

# Catalytic Wet Air Oxidation of Carboxylic Acids on TiO<sub>2</sub>-Supported Ruthenium Catalysts

Jean-Christophe Béziat,<sup>\*</sup> Michèle Besson,<sup>\*1</sup> Pierre Gallezot,<sup>\*</sup> and Sylvain Durécut<sup>†</sup>

<sup>\*</sup>Institut de Recherches sur la Catalyse-CNRS, 69626 Villeurbanne, France; and <sup>†</sup>Département Recherche, TREDI, 54505 Vandœuvre-les-Nancy, France

Received June 16, 1998; revised October 25, 1998; accepted November 9, 1998

The total oxidation of aqueous solutions of carboxylic acids by air was studied in a slurry reactor over the temperature range 180–200°C and oxygen partial pressure of 0.3–1.8 MPa in the presence of a 2.8%Ru/TiO<sub>2</sub> catalyst. The influence of various parameters is presented: the catalytic wet air oxidation of succinic acid is 0 order with respect to succinic acid; the order with respect to oxygen pressure is 0.4, and the activation energy is ca. 125 kJ/mol. It was found that acetic acid, which is one of the intermediates, and CO<sub>2</sub> have no retarding effect on the total organic carbon abatement rate of succinic acid. Substitution of one hydrogen atom of the methyl group in acetic acid by Cl, OH, or NH<sub>2</sub> gives an increase of the oxidation rate. However, it was proposed that the low activity of acetic acid oxidation is due not only to the difficulty to oxidize the methyl group, but also to the low adsorption coefficient of acetic acid on ruthenium surface. Inorganic salts, such as sodium chloride, only slightly decrease the oxidation rate of acetic acid.

The absence of metal ions (Ru, Ti) in the effluents after reaction and the absence of particle sintering indicate also a high stability of the catalyst under the conditions employed. The catalyst can be recycled without loss of activity after the second run. The activity becomes stable after the attainment of a steady-state coverage of the Ru particles by oxygen. The study of the effect of reduction-oxidation treatments of the catalyst showed that the activity depends on the oxidation state of the surface. © 1999 Academic Press

## INTRODUCTION

Interest in new processes for waste water treatment is presently stirred by recent and forthcoming environmental regulations on the disposal of industrial effluents. The main objective for the future is to treat industrial pollutants at their source of emission, particularly chemical and paper pulp plants, and to recycle the treated water in industrial plants, so as to achieve closed loop operations preventing the spilling of industrial water in the hydrosphere. Biological water treatments are not well adapted for this purpose and are also limited by the toxicity or concentration of

effluents. Alternatively, industrial aqueous effluents are generally too diluted to be incinerated economically. The emergent technology of wet air oxidation (WAO), which consists of mineralizing the organic carbon, by oxidation into CO<sub>2</sub>, is very promising for the treatment and recycling of industrial waste waters provided investments and operating cost are reduced significantly. This can be achieved by employing catalysts designed to accelerate the rate of oxidation into CO<sub>2</sub>, thus improving the abatement of total carbon and enabling operation under temperature and pressure conditions milder than those required in the absence of catalysts. Catalytic WAO can be conducted with catalysts dissolved in the reaction medium (1–7). However, soluble catalysts such as transition metal cations (essentially copper) have to be recovered from the treated water by additional separation processes. In contrast, heterogeneous catalysts are easily separated from the liquid phase either in batch or continuous processes, but they have to be stable for a long period of time in the acidic, oxidizing, and often chelating reaction medium; otherwise recovery processes would also be required. Some leaching of solid catalysts such as copper oxides on ZnO–Al<sub>2</sub>O<sub>3</sub> spinel supports (8–10) and manganese–cerium (11) or cobalt–bismuth composite oxides (10, 12) could not be avoided. In previous studies, the total oxidation into carbon dioxide of acetic acid (13) and C<sub>6</sub>–C<sub>4</sub> diacids (14) was achieved at 180–200°C with air on ruthenium catalysts supported on active carbon and graphite. No leaching of ruthenium was observed but the carbon support was partially oxidized, which precludes any prolonged use of carbon-supported catalysts, at least under the operating conditions required to oxidize the most refractory molecules such as acetic acid, i.e., at temperatures higher than 170°C. However, most of the oxides and salts employed as inorganic supports are liable to leach away under hydrothermal conditions in the acidic, oxidizing, and chelating medium. Examination of potential-pH diagrams giving the stability domains of oxides indicates that TiO<sub>2</sub> and ZrO<sub>2</sub> are the most stable of readily available supporting materials (15). Titanium and zirconium oxide supports were actually employed in Nippon Shokubai (16)

<sup>1</sup> To whom correspondence should be addressed. E-mail: mbesson@catalyse.univ-lyon1.fr. Fax: 33 (0)4 72 44 53 99.

and Osaka Gas (17) WAO processes. Ceria, which is also a good candidate for stable supporting materials, was used by Imamura *et al.* (18) and Duprez *et al.* (19, 20).

