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Total Oxidation of Acetic Acid in Aqueous Solutions over Noble Metal Catalysts

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Ruthenium catalysts (1–5 wt%) were prepared by exchange or impregnation of different supports: CeO_2, TiO_2, or ZrO_2. Their activity for acetic acid oxidation in aqueous solutions was investigated in a batch reactor (20 bar O_2, 0.083 *M* CH_3COOH, 200°C). Ru catalysts supported on a high-surface area ceria have an excellent activity for the title reaction. The following order of activity was obtained: $Ru > Ir > Pd \approx Fe \approx Cu > Ag \approx Ni \approx Co \approx Cr \approx$ unpromoted CeO_2, which can be correlated with the tendency of the metals to remain in the metallic form. The operating Ru/CeO_2 catalyst would be composed of large Ru^0 particles with surface Ru^{n+} species: the prereduced catalysts are more active than the preoxidized ones and turnover frequencies are higher on the larger Ru particles which are less oxidizable. The catalysts were examined by XRD and TEM before and after the oxidation reaction. Only metallic Ru could be seen by these techniques which confirmed besides that Ru is remarkably stable (no apparent sintering). A kinetic study was performed on a catalyst with Ru particles of about 20–30 nm. The activation energy was close to 100 kJ mol^{-1} while the kinetic order was negative in acetic acid ($n \approx -0.5$) and positive in oxygen ($n \approx 0.5$). The reaction rate decreased significantly at higher pH values; acetate anion is much less reactive than acetic acid. A mechanism including a homolytic scission of the O–H bond is proposed and discussed in the light of the present results and of the literature data. © 1998 Academic Press

INTRODUCTION

Nowadays, three different processes for removing total organic carbon from industrial waste waters can be envisaged. The choice of one of these processes depends essentially on the loading of the effluent in organic pollutants. The *biological process* is recommended for low chemical oxygen demands of the effluent ($1 < COD < 20$ g L^{-1}) and when the pollutants are easily biodegradable and nontoxic. In the case of high COD ($COD > 100$ g L^{-1}), the *incineration process* is more suitable. At least, *WAO* (wet air oxidation) is an efficient, alternative method allowing to treat effluents with medium COD ($5 < COD < 100$ g L^{-1}). In this process, organic compounds are oxidized into carbon dioxide and water under oxygen pressure and at high temperatures (150–300°C). WAO was applied with success for removing total organic carbon (TOC) such as: insoluble polymers (1, 2), sewage sludge (3), wastewater (4), and certain organic compounds (5–7).

In order to decrease reaction times and to operate under less severe conditions, catalytic wet air oxidation processes (CWAO) have been developed. Homogeneous copper salts (8) or heterogeneous Mn/Ce composite oxide catalysts (9) and Cu/Zn catalysts (10) have been proved to be powerful oxidation catalysts for organic pollutants. However, CWAO processes based on these catalysts induce a partial solubilisation of metal ions during the reaction so that an additional process is necessary to recover toxic ions. To overcome this drawback, attempts to develop stable active heterogeneous catalysts have been made. Noble metal catalysts were recently investigated for the CWAO of phenol (11). These catalysts were found to be more active than homogeneous copper catalysts. Most studies on the WAO of organic compounds have shown that acetic acid was often present at the end of reaction. Actually, acetic acid is a refractory molecule (12) and its oxidation could be a rate determining step in WAO of many organic compounds (13, 14). By contrast with platinum which is almost inactive (15), ruthenium is an active metal for the oxidation of acetic acid in an aqueous medium, particularly when it is supported on carbon or graphite (11, 12). Unfortunately, these carbon materials cannot be employed safely at high temperatures and under high O_2 pressures. Under these conditions, the use of an oxide instead of carbon is therefore recommended as a support. Ceria is often reported as being an efficient component of mixed oxides catalysts for the oxidation of acetic acid. Manganese-cerium composite oxides catalysts were developed by Imamura *et al.* (5, 9, 16) while De Leitenburg *et al.* (17) reported that CeO_2–ZrO_2–CuO catalysts showed a high activity in acid acetic oxidation.

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Ceria was also used as a support of noble metals and it was shown that Ru/CeO$_2$ was interesting for its activity in the oxidation of many organic molecules (18). Moreover, doping ceria with different oxides could improve the activity of Ru for acetic acid oxidation (19).

The purpose of this investigation is to compare the catalytic wet air oxidation of acetic acid on metal catalysts deposited on various supports and then to characterize and to study in detail the behaviour of the most active Ru/CeO$_2$ catalysts.

