases during the reaction, as the oxygen is consumed. Considering the total oxidation stoichiometry for each organic acid (eqs 7–9), the oxygen concentration in the gas phase changes according to eq 10

$$CH_3CH_2CH_2COOH + 5O_2 \rightarrow 4CO_2 + 4H_2O \quad (7)$$

$$CH_3CH_2COOH + 3.5O_2 \rightarrow 3CO_2 + 3H_2O \quad (8)$$

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O \quad (9)$$

$$[O_2]_g V_g = [O_2]_{g_0} V_g - 5([But]_0 - [But])V_L + 3.5[Prop]V_L + 2[Ace]V_L \quad (10)$$

where V_g, V_L, and $[O_2]_{g_0}$ represent the gas-phase volume, the liquid-phase volume, and the initial oxygen concentration in the gas phase, respectively. Taking $[O_2]_g$ from eq 10, the oxygen concentration in the liquid phase can be calculated from eq 6.

The application of the model to the experimental results was accomplished by means of MATLAB software, using as the objective function

$$f_{obj} = \sum_i \sum_j (C_{ij} - \bar{C}_{ij})^2 \quad (11)$$

where C_{ij} represents the calculated concentration of species i at instant j and $\bar{C}_{ij}$ represents the experimental concentration of species i at instant j. The optimization cycle involves solving the set of differential equations (eqs 1–4) to obtain, in each iteration, the value of the calculated concentration as a function of time for each species (C_{ij}). Initially, in eqs 1–3, it was considered that the values of $K_{But}[But]$, $K_{Prop}[Prop]$, and $K_{Ace}[Ace]$ were ≪1. Then, the model parameters with better confidence intervals were fixed, and only the worst parameters were allowed to fluctuate. Different combinations of fixed/free parameters were successively used, and the optimal estimates were obtained. Finally, the parameters were used in the nonsimplified equations to calculate their confidence intervals and to confirm the goodness of the fitting.

Excellent agreement for all of the organic species present in the reaction was obtained by fitting the proposed reaction–deactivation model to the experi-

Table 4. Kinetic Constants (mmol·h^{-1}·g$_{Ir}$$^{-1}$) Obtained with the Proposed Model for the Butyric Acid Oxidation Reaction over the Ir/C Catalyst at Several Temperatures

T (°C)	k_1	k_2	k_3	k_4	k_5	k_6
180	$(3.0 \pm 0.4) \times 10^5$	$(1.3 \pm 0.2) \times 10^6$	$(2.8 \pm 0.4) \times 10^5$	$(1.2 \pm 0.5) \times 10^4$	$(1.4 \pm 0.6) \times 10^3$	$(1.0 \pm 0.8) \times 10^4$
200	$(1.8 \pm 0.1) \times 10^6$	$(7.3 \pm 0.5) \times 10^6$	$(6.4 \pm 0.5) \times 10^6$	$(1 \pm 1) \times 10^5$	$(1.1 \pm 0.1) \times 10^4$	$(5 \pm 5) \times 10^4$
220	$(1.4 \pm 0.1) \times 10^7$	$(4.0 \pm 0.1) \times 10^7$	$(8.8 \pm 0.2) \times 10^7$	$(3 \pm 4) \times 10^6$	$(2.9 \pm 0.5) \times 10^5$	$(1 \pm 4) \times 10^5$

Table 5. Adsorption Equilibrium (L·mmol^{-1}) and Deactivation (h^{-1}) Constants Obtained with the Proposed Model for the Butyric Acid Oxidation Reaction over the Ir/C Catalyst at Several Temperatures