In the present work, WAO of aqueous solutions of succinic and other carboxylic acids was carried out batchwise in a continuously stirred tank reactor pressurized with air in the presence of a commercial TiO<sub>2</sub>-supported ruthenium catalyst in powder form.

## EXPERIMENTAL

### Materials and Characterization

Catalytic studies were carried out with a Ru/TiO<sub>2</sub> catalyst loaded with 2.8 wt% metal obtained from Engelhard (Q500-069). The particle size of the catalyst was less than 0.040 mm. The structure of the catalyst was characterized by X-ray diffraction (Philips PW1050 diffractometer) and by high-resolution transmission electron microscopy (Jeol JEM2010). The BET surface area was measured, after desorption at 200°C under vacuum, by nitrogen adsorption with an automatic sorbometer. The metal dispersion was measured by hydrogen chemisorption with a volumetric apparatus equipped with a Baratron MKS pressure gauge. The catalyst was reduced under hydrogen and outgassed at 300°C; then adsorption isotherm was measured at 45°C. A second isotherm was measured after desorption at 45°C to determine the amount of reversibly adsorbed hydrogen. The treated solutions were analyzed by ICP-AES to determine the concentration of ruthenium and titanium salts.

### Oxidation Procedure

Oxidation of aqueous solutions of carboxylic acids (0.5 wt%) was performed in a 250-ml Hastelloy C22 autoclave, connected to an air reserve and equipped with a magnetically driven turbine. The reactor was loaded with the carboxylic acid solution and with the catalyst. After flushing with argon, the temperature of the mixture was raised to the reaction temperature under stirring. Air was then admitted until the preset pressure was attained and the reaction was started by adjusting the stirring speed at 1800 rpm, which defined time zero. Standard operating conditions were 0.15 liter of 5 g liter<sup>-1</sup> solution, 1 g of 2.8 wt% Ru/TiO<sub>2</sub>, 190°C, and 5 MPa total pressure (i.e., 0.72 MPa of O<sub>2</sub>).

Samples were periodically withdrawn from the reactor through stainless-steel 1/16" tubing, and the pH, total organic carbon (TOC), and product distribution were measured. The pH measurement gave qualitative information on the progress of the reaction, since the pH increased upon oxidation of the acids into CO<sub>2</sub>. Analysis of organic products was performed by HPLC with UV and RID detectors in series and separation with an ion-exchange column

(Sarasep Car-H) using dilute H<sub>2</sub>SO<sub>4</sub> solutions as eluent (0.01 N, 0.5 ml min<sup>-1</sup>). The overall abatement of organic effluents was monitored with a TOC analyzer equipped with an IR detector (Shimadzu 5050A). The TOC was determined by subtracting the inorganic carbon (CO<sub>2</sub> evolved after treatment of the sample in concentrated phosphoric acid) from the total carbon (CO<sub>2</sub> evolved after catalytic combustion on platinum at 700°C). The initial reaction rates were calculated from the curves, giving the concentration of succinic acid or the TOC as a function of time at low conversion; they were expressed either in mol<sub>acid</sub> h<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup> (*r*<sub>0(acid)</sub>) or in mol<sub>C</sub> h<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup> (*r*<sub>0(TOC)</sub>). The percentage of TOC abatement was defined as 100 (TOC<sub>0</sub> - TOC)/TOC<sub>0</sub>.

## RESULTS

### Catalyst Characterization

Nitrogen adsorption measurements showed that the BET surface area of the 2.8%Ru/TiO<sub>2</sub> catalyst was 50 m<sup>2</sup> g<sup>-1</sup>. The X-ray diffraction pattern exhibited only the reflections of the anatase form of TiO<sub>2</sub>, except for a small peak corresponding to the main reflection of rutile. Hydrogen chemisorption measurements, assuming a H/Ru = 1 stoichiometry, indicated that the ruthenium dispersion in the fresh catalyst was 36%. This is in reasonable agreement with TEM micrographs showing that Ru particles are in the size range 4–5 nm. These particles are not homogeneously distributed on the support but tend to agglomerate in specific domains as large as 1 μm<sup>2</sup>. The 2.8%Ru/TiO<sub>2</sub> catalyst was also studied after complete oxidation of the solution of succinic acid at 190°C. The TEM view given in Fig. 1 shows the presence of 4-nm ruthenium particles, indicating that the ruthenium dispersion was not modified during catalytic reaction. The solutions analyzed after reaction contained no ruthenium and titanium within the detection limit of ICP-AES (0.5 and 0.1 ppm, respectively).

### Preliminary Experiments

It was first verified that TiO<sub>2</sub> was not active for the oxidation of succinic acid in the absence of ruthenium. The oxidation reaction was run under standard conditions using 1 g of TiO<sub>2</sub> (Degussa P25) for 4 h. The TOC did not change after 4 h, whereas a nearly complete TOC abatement was observed during the same period of time in the presence of the 2.8%Ru/TiO<sub>2</sub> catalyst (*vide infra*).