EXPERIMENTAL

Catalyst Preparation

Cerium dioxide (Rhône-Poulenc HSA5, 200 m^2 g^{-1} and HSA5M 40 m^2 g^{-1}), titanium dioxide (Rhône Poulenc DT51, 80 m^2 g^{-1}) and zirconium dioxide (Degussa Zirkonoxid, 40 m^2 g^{-1}) were used as supports. They were calcined at 500°C in air before impregnation. This treatment did not change the surface area, except for HSA5 whose area decreased by about 20% (163 m^2 g^{-1}, instead of 200 m^2 g^{-1}). Hence, the ceria will be referred to as CeO$_2$ 160 for HSA5 and to as CeO$_2$ 40 for HSA5M. A 0.2 *M* aqueous solution of group Ib, VIb, or VIII metal salts (mostly nitrates, except Ru hexammine chloride, Pd chloride, and chloroiridic acid) was contacted with the support (10 g), the slurry being slowly stirred at room temperature for 20 h. After drying the solution in air at 120°C, the resulting solid was reduced at 350°C for 3 h in a hydrogen flow or, in some experiments, calcined for 3 h in an air flow. The amount of metal precursor was adjusted so as to obtain a 5 wt% metal loading for all the impregnated catalysts. A 1% and a 2% Ru/CeO$_2$ 160 were also prepared according to this procedure.

In order to increase the metal dispersion, a 2% Ru/CeO$_2$ catalyst was prepared by exchange of an aqueous solution of ruthenium trichloride in HCl 0.03 N with the HSA5 ceria powder suspended in water. The exchange occurred while the slurry was slowly stirred at room temperature for 20 h at a fixed pH of 2.4. After the filtration of the solution, the catalysts underwent the same final treatment as the impregnated catalysts. The metal accessibility of this exchanged catalyst was varied by treating the fresh sample in a H$_2$ flow at different temperatures between 350 and 700°C.

Oxidation Reactions

The reactions were carried out in a 0.5 L Hastelloy C22 autoclave equipped with a magnetically driven stirrer. The reactor was loaded with 250 mL of distilled water containing 1 g of catalyst and generally 5 g L^{-1} of acetic acid (concentration: 0.083 *M*). Typical operating conditions were: 38 bar total pressure ($H_2O + O_2$), 200°C, and 3 h residence time. The run started when 20 bar of oxygen were added to the hot reactor (200°C). Aliquot samples of the gas phase and of the solution (3 mL) were analyzed at different reaction times. The kinetic orders with respect to acetic acid or with respect to oxygen were determined by varying the initial CH_3COOH concentration in the 0.06–0.2 *M* range or the O$_2$ partial pressure in the 5–20 bar range while the activation energy was obtained by varying the temperature in the 100–200°C range. Possible pH effects on the reaction rate were investigated by studying the oxidation of sodium acetate at pH 8.8, as well as the oxidation of an equimolar mixture of acetic acid and sodium acetate at pH 4.7.

The gases (oxygen and carbon dioxide) were analyzed on a catharometer gas chromatograph equipped with a Porapak Q packed column (1/4 inch, 1 m). Carboxylic acids were analyzed on an Aminex 87H column. The mobile phase was H_2SO_4 0.004 *M*. A UV/visible detector was used at a 235-nm wavelength.

Catalyst Characterizations

Ru/CeO$_2$ catalysts, very active in CH_3COOH oxidation, were characterized by different techniques.

Metal dispersions were determined by hydrogen chemisorption in a chromatographic microreactor previously described (20): H$_2$ pulses (0.26 cm^3) were injected, every other minute, over the sample prereduced in H$_2$ (350°C, 10 h) and degassed under a flow of argon (350°C, 3 h). Ultrapure H$_2$ and Ar gases (less than 1 ppm impurities) were used throughout this technique of characterization.

XRD analyses were carried out in a Siemens D500 powder diffractometer using CuKα_1 radiation (0.15406 nm). About 50 mg of catalyst were pressed in the sample holder. Fresh reduced catalysts were passivated in 200 ppm O$_2$ in N$_2$ while used catalysts were dried at 120°C before XRD analysis. The crystalline phases were identified by comparison with JCPDS files: metallic ruthenium (06-0663), ruthenium dioxide (40-1290).

TEM was performed in a Philips CM120 microscope with a resolution of 0.35 nm. The sample was crushed, ultrasonically suspended in ethanol and deposited on a Cu grid recovered with a thin layer of carbon. The presence of Ru was controlled by EDX carried out in the STEM mode. Selected area electron diffraction (SAED) were also carried out on some Ru particles.

RESULTS AND DISCUSSION

Activity of the Ruthenium-Supported Catalysts

Acetic acid oxidation (Eq. [1]) was first investigated over the bare supports calcined at 450°C,

$$CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O. \qquad [1]$$

Comparison with blank experiments (thermal oxidation in the absence of any catalyst) indicates that these supports possess catalytic properties (Table 1). The oxides could

TABLE 1

Activity of the Bare Supports for Acetic Acid Oxidation (200°C, 20 bar O_2, Initial Concentration of CH_3COOH: 83 mmol L^{-1}, Support: 4 g L^{-1})

Oxide	Specific area ($m^2\,g^{-1}$)	Initial rate[a] ($mmol\,h^{-1}\,g^{-1}$)	Initial rate[a] ($\mu mol\,h^{-1}\,m^{-2}$)	(%) Conversion at 1 h
CeO_2 160	163	0.75	4.7	4.0
CeO_2 40	41	0.25	6.2	1.6
TiO_2	78	0.23	2.9	1.5
ZrO_2	39	0.15	3.6	1.1
Blank	—	—	—	0.4

[a] Corrected from the conversion of the thermal reaction.

favour the oxygen transfer between the solution and the adsorbed species by a redox mechanism. The initial rates of oxidation reported in Table 1 show that ceria has the highest intrinsic activity (per m^2). Moreover, owing to its high surface area, HSA5 ceria has a high specific activity (per gram). Even for this active support, however, the conversion remained below 10% after a 3-h reaction. Carbon dioxide was the only oxidation product: no organic compound but CH_3COOH was detected in the liquid phase. ICP-MS analyses carried out after a 3-h reaction revealed that practically no cerium ion was dissolved in the liquid phase (0.05 to 0.2 mg L^{-1}).