T (°C)	K_{But} (L·mmol^{-1})	K_{Prop} (L·mmol^{-1})	K_{Ace} (L·mmol^{-1})	K_{O_2} (L·mmol^{-1})	k (h^{-1})
180	$(5 \pm 1) \times 10^{-7}$	$(5 \pm 1) \times 10^{-5}$	$(7 \pm 3) \times 10^{-4}$	$(2 \pm 1) \times 10^{-2}$	0.04 ± 0.19
200	$(3.8 \pm 0.4) \times 10^{-7}$	$(3 \pm 1) \times 10^{-5}$	$(5.0 \pm 0.2) \times 10^{-4}$	$(3.6 \pm 0.2) \times 10^{-3}$	0.4 ± 0.1
220	$(2.4 \pm 0.1) \times 10^{-7}$	$(1 \pm 2) \times 10^{-5}$	$(1.8 \pm 0.3) \times 10^{-4}$	$(3.2 \pm 0.1) \times 10^{-4}$	0.5 ± 0.1
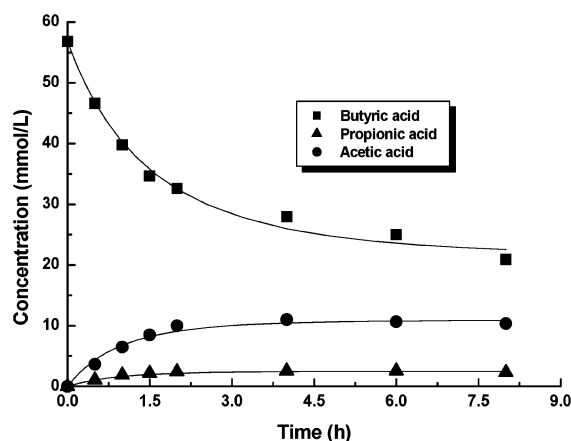
Figure 3. Comparison between the reaction−deactivation kinetic model proposed and the experimental results obtained in butyric acid oxidation with the Ir/C catalyst at 200 °C and 6.9 bar of oxygen partial pressure.

Table 6. Activation Energies and Adsorption Enthalpies

	activation energy (kJ/mol)		adsorption enthalpy (kJ/mol)
E_1	177 ± 5	ΔH^0_{But}	-34 ± 12
E_2	158 ± 6	ΔH^0_{Prop}	-66 ± 34
E_3	266 ± 7	ΔH^0_{Ace}	-61 ± 12
E_4	249 ± 75	$\Delta H^0_{O_2}$	-182 ± 11
E_5	247 ± 40		
E_6	112 ± 118		

mental results in the butyric acid oxidation, for the Ir/C catalyst at 200 °C and 6.9 bar of oxygen partial pressure (Figure 3).

The parameters (with the corresponding 95% confidence intervals) are grouped in terms of the kinetic constants (Table 4) and adsorption equilibrium constants (Table 5) for the different temperatures studied.

The results confirm the high tendency of the iridium catalyst to adsorb oxygen, which is the cause of deactivation. It can also be concluded that the refractory intermediates, propionic and acetic acids, are more strongly adsorbed than the initial organic substrate, butyric acid. From the values of the deactivation constant listed in Table 5, it can be concluded that catalyst deactivation increases significantly from 180 to 200 °C.

With the values presented in Tables 4 and 5, it was possible to calculate the apparent activation energy of each surface reaction and the corresponding adsorption enthalpy by means of Arrhenius and van't Hoff plots, respectively. The results are reported in Table 6, with the corresponding 95% confidence intervals, considering the 95% confidence intervals of the corresponding kinetic and equilibrium constants.

The values obtained are coherent with those found in the literature for a variety of compounds.[44] The reaction−deactivation model developed here allows for a more realistic approach to the study of butyric acid oxidation over carbon-supported iridium catalysts.