The reaction rates were measured under standard reaction conditions as a function of the mass of 2.8%Ru/TiO<sub>2</sub> catalyst. It was verified that the initial reaction rates expressed in mol<sub>acid</sub> h<sup>-1</sup> or in mol<sub>C</sub> h<sup>-1</sup> were proportional to the catalyst mass up to 1.5 g. It can be concluded that the reaction rates were not limited by external mass transfer under the standard reaction conditions involving 1 g of catalyst. It was also verified that the activity did not depend

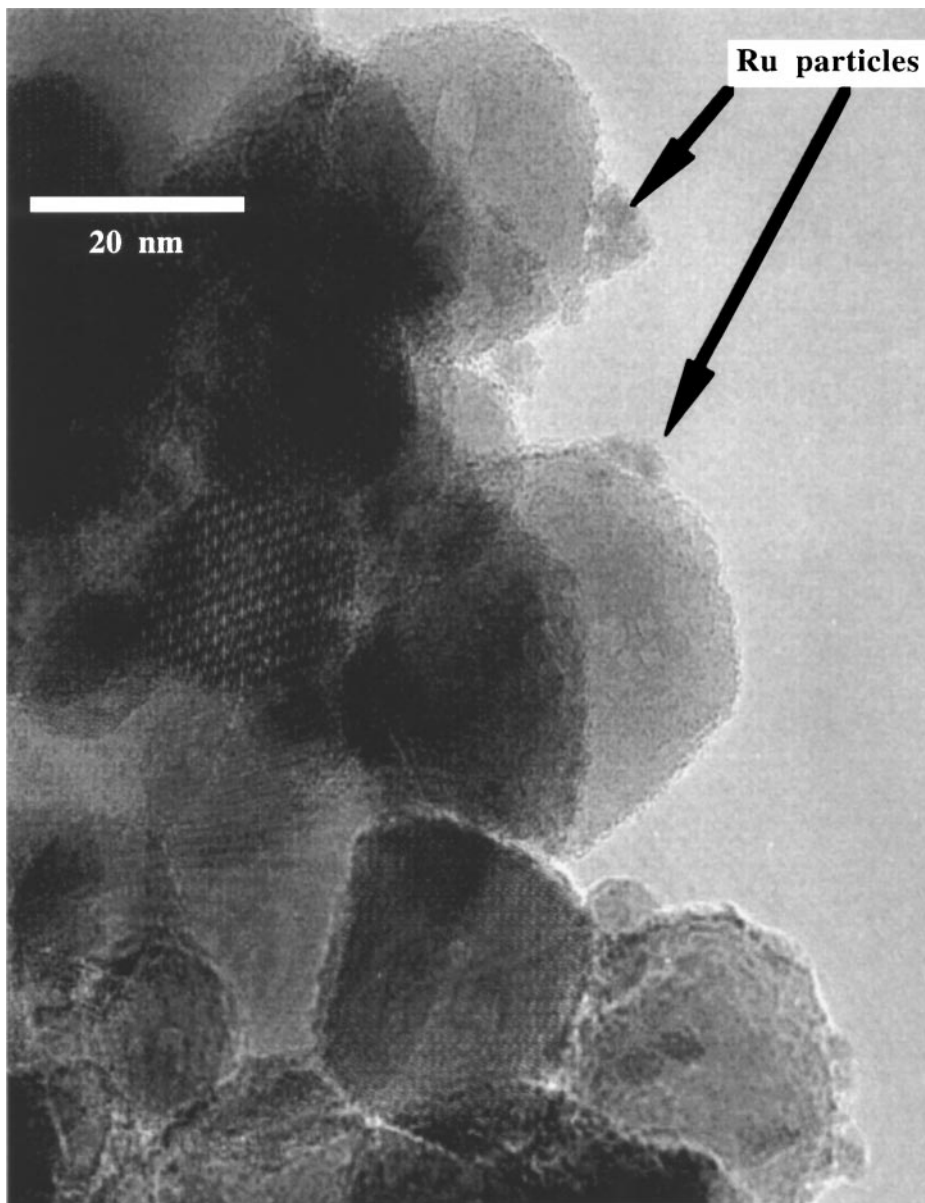


FIG. 1. TEM view of the 2.8%Ru/TiO<sub>2</sub> catalyst after total oxidation of succinic acid.

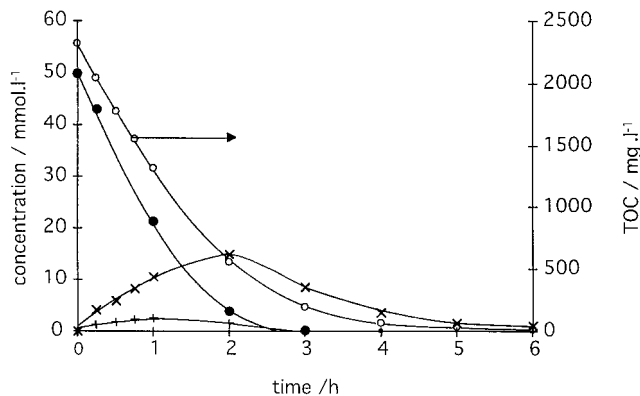
upon the stirring speed under the standard conditions and that the adsorption of succinic acid on the support was negligible.