Table 2 gives the results obtained with Ru catalysts impregnated on these supports. The results obtained with Ru/C catalysts (11, 12) are also reported in the table. Ruthenium was chosen for the comparison because it has been shown previously that it exhibits a good activity for CH_3COOH oxidation in aqueous media (11, 12, 18). Ceria and graphite lead to very active catalysts. For a 5% Ru catalyst, the initial activity is about 20 mmol $h^{-1}\,g_{cata}^{-1}$ corresponding to a DCO abatement of 1.2 g per hour and per gram of catalyst. However, ceria must possess a very high surface area; the catalyst prepared with CeO_2 160 is at least five times as active as the catalyst prepared with CeO_2 40. This is not due to a better dispersion of Ru/CeO_2 160; we will see further on that turnover frequencies (TOF) are higher on large Ru particles than on small ones. A likely explanation is that these large Ru particles keep a close contact with CeO_2 clusters when the support has a high surface area.

TABLE 2

Activity of Supported Ru Catalysts for Acetic Acid Oxidation at 200°C

Catalyst	Surface area ($m^2\,g^{-1}$)	Initial activity ($mmol\,h^{-1}\,g_{Ru}^{-1}$)	Conversion at 1 h (%)
5% Ru/CeO_2 160	125	385	82
2% Ru/CeO_2 160	140	560	53
1% Ru/CeO_2 160	145	470	23
3.4% Ru/Graphite[a]	300	400	—
5% Ru/C[b]	850	210	49
5% Ru/TiO_2	75	80	14
5% Ru/CeO_2 40	38	74	13
5% Ru/ZrO_2	35	64	12

[a] Lonza HSA graphite; after Gallezot *et al.* (12).

[b] Lurgi BA special carbon; data taken from Ref. (11).

Activity of the Ceria-Supported Metal Catalysts

Owing to the good performance of the high-surface area ceria in CH_3COOH oxidation (very low leaching, good intrinsic activity), it was decided to investigate further the catalytic behaviour of metals supported on HSA5 ceria. The results are reported in Figs. 1a, b, and c, where different catalytic behaviours can be observed. In comparison with the activity of the metal-free ceria, Ru and Ir (class I, Fig. 1a) are very active metals in wet air oxidation of acetic acid. Under our operating conditions (200°C, 20 bar O_2), the initial oxidation rate of the Ru catalyst is close to 20 mmol $h^{-1}\,g_{cata}^{-1}$. Class II catalysts are those metals (Pd, Fe, and Cu) with an initial activity between 1 and 2 mmol $h^{-1}\,g_{cata}^{-1}$, slightly higher than the activity of the bare support (0.73 mmol $h^{-1}\,g_{cata}^{-1}$). Class III corresponds to inactive catalysts (Ag, Ni, Cr, Co) with virtually no additional activity, due to the presence of the metal.

These results could be correlated with the differences of stability of the metals in the reactant mixture. Actually, the potential measured at a ruthenium electrode placed into a 83 mmol L^{-1} acetic acid solution saturated with O_2 is about 0.5V/SHE under the standard conditions (25°C, 1 bar). Figure 2 compares the Pourbaix diagrams (22) of each metal at the pH 2.9 of the acetic acid solution. Only noble metals (Ru, Ir, and Pd) remain in their immunity domain while Cu and Fe pass into the corrosion zone. Class III metals can be dissolved and become totally inactive. There is apparently a correlation between the catalytic activity and the ability of the metal to remain in its reduced solid form. Although Cu and Fe ions can exhibit a significant activity for WAO by homogeneous catalysis (8, 23, 24), these results show that the activity of metallic ions in solution for acetic acid oxidation is negligible. Concerning leaching phenomena, ICP-MS analysis confirm the thermodynamic predictions, since, contrary to what can be observed with noble metals ($<$0.05 mg L^{-1}), significant amounts of nonnoble metals are present in the solution after the reaction. Accordingly, Ru/CeO_2 is an appropriate catalyst for the total oxidation of acetic acid. We can remark that ruthenium is not so noble as certain group 8 metals (Pt, Pd, and even Rh); in gaseous O_2 Ru is easily oxidized into RuO_2 and, above 200°C, into RuO_3 and RuO_4 (25). Owing to the relatively low concentration of O_2 in water (about 3 g L^{-1} at 200°C under 20 bar of O_2), the bulk of Ru particles remains metallic in the course of the oxidation reaction.