Conclusions

The carbon-supported platinum (Pt/C) and iridium (Ir/C) catalysts prepared in this work are very efficient in butyric acid removal by CWAO. The prepared catalysts are very stable under the reaction conditions, with no significant leaching of the metal phase being observed. The platinum catalysts are more resistant to deactivation than the corresponding iridium catalysts. Gasification of the carbon support is not a probable cause of deactivation in this specific case. Blockage of the pores by coke deposition does not seem to be significant. Metal sintering is also not likely to occur significantly under the reaction conditions. The iridium catalyst undergoes deactivation due to overoxidation of the metal surface in a mechanism similar to that ascribed to the platinum catalysts. The introduction of a simple deactivation function ($\alpha = e^{-kt}$) in the proposed kinetic model leads to an excellent fit of the experimental results.

The proposed reaction−deactivation model is of practical interest for the design of continuous catalyst systems, accounting for the description of mechanistic aspects of catalyst deactivation in CWAO.

Acknowledgment

Literature Cited

(1) Katzer, J. R.; Ficke, H. H.; Sadana, A. An Evaluation of Aqueous Phase Catalytic Oxidation. *J. Water Pollut. Control Fed.* **1976**, *48*, 920.

(2) Debellefontaine, H.; Foussard, J. N. Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. *Waste Manage.* **2000**, *20*, 15.

(3) Gimeno, O.; Plucinski, P.; Kolaczkowski, S. T.; Rivas, F. J.; Alvarez, P. M. Removal of the herbicide MCPA by commercial activated carbons: Equilibrium, kinetics, and reversibility. *Ind. Eng. Chem. Res.* **2003**, *42*, 1076.

(4) Garg, A.; Saha, S.; Rastogi, V.; Chand, S. Catalytic wet air oxidation of pulp and paper mill effluent. *Indian J. Chem. Technol.* **2003**, *10*, 305.

(5) Kacar, Y.; Alpay, E.; Ceylan, V. K. Pretreatment of Afyon alcaloide factory's wastewater by wet air oxidation (WAO). *Water Res.* **2003**, *37*, 1170.

(6) Chen, G. H.; Lei, L. C.; Hu, X. J.; Yue, P. L. Kinetic study into the wet air oxidation of printing and dyeing wastewater. *Sep. Purif. Technol.* **2003**, *31*, 71.

(7) Hu, X. J.; Lei, L. C.; Chen, G. H.; Yue, P. L. On the degradability of printing and dyeing wastewater by wet air oxidation. *Water Res.* **2001**, *35*, 2078.

(8) Lei, L. C.; Hu, X. J.; Chen, G. H.; Porter, J. F.; Yue, P. L. Wet air oxidation of desizing wastewater from the textile industry. *Ind. Eng. Chem. Res.* **2000**, *39*, 2896.

(9) Zhu, W. P.; Bin, Y. J.; Li, Z. H.; Jiang, Z. P.; Yin, T. Application of catalytic wet air oxidation for the treatment of H-acid manufacturing process wastewater. *Water Res.* **2002**, *36*, 1947.

(10) Mishra, V. S.; Mahajani, V. V.; Joshi, J. B. Wet Air Oxidation (Review). *Ind. Eng. Chem. Res.* **1995**, *34*, 2.

(11) Kolaczkowski, S. T.; Plucinski, P.; Beltran, F. J.; Rivas, F. J.; McLurgh, D. B. Wet air oxidation: A review of process technologies and aspects in reactor design. *Chem. Eng. Sci.* **1999**, *73*, 143.

(12) Hu, X.; Lei, L.; Chu, H. P.; Yue, P. L. Copper/Activated Carbon as Catalyst for Organic Wastewater Treatment. *Carbon* **1999**, *37*, 631.

(13) Pirkanniemi, K.; Sillanpaa, M. Heterogeneous water phase catalysis as an environmental application: A review. *Chemosphere* **2002**, *48*, 1047.

(14) Pintar, A. Catalytic processes for the purification of drinking water and industrial effluents. *Catal. Today* **2003**, *77*, 451.

(15) Imamura, S.; Hirano, A.; Kawabata, N. Wet Oxidation of Acetic Acid Catalyzed by Co—Bi Complex Oxides. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 570.