#### *Kinetics of Succinic Acid Oxidation*

Figure 2 gives the composition of the reaction medium as a function of time under standard reaction conditions. Succinic acid was totally converted within 150 min; the only reaction products detected were CO<sub>2</sub>, acetic acid, and acrylic acid, which all appear as initial products. Other oxidation products may well be formed transiently but are not detected because they are rapidly oxidized at 190°C. Acrylic acid was rapidly converted into CO<sub>2</sub> but the con-

centration of acetic acid started to decrease only after succinic acid disappeared from the reaction medium. The initial rate of reaction was 16 mol<sub>acid</sub> h<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup> or 43 mol<sub>C</sub> h<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup>, and the TOC abatement was 97.6% after a period of 4 h.

The influence of the partial pressure of oxygen was studied by measuring the initial reaction rate,  $r_0$ , at different total pressures between 3 and 10 MPa, i.e., between 0.32 and 1.72 MPa of oxygen, taking into account the pressure of nitrogen and the partial pressure of water vapor at 190°C. The plot of  $\ln r_{0(\text{acid})}$  as a function of  $\ln P_{\text{ox}}$  (Fig. 3) gives a straight line from which a 0.4 reaction order can be determined.



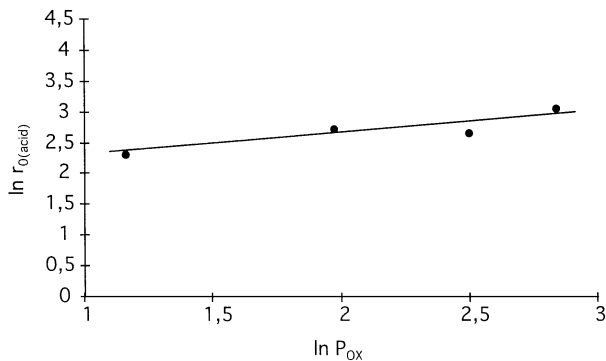
**FIG. 2.** Oxidation of succinic acid with air; composition of reaction medium and TOC as a function of time under standard reactions conditions (1 g of 2.8%Ru/TiO<sub>2</sub>, 150 ml of 5 g liter<sup>-1</sup> aqueous solution of succinic acid, autoclave pressurized with air at 5 MPa,  $T=190^{\circ}\text{C}$ ). TOC (○); succinic acid (●); acetic acid (×); acrylic acid (+).

The influence of temperature was studied by running the reaction at 180, 190, and 200°C. From the Arrhenius plot of  $\ln r_{0(\text{acid})}$  and  $\ln r_{0(\text{TOC})}$  as a function of  $1/T$  (Fig. 4), activation energies of 124 and 129 kJ mol<sup>-1</sup>, respectively, were measured.

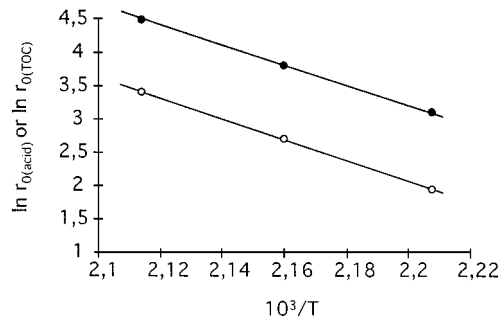
The linearity of the curve giving conversion as a function of time (Fig. 5) suggests that the reaction order is zero with respect to succinic acid up to nearly complete conversion; this indicates a strong adsorption of the molecule on the surface.

#### Influence of Sodium Chloride

Since most industrial effluents contain inorganic salts, particularly chlorides, succinic acid oxidation was conducted in the presence of 6.7 g liter<sup>-1</sup> of NaCl. The data given in Table 1 indicate that both activity and TOC abatement were decreased, the oxidation of acetic acid being the most affected. However, the oxidation process was still very



**FIG. 3.** Influence of the partial pressure of oxygen on the oxidation of succinic acid with air. Plot of  $\ln r_0$  vs  $\ln P_{\text{ox}}$  where  $r_0$  is the initial reaction rate and  $P_{\text{ox}}$  the partial pressure of oxygen at 190°C calculated from the total pressure  $P_T$  ( $P_{\text{ox}} = (P_T - 0.14)/5$ ).



**FIG. 4.** Arrhenius plot of succinic acid oxidation at 180, 190, and 200°C. (○)  $r_{0(\text{acid})}$ ; (●)  $r_{0(\text{TOC})}$ .