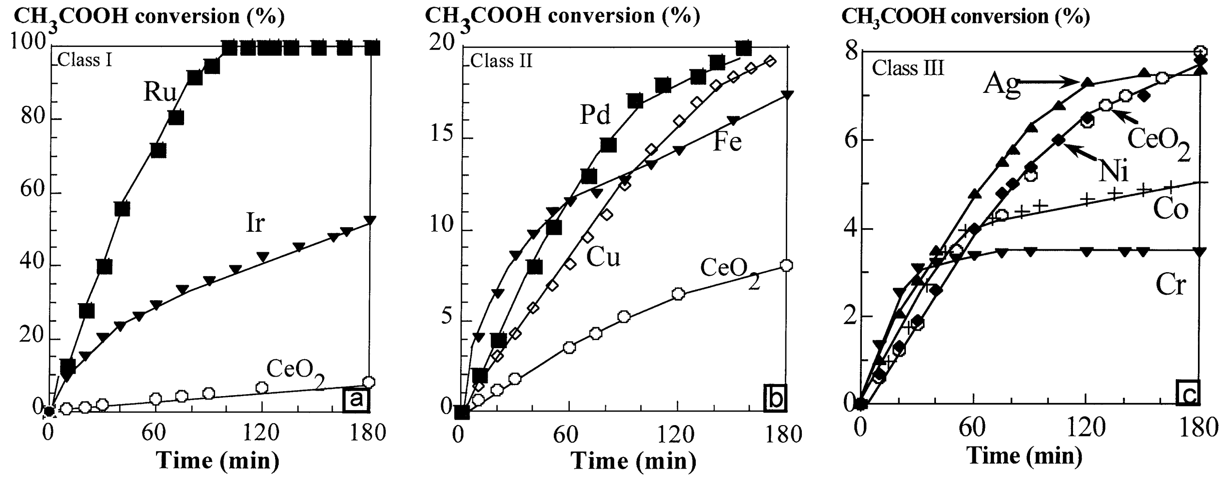

FIG. 1. Acetic acid oxidation over metal catalysts (5 wt%) supported on CeO_2 160. (200°C; 20 bar O_2; $[CH_3COOH] = 0.083$ *M*; catalyst: 4 g L^{-1}): a, class I catalysts (Ru, Ir); b, class II catalysts (Pd, Fe, Cu); c, class III catalysts (Ag, Ni, Co, Cr). The curve denoted "CeO_2" refers to as the experiment with unpromoted ceria.

Catalytic Behaviour of Ru/CeO_2 for Oxidation Reactions in Aqueous Media

The metal catalysts investigated in acetic acid oxidation are initially reduced in H_2 (Fig. 1). Moreover, electrochemical data (Fig. 2) show that the most active catalysts should remain reduced under the standard conditions. As it is difficult to extrapolate these data under the actual reaction conditions, the effect of the metal state on the oxidation rate was investigated catalyst by comparing the activity of the prereduced and of the preoxidized Ru/CeO_2 sample (Table 3). When reduced, Ru/CeO_2 is significantly more active than when it is oxidized. The ruthenium accessibility in the preoxidized catalyst is slightly higher (6%) than in the prereduced sample (4.8%). However, this small difference cannot explain the change of activity. It is thus confirmed that metallic Ru is more active than RuO_2.

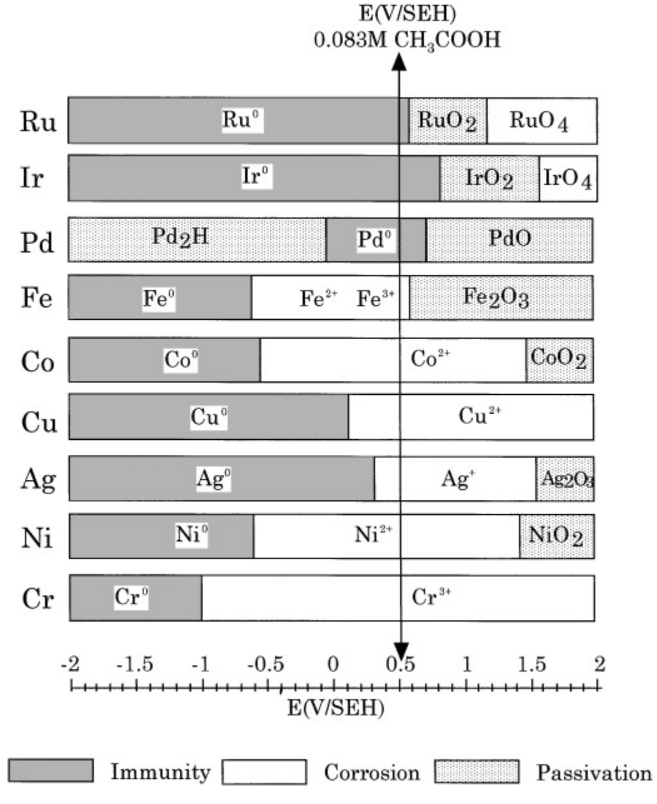

FIG. 2. Changes of the chemical state of the metals with their electrochemical potential (after Ref. (22)). The solid line corresponds to the potential of Ru measured in a 0.083 *M* acetic acid solution in the presence of oxygen.