(16) Imamura, S.; Fukuda, I.; Ishida, S. Wet Oxidation Catalyzed by Ruthenium Supported on Cerium(IV) Oxides. *Ind. Eng. Chem. Res.* **1988**, *27*, 718.

(17) Kulkarni, U. S.; Dixit, S. G. Destruction of Phenol from Wastewater by Oxidation with SO_3^{2-}—O_2. *Ind. Eng. Chem. Res.* **1991**, *30*, 1916.

(18) Shende, R. V.; Mahajani, V. V. Kinetics of Wet Air Oxidation of Glyoxalic Acid and Oxalic Acid. *Ind. Eng. Chem. Res.* **1994**, *33*, 3125.

(19) Lin, S. H.; Ho, S. J. Catalytic Wet-Air Oxidation of High Strength Industrial Wastewater. *Appl. Catal. B* **1996**, *9*, 133.

(20) Sadana, A.; Katzer, J. R. Catalytic Oxidation of Phenol in Aqueous Solution over Copper Oxide. *Ind. Eng. Chem. Fundam.* **1974**, *13*, 127.

(21) Imamura, S.; Doi, A.; Ishida, S. Wet Oxidation of Ammonia Catalyzed by Cerium-Based Composite Oxides. *Ind. Eng. Chem. Prod. Res. Dev.* **1985**, *24*, 75.

(22) Imamura, S.; Nakamura, M.; Kawabata, N.; Yoshida, J.; Ishida, S. Wet Oxidation of Poly(ethylene glycol) Catalyzed by Manganese—Cerium Composite Oxide. *Ind. Eng. Chem. Prod. Res. Dev.* **1986**, *25*, 34.

(23) Levec, J. Catalytic Oxidation of Toxic Organics in Aqueous Solution. *Appl. Catal.* **1990**, *63*, L1.

(24) Pintar, A.; Levec, J. Catalytic Oxidation of Organics in Aqueous Solutions: I. Kinetics of Phenol Oxidation. *J. Catal.* **1992**, *135*, 345.

(25) Gallezot, P.; Chaumet, S.; Perrard, A.; Isnard, P. Catalytic Wet Air Oxidation of Acetic Acid on Carbon-Supported Ruthenium Catalysts. *J. Catal.* **1997**, *168*, 104.

(26) Gomes, H. T.; Figueiredo, J. L.; Faria, J. L. Catalytic Wet Air Oxidation of Low Molecular Weight Carboxylic Acids Using a Carbon Supported Platinum Catalyst. *Appl. Catal. B* **2000**, *27*, L217.

(27) Gomes, H. T.; Figueiredo, J. L.; Faria, J. L. Catalytic Wet Air Oxidation of Butyric Acid Solutions Using Carbon Supported Iridium Catalysts. *Catal. Today* **2002**, *75*, 23.

(28) Gomes, H. T.; Figueiredo, J. L.; Faria, J. L.; Serp, P.; Kalck, P. Carbon Supported Iridium Catalysts in the Catalytic Wet Air Oxidation of Carboxylic Acids: Kinetics and Mechanistic Interpretation. *J. Mol. Catal. A* **2002**, *182—183*, 48.

(29) Gallezot, P.; Laurain, N.; Isnard, P. Catalytic Wet-Air Oxidation of Carboxylic Acids on Carbon-Supported Platinum Catalysts. *Appl. Catal. B* **1996**, *9*, L11.

(30) Mantzavinos, D.; Hellenbrand, R.; Livingston, A. G.; Metcalfe, I. S. Catalytic Wet Oxidation of *p*-Coumaric Acid: Partial Oxidation Intermediates, Reaction Pathways and Catalyst Leaching. *Appl. Catal. B* **1996**, *7*, 379.

(31) Hamoudi, S.; Larachi, F.; Sayari, A. Wet Oxidation of Phenolic Solutions over Heterogeneous Catalysts: Degradation Profile and Catalyst Behavior. *J. Catal.* **1998**, *177*, 247.