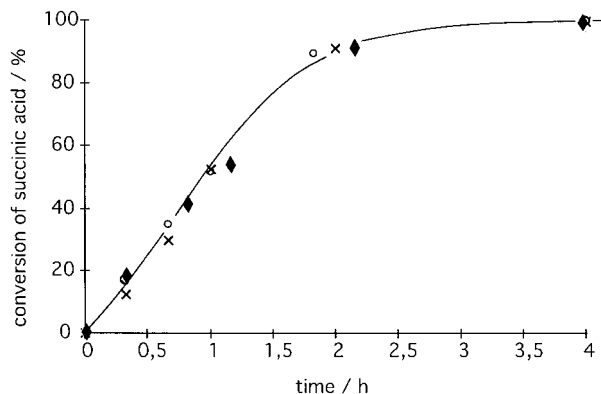
effective since the final TOC abatement after 6 h was more than 99%.

#### Influence of Reaction Products

In the course of succinic acid oxidation, the main products present in the reaction medium were CO<sub>2</sub> and CH<sub>3</sub>COOH. In order to verify that the rate of succinic acid oxidation was not affected by the increasing concentration of these molecules, acetic acid was initially added in the reaction medium with an initial concentration of 14 mmol liter<sup>-1</sup>. Another experiment was carried out in the presence of 182 mmol of CO<sub>2</sub> added in the form of 8 g of solid CO<sub>2</sub>; the total pressure was adjusted to keep the same partial pressure of oxygen as in other experiments. Figure 5 shows that the conversion of succinic acid was not affected by the presence of additional amounts of acetic acid or of carbon dioxide.

#### Influence of Catalyst Pretreatment

The catalytic data reported above were obtained on catalyst 2.8%Ru/TiO<sub>2</sub> as received from Engelhard and stocked in the presence of air. Different reduction or oxidation pretreatments were carried out before reaction; passivation



**FIG. 5.** Influence of additional amount of acetic acid (◆) and carbon dioxide (×) in the reaction medium on succinic acid conversion, (○) reference experiment.

TABLE 1

## Influence of Sodium Chloride on Activity and TOC Abatement

[NaCl] (g liter <sup>-1</sup> )	$r_0(\text{acid})$ (mol <sub>acide</sub> h <sup>-1</sup> mol <sub>Ru</sub> <sup>-1</sup> )	$r_0(\text{TOC})$ (mol <sub>C</sub> h <sup>-1</sup> mol <sub>Ru</sub> <sup>-1</sup> )	TOC abatement at 4 h (%)	[Acetic acid] at 4 h (mmol l <sup>-1</sup> )
0	16	43	97.6	2.7
6.7	10	31	92.3	7.3

treatment consisted of contacting the freshly reduced samples with a flowing mixture of 1% O<sub>2</sub> in N<sub>2</sub> for 6 h at room temperature. Table 2 gives the corresponding activity data for TOC abatement in succinic acid oxidation.

The data clearly show that the initial activities are significantly higher on well-reduced ruthenium particles. The activity decreased as the surface was covered by oxygen: the higher the oxygen coverage of the ruthenium surface, the lower the reaction rate. The rates were particularly slow as the catalyst was heated in air at 300°C, which probably resulted in the formation of an overlayer of RuO<sub>2</sub> on the surface and subsurface.

## Catalyst Recycling

Starting from the as-received 2.8% Ru/TiO<sub>2</sub> catalyst, four experiments of succinic oxidation were conducted with the same catalyst recycled after separation from the oxidized solutions by filtration. The recovered catalyst was reused as such for the WAO of fresh solutions. The initial activity and TOC abatement after 4 h are given in Table 3. The activity decreased after the first catalyst recycle, then was stable in the three subsequent oxidation runs. A close examination of the product distribution showed that the loss of activity was mainly due to a decrease of the rate of acetic acid oxidation. This appears clearly in Fig. 6, giving the concentration of acetic acid in the reaction medium as a function of time.

TABLE 2

## Influence of Catalyst Pretreatment on the Activity for TOC Abatement in Succinic Acid Oxidation

Pretreatment of 2.8% Ru/TiO <sub>2</sub>	Initial activities for TOC abatement (mol <sub>C</sub> h <sup>-1</sup> mol <sub>Ru</sub> <sup>-1</sup> )
Sample 1: catalyst as received stocked in air	43
Sample 2: catalyst reduced <sup>a</sup> under H <sub>2</sub> at 300°C, passivated, kept under Ar	75
Sample 3: catalyst reduced <sup>a</sup> under H <sub>2</sub> at 500°C, passivated, kept under Ar	73
Sample 4: sample 3 heated under air at 300°C	13
Sample 5: sample 4 reduced <sup>a</sup> under hydrogen at 300°C, passivated, kept under Ar	63
Sample 6: sample 5 kept in air three weeks	31

<sup>a</sup> Heating rate 1 K min<sup>-1</sup>, 2 h at reduction temperature, cooling under Ar.