The reduced catalyst was characterized by XRD before and after the test reaction (3 h at 200°C). Figure 3 shows the corresponding diffractograms with the peaks at $2\theta = 38.4°$, $42.2°$, and $44.1°$, corresponding to the (100), (200), and (101) planes of Ru^0. As expected, no RuO_2 peak can be detected on the fresh catalyst while a very small peak at $2\theta = 35.16°$ could reveal the presence of ruthenium oxide in the used catalyst. However, Ru remains essentially in the metallic form after reaction. The mean particle size of Ru^0 calculated by the Debye–Scherrer equation from peak width broadening is 19.5 nm in the fresh catalyst and 21.5 nm in the used catalyst. Meanwhile, no change in the particle size of CeO_2 (close to 15 nm) can be observed. The Ru/CeO_2 catalyst appears to be very stable during the oxidation reaction.

TABLE 3

Effect of the Catalyst Pretreatment at 350°C on the Catalytic Activity of 5% Ru/CeO_2 for Acetic Acid Oxidation at 200°C

Pretreatment	Surface area ($m^2\,g^{-1}$)	Dispersion (%)	Conversion at 1 h	Initial rate (mmol $h^{-1}\,g_{Ru}^{-1}$)	T.O.F. (h^{-1})
Reduced, H_2	125	4.8	82	385	800
Calcined, air	155	6.0	39	185	310

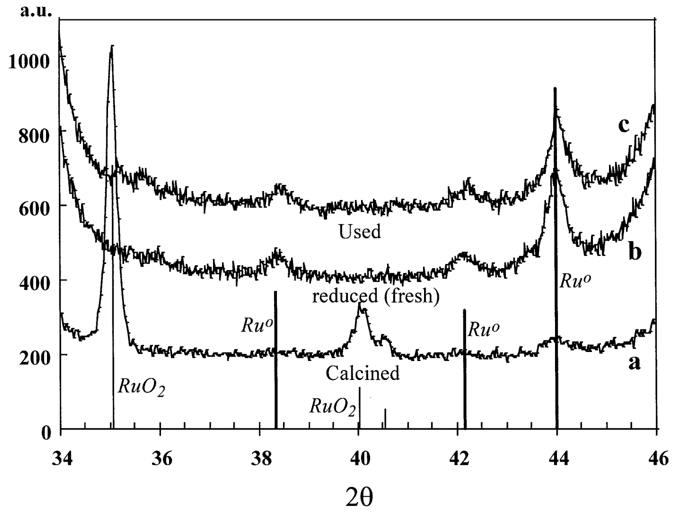

FIG. 3. X-ray diffractograms of the 5% Ru/CeO_2 160 catalyst: a, calcined, b, reduced (fresh), and c, after reaction (used).

TABLE 4

Metal Dispersion of the 2 wt% Ru/CeO_2 Catalyst Prepared via Ion-Exchange and Reduced at Different Temperatures

Temperature of reduction (°C)	Specific area ($m^2 g^{-1}$)	Ru dispersion (%)
350	140	57
500	129	55
575	121	48
625	115	35
660	108	20
680	95	7
700	87	2

The Ru/CeO_2 catalyst was also examined by electron microscopy. Figure 4 shows TEM pictures of this catalyst before (just after H_2 reduction at 350°C) and after reaction. Ruthenium particles of hexagonal shape, surrounded by clusters of small CeO_2 particles, were clearly identified by EDX and SAED. This technique showed that metallic Ru particles were preferentially orientated along their $[\bar{1}, 1, 1]$ axis (26). Ru particles are between 20 and 30 nm (TEM), close to the size found by XRD. Neither their size nor their orientation changes during the reaction. By contrast, ceria particles appear to be much smaller on the TEM pictures (about 7–9 nm) than expected by XRD (15 nm). This could be due to an agglomeration of small clusters of ceria.

Dispersion Effects

A highly dispersed 2 wt% Ru/CeO_2 catalyst was prepared by acidic exchange and then treated in a reducing medium (H_2, 30 mL min^{-1}, 3 h) at different temperatures so as to obtain a varying dispersion of ruthenium in the catalyst (Table 4). The catalytic behaviour of the fresh and sintered catalysts (Fig. 5) shows that acetic acid oxidation is a