(32) Matatov-Meytal, Y. I.; Sheintuch, M. Catalytic Abatement of Water Pollutants. *Ind. Eng. Chem. Res.* **1998**, *37*, 309.

(33) Wu, Q.; Hu, X.; Yue, P. L.; Zhao, X. S.; Lu, G. Q. Copper/MCM-41 as Catalyst for the Wet Oxidation of Phenol. *Appl. Catal. B* **2001**, *32*, 151.

(34) Dam, H. E. V.; Wisse, L. J.; Bekkum, H. V. Platinum/Carbon Oxidation Catalysts: VIII. Selecting a Metal for Liquid-Phase Alcohol Oxidations. *Appl. Catal.* **1990**, *61*, 187.

(35) Gallezot, P.; de Mésanstourne, R.; Christidis, Y.; Mattioda, G.; Schouteeten, A. Catalytic Oxidation of Glyoxal to Glyoxilic Acid on Platinum Metals. *J. Catal.* **1992**, *133*, 479.

(36) Béziat, J.-C.; Besson, M.; Gallezot, P.; Durécu, S. Catalytic Wet Air Oxidation of Carboxylic Acids on TiO_2-Supported Ruthenium Catalysts. *J. Catal.* **1999**, *182*, 129.

(37) Dirkx, J. M. H.; van der Baan, H. S. The Oxidation of Glucose with Platinum on Carbon as Catalyst. *J. Catal.* **1981**, *67*, 1.

(38) Vleeming, J. H.; Bruijn, F. A.; Kuster, B. F. M.; Marin, G. B. Deactivation of Carbon-Supported Platinum Catalysts during Oxidations in Aqueous Media. *Stud. Surf. Sci. Catal.* **1994**, *88*, 467.

(39) Imamura, S.; Nishimura, H.; Ishida, S. Preparation of Mn/Ce Composite Oxide Catalysts for the Wet Oxidation of Acetic Acid and Their Catalytic Activities. *J. Jpn. Pet. Inst.* **1987**, *30*, 199.

(40) Mallat, T.; Bodnar, Z.; Baiker, A.; Greis, O.; Strubig, H.; Reller, A. Preparation of Promoted Platinum Catalysts of Designed Geometry and the Role of Promoters in the Liquid-Phase of 1-Methoxy-2-propanol. *J. Catal.* **1993**, *142*, 237.

(41) Besson, M.; Lahmer, F.; Gallezot, P.; Fuertes, P.; Flèche, G. Catalytic Oxidation of Glucose on Bismuth-Promoted Palladium Catalysts. *J. Catal.* **1995**, *152*, 116.

(42) Gallezot, P. Selective Oxidation with Air on Metal Catalysts. *Catal. Today* **1997**, *37*, 405.

(43) Trimm, D. L. In *Progress in Catalyst Deactivation*; Figueiredo, J. L., Ed.; Martinus Nijhoff: Dordrecht, The Netherlands, 1982; p 3.

(44) Hamoudi, S.; Belkacemi, K.; Larachi, F. Catalytic Oxidation of Aqueous Phenolic Solutions Catalyst Deactivation and Kinetics. *Chem. Eng. Sci.* **1999**, *54*, 3569.

(45) Belkacemi, K.; Larachi, F.; Hamoudi, S.; Sayari, A. Catalytic Wet Oxidation of High-Strength Alcohol-Distillery Liquors. *Appl. Catal. A* **2000**, *199*, 199.

(46) Larachi, F.; Iliuta, I.; Belkacemi, K. Catalytic Wet Air Oxidation with a Deactivating Catalyst Analysis of Fixed and Sparged Three-Phase Reactors. *Catal. Today* **2001**, *64*, 309.

(47) Froment, G. F.; Bishoff, K. B. *Chemical Reactor Analysis and Design*, 2nd ed.; John Wiley & Sons: New York, 1990.