TABLE 3

## Activity in TOC Abatement in Succinic Acid Oxidation after Three Recycling Operations

	Activity (mol <sub>SUC</sub> h <sup>-1</sup> mol <sub>Ru</sub> <sup>-1</sup> )	Activity (mol <sub>C</sub> h <sup>-1</sup> mol <sub>Ru</sub> <sup>-1</sup> )	TOC abatement after 4 h (%)
As-received catalyst	16	43	97.5
First recycle	12	33	90
Second recycle	12	33	90
Third recycle	12	33	90

## Wet Air Oxidation of Other Carboxylic Acids

Wet air oxidation of aqueous solutions containing 5 g liter<sup>-1</sup> of the following four molecules containing carboxylic acid functions was carried out under the standard conditions employed for succinic acid oxidation. The TOC abatement as a function of time is given in Fig. 7. The initial activities expressed in mol<sub>C</sub> h<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup> were in the following series: acetic (17) < succinic (43) < glycine (64) < chloracetic (151) < glycolic (230). Substitution of one hydrogen atom of the methyl group in acetic acid by Cl, hydroxyl, or amino group increased the rate of oxidation.

## DISCUSSION

This study shows that succinic acid and other carboxylic acids, particularly acetic acid, can be completely mineralized into CO<sub>2</sub> with high specific activity on Ru/TiO<sub>2</sub> catalysts using air as an oxidizing agent. Previous studies in our laboratory showed that similar results, and even better activities, were obtained on carbon-supported catalysts (14), but the slow oxidation of carbons limits their practical application as catalyst support at temperatures higher than 150°C. In contrast, this study demonstrates that titanium dioxide was stable in both acidic and oxidizing medium since no titanium leaching was detected. As ruthenium is

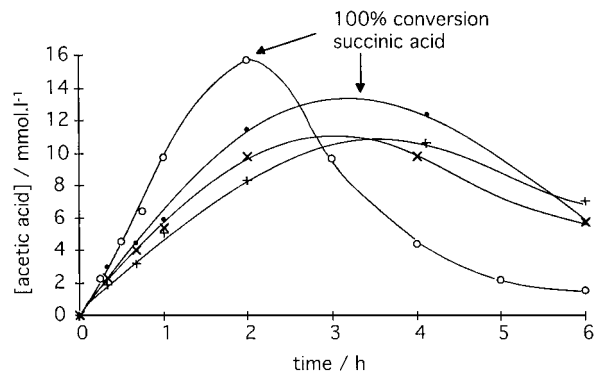
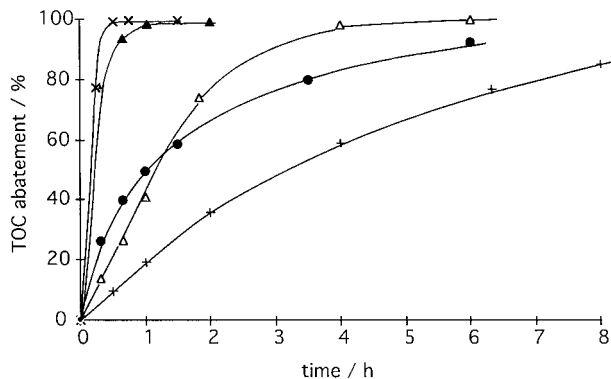


FIG. 6. Concentration of acetic acid formed by succinic acid oxidation during four successive run with recycled catalysts. First run (○); second run (●); third run (×); fourth run (+).



**FIG. 7.** TOC abatement as a function of time: acetic acid (+); succinic acid ( $\Delta$ ); chloroacetic acid ( $\blacktriangle$ ); glycolic acid ( $\times$ ); glycine ( $\bullet$ ). (1 g of 2.8% Ru/TiO<sub>2</sub>, 150 ml of 5 g liter<sup>-1</sup> aqueous solution, autoclave pressurized with air at 5 MPa,  $T = 190^\circ\text{C}$ .)

also stable in the reaction medium, as shown in this and previous studies (13, 14), Ru/TiO<sub>2</sub> catalysts are ideally suited for heterogeneous WAO processes. Indeed, the data presented in Fig. 7 indicate that they can be recycled without loss of activity after the second run so that they are potentially well adapted to continuous WAO process. Accordingly, subsequent studies conducted in trickle-bed reactor on the same catalyst in pellet form have shown that its activity in succinic acid oxidation was stable during several weeks on stream (21). The fact that the presence of sodium chloride in solution moderately affects the rate of TOC abatement (Table 1) is also encouraging. Discussion on the potential interest of Ru/TiO<sub>2</sub> catalysts in industrial application will await forthcoming results on the WAO of real effluents. The present discussion will focus on more fundamental aspects such as the effect of oxygen coverage on the ruthenium surface and why carboxylic acids exhibit different reactivities toward oxidation.