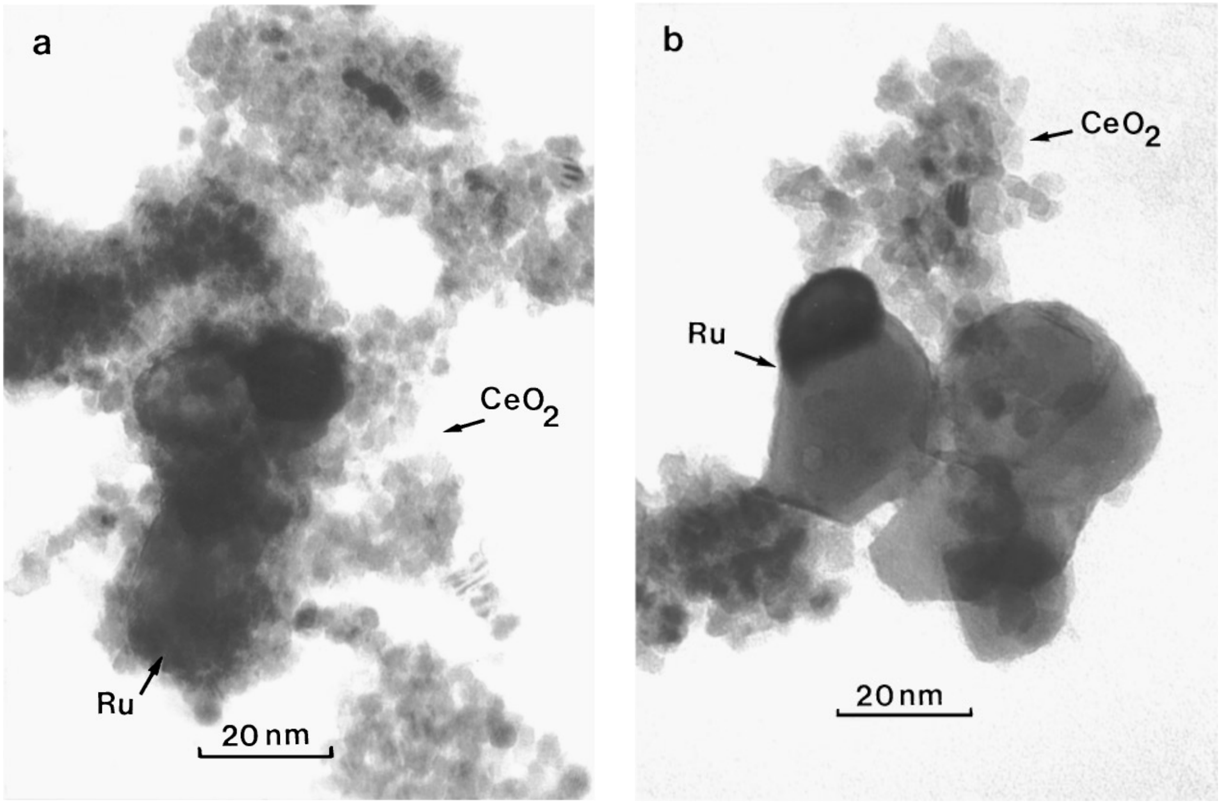

FIG. 4. TEM pictures of 5% Ru/CeO_2: a, fresh catalyst; b, used catalyst.

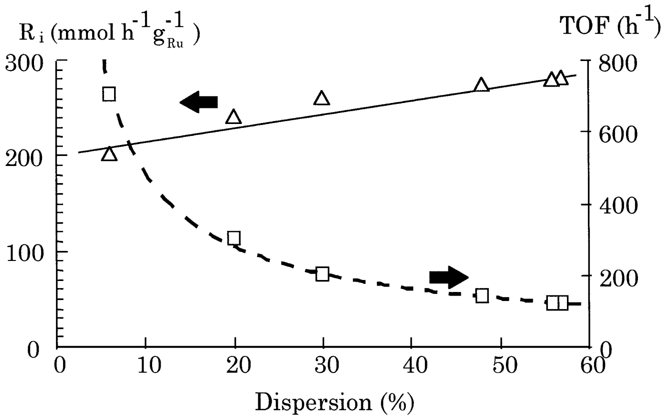

FIG. 5. Effect of metal dispersion on initial activity (R_i) and on turnover frequency (TON) of 2% Ru/CeO$_2$ catalysts for acetic acid oxidation at 200°C.

reaction sensitive to the particle size; the turnover frequency increases by a factor of 5 when the metal dispersion decreases by a factor of 8, from 57 to 7%. A similar effect was noticed by Gallezot *et al.* with Ru/C catalysts (12); the specific activity of these catalysts for acetic acid oxidation at 200°C increased from 0.01 to 0.09 mmol h^{-1} g$_{\mathrm{Ru}}^{-1}$ when the particle size of Ru increased from below 1 to 2 nm. We noticed (result not shown in Fig. 5) that the TOF ceased to increase for the catalyst sintered at the highest temperature (2% dispersion after sintering in H$_2$ at 700°C). A SMSI (strong metal–support interaction) effect with partial coverage of Ru particles by ceria could have occurred in this catalyst sample. The decrease of the Ru metal area being compensated by an increase of the turnover frequency, the specific activity (mmol h^{-1} g$_{\mathrm{cata}}^{-1}$) is almost constant over the 7–57% range of dispersion. Moreover, the exchanged catalysts are less stable than the impregnated catalysts probably because small Ru particles are more easily oxidized than the large particles present in impregnated catalysts. For this reaction, there is no need to look for very dispersed catalysts.