The activity of Ru/TiO<sub>2</sub> catalysts was shown to depend upon reduction or oxidation pretreatments (Table 2). Ruthenium was most active for succinic acid oxidation when it was freshly reduced and kept under argon before use; the activity became significantly lower when it was stocked in air, and ruthenium heated in air at 300°C exhibited a weak activity. These simple facts point to a detrimental effect on the WAO of increasingly higher oxygen coverages of the surface or of the incorporation of oxygen in subsurface. Assuming that the organic molecules need to be adsorbed on the surface of the metal to be oxidized, the activity pattern could be easily rationalized: higher oxygen coverage hampers the adsorption of the molecule. It was shown that this type of interpretation holds for the selective oxidation of oxygenates at low temperatures on platinum and palladium catalysts which occurs via a mechanism of oxidative dehydrogenation. The total or partial poisoning of the catalysts was interpreted by an overoxidation of the metal surface (22–24), whereas high oxidation activi-

ties were obtained when the competitive adsorption on the metal surface of oxygen and of the organic substrate was equilibrated. In the case of WAO on ruthenium at 190°C, the mechanism of oxidation reaction is probably different and may involve the formation of radicals. However, the modeling of the oxidation kinetics of succinic acid in trickle-bed reactor (21) suggests that adsorption of the organic molecule on ruthenium surface, whatever its oxidized state, is still a necessary and rate controlling step. Therefore, the different activities for TOC abatement as a function of catalyst pretreatment could be attributed to the different oxygen coverage of the surface: lower oxygen coverage gives higher WAO activities because of easier adsorption of the molecule or because of easier electron transfer from the metal to the adsorbed molecule. Note that the deactivation which occurs during the first recycling operation (Table 3) can be attributed to a partial oxidation of the surface; the catalyst did not deactivate in further recycling because the oxidation state did not change. This means that the oxygen coverage should stabilize before a steady state was attained; this point will be better highlighted by the continuous WAO study in trickle-bed reactor (21).

Literature data on WAO and previous works in this laboratory (13, 19, 20, 25–28) have shown that acetic acid is one of the most difficult molecules to oxidize into CO<sub>2</sub>. This was confirmed by the present study. Thus, the oxidation of acetic acid started only after succinic acid was consumed (Fig. 2), and the rate of acetic acid oxidation was much smaller than the rates of C<sub>2</sub> carboxylic acids derived by substitution of one hydrogen atom of the methyl group by Cl, NH<sub>2</sub>, and OH groups. The difficulty in oxidizing acetic acid could be due to a low adsorption coefficient of the molecule on the metal surface (effect 1), to a weak reactivity in the adsorbed state with respect to oxidation (effect 2), or to the combination of both. Effect 1 is supported by two experimental observations: acetic acid started to oxidize only after succinic acid was no longer present in the reaction medium (Fig. 2), and acetic acid added initially did not modify the kinetics of succinic acid oxidation (Fig. 5). Thus, it can be inferred that the adsorption coefficient of acetic acid is much lower than that of succinic acid. This is further supported by a modeling study of the oxidation kinetics in trickle-bed reactor, from which a comparatively weak adsorption coefficient of acetic acid was calculated (21). Effect 2, which accounts for the so-called refractory character of acetic acid, is usually attributed to the difficulty to activate the C–H bond of the methyl group in  $\alpha$ -position from the carboxylic function. This effect is supported by the fact that by substituting one hydrogen atom with a NH<sub>2</sub> or OH group or Cl, the molecule is then oxidized very rapidly (the rate of TOC abatement under standard conditions was 17, 64, 151, and 230 mol<sub>c</sub> h<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup>, for acetic, glycine chloroacetic, and glycolic acid, respectively). With the presently available experimental data, none of these effects could be definitively

ruled out, and a negative synergy due to the combination of the two effects is quite possible.

### CONCLUSION

This investigation highlights the following points:

(i) Complete mineralization into CO<sub>2</sub> of aqueous solutions of carboxylic acid (5 g liter<sup>-1</sup>) was obtained by oxidation with air at 190°C on a commercially available Ru/TiO<sub>2</sub> catalyst. This was supported by the fact that the treated water did not contain any organic products (100% TOC abatement) and that the catalyst can be recycled without loss of activity after the first recycling operation, which rules out formation of polymeric deposit as observed in the WAO of phenol on CuO–ZnO–Al<sub>2</sub>O<sub>3</sub> or Mn/Ce oxide catalysts (9, 29).

(ii) No leaching of ruthenium or titanium was detected. The stability of heterogeneous catalysts in the acidic and oxidizing reaction medium is a key issue in WAO processes.

(iii) Different reduction and oxidation treatments of the Ru/TiO<sub>2</sub> catalyst prior to WAO of succinic acid resulted in different initial activities: high oxygen coverages of the ruthenium surface result in low activities. This can be rationalized by assuming that the adsorption coefficient of the organic molecule is lower on surface highly covered by oxygen or that the interaction of the adsorbed molecule with the metal protected by an oxygen layer is weaker. A steady state of activity is attained only after the metal surface is equilibrated and reaches a constant oxygen coverage. This accounts for the fact that the catalyst deactivated during a first reaction run, but its activity was stable in subsequent recycling operations.

(iv) This investigation, supported by the modeling study reported elsewhere (21), brings a new interpretation for the different rates of oxidation of carboxylic acids, and particularly for the difficulty in oxidizing acetic acid in WAO processes. The first step of the reaction on heterogeneous catalysts involves the adsorption of the molecule on the metal surface. Therefore the respective adsorption coefficients of carboxylic acids have to be taken into account to interpret the different rates of TOC abatement. However, this does not rule out the influence of other factors such as those associated with the electronic structure of the molecules.

### ACKNOWLEDGMENTS

We gratefully acknowledge Engelhard for providing the catalyst sample. We thank Marion Sergent for her assistance with the TOC and HPLC measurements.

### REFERENCES

- Mantzavinos, D., Hellenbrand, R., Livingston, A. G., and Metcalfe, I. S., *Appl. Catal. B* **7**, 379 (1996).
- Chang, C. J., and Lin, J. C., *J. Chem. Technol. Biotechnol.* **57**, 355 (1993).
- Lin, S. H., and Ho, S. J., *Appl. Catal. B* **9**, 133 (1996).
- Phull, K. K., and Hao, O. J., *Ind. Eng. Chem. Res.* **32**, 1772 (1993).
- Hao, O. J., Phull, K. K., Chen, J. M., Davis, A. P., and Maloney, S. W., *J. Hazardous Mater.* **34**, 51 (1993).
- Mishra, V. S., Joshi, J. B., and Mahajani, V. V., *Ind. Chem. Eng.* **35**, 211 (1993).
- Shende, R. V., and Mahajani, V. V., *Ind. Eng. Chem. Res.* **33**, 3125 (1994).
- Pintar, A., and Levec, J., *Chem. Eng. Sci.* **47**, 2395 (1992).
- Levec, J., and Pintar, A., *Catal. Today* **24**, 51 (1995).
- Hellenbrand, R., Mantzavinos, R., Livingston, A. G., and Metcalfe, I. S., in "Environmental Catalysis—For a Better World and Life" (G. Centi, C. Cristiani, P. Forzatti, and S. Perathoner, Eds.), p. 487. Società Chimica Italiana, Rome, Italy, 1995.
- Imamura, S., Nishimura, H., and Ishida, S., *Sekiyu Gakkaishi* **30**, 199 (1987).
- Imamura, S., Matsushige, H., and Kawabata, N., *J. Catal.* **78**, 217 (1982).
- Gallezot, P., Chaumet, S., Perrard, A., and Isnard, P., *J. Catal.* **168**, 104 (1997).
- Béziat, J. C., Besson, M., Gallezot, P., Juif, S., and Durecu, S., in "3rd World Congress on Oxidation Catalysis" (R. K. Grasselli, S. T. Oyama, A. M. Gaffney, and J. E. Lyons, Eds.), p. 615, Studies in Surface Science and Catalysts, Vol. 110. Elsevier, Amsterdam, 1997.
- Pourbaix, M., "Atlas d'équilibres électrochimiques," Gauthier-Villars, Paris, 1963.
- Ishii, T., Mitsui, K., Sano, K., and Inoue, A., EP 0431 932A1 to Nippon Shokubai (1990).
- Harada, Y., and Yamasaki, K., *Desalination* **98**, 27 (1994).
- Imamura, S., Fukuda, I., and Ishida, S., *Ind. Eng. Chem. Res.* **27**, 718 (1988).
- Duprez, D., Delanoë, F., Barbier, J., Jr., Isnard, P., and Blanchard, G., *Catal. Today* **29**, 317 (1996).
- Duprez, D., Delanoë, F., Barbier, J., Jr., Isnard, P., and Blanchard, G., in "Environmental Catalysis—For a Better World and Life" (G. Centi, C. Cristiani, P. Forzatti, and S. Perathoner, Eds.), p. 495. Società Chimica Italiana, Rome, Italy 1995.
- Béziat, J. C., Besson, M., Gallezot, P., and Durecu, S., submitted for publication.
- Mallat, T., and Baiker, A., *Catal. Today* **19**, 247 (1994).
- Imamura, I., Nishimura, H., and Ishida, S., *Sekiyu Gakkaishi* **30**, 199 (1987).
- Besson, M., Lahmer, F., Gallezot, P., Fuertes, P., and Flèche, G., *J. Catal.* **152**, 116 (1995).
- Gallezot, P., Besson, M., and Fache, F., in "Chem. Ind. 62: Catalysis of Organic Reactions" (M. G. Scaros and M. L. Prunier, Eds.), p. 331. Dekker, New York, 1995.
- Mishra, V. S., Mahajani, V. V., and Joshi, J. B., *Ind. Eng. Chem. Res.* **34**, 2 (1995).
- Krajnc, M., and Levec, J., *Appl. Catal. B* **13**, 93 (1997).
- Mantzavinos, D., Hellenbrand, R., Livingston, A. G., and Metcalfe, I. S., *Wat. Sci. Technol.* **35**, 119 (1997).
- Hamoudi, S., Larachi, F., and Sayari, A., *J. Catal.* **177**, 247 (1998).