Kinetic Study and pH Effects

Kinetic parameters (activation energy; orders with respect to acetic acid and to oxygen) were determined on the reduced 5 wt% Ru/CeO$_2$ catalyst prepared by impregnation (Table 5). This kinetic study led to the following expression of the rate equation,

$$r_i = 1.13 \times 10^9 \exp\left(-\frac{96600}{RT}\right) [\mathrm{CH_3COOH}]^{-0.5} P_{\mathrm{O_2}}^{0.5},$$

r_i being the initial rate (mol h^{-1} g$_{\mathrm{Ru}}^{-1}$), [CH$_3$COOH] being the acetic acid concentration (mol L^{-1}), and $P_{\mathrm{O_2}}$ being the dioxygen pressure (bar). The values found for the activation energy and the kinetic order m with respect to oxygen are very close to those reported by Gallezot *et al.* (12) for CH$_3$COOH oxidation over Ru/graphite at 200°C (100.5 kJ mol^{-1} and $m = 0.65$). By contrast, these authors found a zero order in acetic acid instead of −0.5 in this study. As the two kinetic studies (12, this study) have been carried out within the same range of concentration (60–300 mmol L^{-1}), we can conclude that acetic acid is not so strongly adsorbed on Ru/C as on Ru/CeO$_2$ catalysts.

The change with time of the pH of the solution was measured. It has been observed that the pH decreased (from pH 2.9 at $t = 0$ to about pH 2.4) as long as the acetic acid was not totally converted ($t < 60$ min). Above a 98–99% conversion, the pH tends to recover its initial value. The formation of CO$_2$ (p$K_a = 6.34$ for the equilibrium H$_2$CO$_3$/HCO$_3^-$) cannot explain these results. The presence of oxalic acid in the products could decrease the pH of the solution (p$K_a = 1.23$ for the equilibrium C$_2$O$_4$H$_2$/C$_2$O$_4$H$^-$). However, the traces of oxalic acid detected in the products (<0.1 mmol L^{-1}) cannot account completely for the decrease of pH. Apparently protons are produced during the catalytic cycle by interaction of certain intermediates with the catalyst.

We can remark that in the 2.4–2.9 range of pH, acetic acid is virtually not ionized (less than 1.4% acetate ions). The effect of pH on the reaction rate was also investigated by studying the oxidation of sodium acetate (initial pH = 8.8) and of an equimolar mixture of acetic acid and sodium acetate (initial pH = 4.7). The results (Fig. 6) show that the acetate anion is much more difficult to oxidize than the acetic acid. The same phenomenon was observed by Imamura *et al.* (18) who reported that acetic acid oxidation over Ru catalysts was faster at pH 2.7 than at pH 6.9 (by a factor of three). Definite pH effects were also observed by Harmsen *et al.* (27) in oxidation of formic acid over Pt/C catalysts at 25°C. The reaction rate reached a maximum at pH 4, a value slightly higher than the isoelectric point of the catalyst (pH$_{\mathrm{iep}} \approx 3$) and of the p$K_a$ of formic acid (equal to 3.75). After Harmsen *et al.* (27), formic acid oxidation would proceed via a surface reaction between formate anions and

TABLE 5

Acetic Acid Oxidation over the 5 wt% Ru/CeO$_2$ Prepared by Impregnation: Kinetic Results

AcOH concentration (mmol L^{-1})	O$_2$ partial pressure (bar)	Temperature (°C)	Initial rate (mmol h^{-1} g$_{\mathrm{Ru}}^{-1}$)
0.060	20	200	442
0.083	20	200	385
0.120	20	200	320
0.166	20	200	250
0.083	5	200	178
0.083	10	200	266
0.083	15	200	318
0.083	20	170	60
0.083	20	140	10
0.083	20	100	0.5

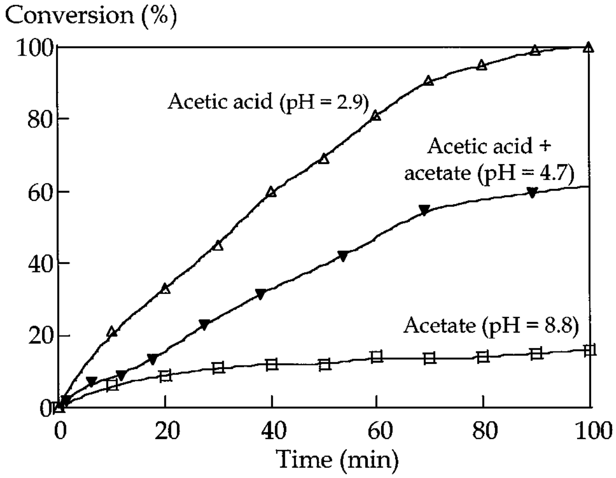

FIG. 6. Oxidation of acetic acid (initial pH: 2.9), of an equimolar mixture of acetic acid and sodium acetate (initial pH: 4.7) and of sodium acetate (initial pH: 8.8) over Ru/CeO$_2$ at 200°C.

oxygen atoms. They explained the decrease of the reaction rate with increasing pH by a repulsion phenomenon at pH $>$ pH$_{iep}$, between the formate anions and the negative charge of the catalyst while the decrease observed at pH $<$ pK$_a$ would be due to a diminution of formate ion concentration.

The mechanism of acetic acid oxidation cannot be established on the basis of the data obtained in this study. However, certain kinetic schemes can be proposed in the light of our results and those of the literature (27–32). The isoelectric point of ceria is close to 6.7 (33, 34) while the pK$_a$ of acetic acid equals 4.75. As the reaction rate decreases with increasing pH from 2.9 to 8.8, acetic acid appears to be more reactive than acetate ion (Fig. 6). The oxidation reaction could occur via a homolytic splitting of the acetic acid molecule including a hydrogen abstraction by the metal assisted by oxygen reactive species (ORS). Hydroxyl radicals HO$^\bullet$ and, to a lesser extent, hydroperoxyl radicals HO$_2^\bullet$ are strong ORS, commonly used for oxidation in aqueous media (28, 29). However, the production of hydroxyl radicals at low temperature requires the use of strong oxidant agents: O$_3$, H$_2$O$_2$ (under UV light) or O$_3$ + H$_2$O$_2$ (29) or the use of radiation-chemical techniques such as pulse radiolysis (28). With dioxygen, the production of hydroxyl radicals is quite unlikely but superoxide radicals could be catalytically produced according to Eq. [1]:

$$\mathrm{M}^{n+} + \mathrm{O}_2 \rightarrow \mathrm{M}^{(n+1)+} + \mathrm{O}_2^{\bullet -}. \qquad [1]$$

A certain number of transition metals can activate O$_2$ via reaction [1] (35, 36). Ruthenium III and IV species are known to be good candidates for catalyzing this reaction. Similarly, cerium oxide interacting with dioxygen is able to produce superoxide and even peroxide species (37, 38). As the hydroperoxyl radical is the acid form of the superoxide radical (Eq. [2]) with a pK$_a$ of 4.8 (28), it predominates at pH 2.9:

$$\mathrm{O}_2^{\bullet -} + \mathrm{H}^+ \rightleftharpoons \mathrm{HO}_2^\bullet. \qquad [2]$$

For a compound ZH, three reactions can occur, with the transition metal (Eq. [3]), with O$_2$ (Eq. [4]) or with HO$_2^\bullet$ (Eq. [5]):

$$\mathrm{ZH} + \mathrm{M}^{(n+1)+} \rightarrow \mathrm{Z}^\bullet + \mathrm{M}^{n+} + \mathrm{H}^+ \qquad [3]$$

$$\mathrm{ZH} + \mathrm{O}_2 \rightarrow \mathrm{Z}^\bullet + \mathrm{HO}_2^\bullet \qquad [4]$$

$$\mathrm{ZH} + \mathrm{HO}_2^\bullet \rightarrow \mathrm{Z}^\bullet + \mathrm{H}_2\mathrm{O}_2. \qquad [5]$$

Reaction [3] occurs in adsorbed phase on surface Ru^{n+} species. It accounts for the formation of protons and was proposed by Chen and Chou to occur in the oxidation of propionaldehyde over heterogenized cobalt and manganese catalysts (39). Reactions [4] and [5] can occur either in adsorbed phase or in homogeneous phase. With acetic acid, two radicals can be formed, CH$_3$COO$^\bullet$ and $^\bullet$CH$_2$COOH. Nevertheless, COOH being an electron-withdrawing group, the attack of the α position by electrophilic species (such as oxygen species) is extremely difficult (40). Moreover, by means of surface science techniques, Bowker *et al.* showed that acetic acid was adsorbed on noble metals as CH$_3$COO species (31, 32). Schuchmann reported however that H abstraction from the methyl group of acetate anions could occur in the presence of hydroxyl radicals (41). In this case, acetate oxidation led to numerous intermediates (formaldehyde, oxalic, glyoxylic, and glycolic acids) not observed here. Once formed, adsorbed acetate species are rapidly decarboxylated and the resulting methyl group is oxidized into CO$_2$ and H$_2$O through the formation of methylperoxyl species (11, 16).

CONCLUSIONS

1. Ruthenium catalysts are very active for acetic acid oxidation in aqueous media, particularly when the metal is supported on high-surface area ceria (160 m^2 g^{-1}). Ru is significantly less active when supported on low-surface area ceria (40 m^2 g^{-1}) or on other supports such as TiO$_2$ or ZrO$_2$.

2. The best catalyst is composed of large Ru^0 particles covered with Ru^{n+} species and surrounded of small clusters of ceria. The catalyst must be reduced before reaction and turnover frequencies are higher on large Ru particles.

3. A kinetic study performed on a catalyst with 20–30 nm particles led to the equation for the initial rate (mol h^{-1} g$_{\mathrm{Ru}}^{-1}$),

$$r_i = 1.13 \times 10^9 \exp\left(-\frac{96600}{RT}\right) [\mathrm{CH_3COOH}]^{-0.5} P_{\mathrm{O}_2}^{0.5},$$

with $[CH_3COOH]$ the acetic acid concentration (mol L^{-1}) and P_{O_2} the dioxygen pressure (bar).

4. Protons are produced during the oxidation reaction and the rate significantly decreases with increasing pH. Acetate anions are less easily oxidized than acetic acid.

5. A mechanism with homolytic cleavage of the O–H bond of CH_3COOH has been proposed. H abstraction by the metal assisted by oxygen reactive species is a keystep of this mechanism. Other steps would include decarboxylation/oxidation of the acetate species.

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