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Catalytic Wet Air Oxidation of Acetic Acid on Carbon-Supported Ruthenium Catalysts

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Ruthenium catalysts prepared by ion exchange of active carbons and high-surface-area graphites are active for the wet air oxidation of aqueous solutions of acetic acid (5–20 g/liter). A total conversion into CO_2 can be achieved between 448 and 473 K using air as oxidizing agent. No leaching of ruthenium can be detected which indicates that the reaction proceeds on the heterogeneous catalysts. For the same particle size (1 nm), graphite-supported ruthenium catalysts are much more active (up to 0.4 mol h^{-1} g_{Ru}^{-1} at 473 K in a stirred batch reactor pressurized with air at 10 MPa) than active carbon-supported catalysts. The lower activities of the latters could be due to internal diffusion limitation since the 1-nm Ru particles are located inside the micropores. However, graphite-supported catalysts might be intrinsically more active because of an electron transfer from graphite to metal particles which would increase the resistance of ruthenium to oxygen poisoning. It was also shown that the activity of ruthenium is particle size dependent: the smaller the sizes, the lower the activities. This effect could be interpreted by the higher adsorption energy of oxygen on the small particles which produces a poisoning of the metal surface. From measurements of the reaction rates on the Ru/HSAG graphite catalyst at different temperatures, pressures, and acetic acid concentrations, it was established that the reaction orders were zero and 0.65 with respect to the concentration and oxygen pressure, respectively; the activation energy of the reaction was 100.5 kJ mol^{-1}. An equation describing the reaction kinetics was proposed. © 1997 Academic Press

INTRODUCTION

Wet air oxidation (WAO) processes are aimed at reducing the chemical oxygen demand (COD) of waste waters by total oxidation with air of dissolved or suspended organic and inorganic effluents. WAO is well suited to treat effluents where the concentrations of organic pollutants are too low for the economy of an incineration process and when biological treatments are ineffective, e.g., in the case of toxic effluents. However, to be effective, WAO processes require very high temperatures and pressures, typically in the range 473–573 K and 7–15 MPa, respectively, which severely affects the economy of this technology. R&D efforts in this field are currently under way to achieve the oxidation of organic effluents under milder conditions by catalytic WAO processes using homogeneous or heterogeneous catalysts (1–3). Homogeneous catalysts, which usually consist of transition metal ions of the first row dissolved in the reaction medium, are efficient to destroy organic effluents under less drastic conditions, but the dissolved species must be recovered from the treated waters. Most of the heterogeneous catalysts employed so far were not stable enough in strongly corrosive reaction media, so that a treatment is required to recover the mineral species leached from supports and/or active phases. The most promising processes involving heterogeneous catalysts, which do not dissolve readily in the reaction medium, are based on precious metals (Pt, Pd, Ru) on acid-resistant supports. Thus, industrial catalytic WAO processes have been developed in Japan by Nipon Shokubai using palladium and platinum supported on titania or titania–zirconia (4). Imamura *et al.* (5) have shown that ceria-supported ruthenium catalysts, working at 473 K under 2 MPa of a 50–50 mixture of O_2 and N_2, performed better than copper-based homogeneous catalysts for the oxidation of various chemicals including acetic acid. More recently, Duprez *et al.* (6) found that Ru/C catalysts exhibited higher activities in acetic acid oxidation than Mn–Ce oxides or Ru/TiO_2 catalysts.

The present work, conducted within the framework of the "Environment Programme" of the EEC, was intended to study the total oxidation into carbon dioxide of aqueous solutions of carboxylic acids on platinum metals supported on carbons, using air as the oxidizing agent under moderate temperature and pressure conditions. So far, carbon-supported, platinum-group metals have been little employed in WAO although they are much more resistant to acid leaching than catalysts based on oxide supports and transition metals of the first row. The idea of using carbon-supported catalysts stemmed from earlier studies on the selective oxidation with air of glyoxal (7, 8), glucose (9–11), and glycerol (12–14) on platinum catalysts supported on

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active carbons, showing that the oxidation may proceed to completion, i.e., to carbon dioxide, under slightly more severe conditions than those required for partial oxidation. In a previous paper (15), it was shown that platinum catalysts supported on active carbons were efficient for the total oxidation of formic or oxalic acids aqueous solutions under air at atmospheric pressure and slightly above room temperature. Solutions of maleic acid were also totally oxidized on Pt/C catalysts, albeit above 373 K (15).

It is well known that acetic acid is one of the most resistant chemicals to oxidation because of the difficulty to oxidize the methyl group in α-position of the carboxylic group. Thus, in the oxidation scheme of phenol proposed by Devlin and Harris (16), the route conducting to acetic acid is a dead-end. The present paper reports a WAO study of acetic acid solutions carried out on carbon-supported ruthenium catalysts. Ruthenium was employed as active component because Pt/C catalysts were unable to convert acetic acid (15) and there were strong indications from previous works (5, 6) that ruthenium was the most active metal for this oxidation reaction. Active carbons and high-surface-area graphites were used as supporting materials. Graphite was chosen because it can modify, via electronic effects, the catalytic properties of metal particles (17–21). Also, the metal particles located on graphite steps are much more accessible to reactants in the liquid phase than particles inside microporous active carbon supports.

EXPERIMENTAL

Catalyst Preparation and Characterization

Two active carbons (CECA 50S and Norit rox 0.8) and a high-surface graphite (Lonza HSAG 300) were employed as supporting materials to prepare ruthenium catalysts. The characteristics of these supports are given in Table 1. The Norit extrudates were ground into powder and sieved to keep the particles under 50 μm. All the carbon supports were oxidized to create exchangeable carboxylic acid groups by stirring 20-g batches in 500 ml sodium hypochlorite solutions (15% active chlorine) for 24 h at room temperature. After filtration, the carbons were washed with 500 ml of HCl (1 mol liter^{-1}) and then with water until neutrality of the wash-waters and dried overnight at 373 K under reduced pressure. The functionalized supports were ion exchanged with aqueous solutions of $[Ru(NH_3)_6](OH)_3$ obtained by exchanging $Ru(NH_3)_6Cl_3$ solutions through a column of anionic-exchange resin. The exchange was performed by stirring 20 g of the support for 18 h under nitrogen atmosphere in ammoniacal solutions containing the required amounts of $[Ru(NH_3)_6](OH)_3$. The suspension was filtered, washed with water, and dried overnight at 373 K under flowing nitrogen atmosphere. Reduction of ruthenium was carried out in a glass cell under a flow of hydrogen by heating at 1 K min^{-1} from 298 to 573 K and maintaining this temperature for 2 h. The reduced catalysts were cooled to 300 K under argon and finally brought into contact with air diluted with argon to avoid deep metal oxidation. The characteristics of the catalysts are given in Table 2.

TABLE 1

Characteristics of Carbon Supports

	Graphite	Active carbons		
	HSAG 300	CECA 50S	ESCAT 40	Norit rox 0.8
Granulometry	powder (<50 μm)	powder (<80 μm)	powder (<21 μm)	extrudates (1 mm)[a]
Specific area	300 m^2 g^{-1}	1450 m^2 g^{-1}	850 m^2 g^{-1}	900 m^2 g^{-1}

[a] The extrudates were ground and sieved to powder (<50 μm).

TABLE 2

Characteristics of Ruthenium Catalysts and Activities in Acetic Acid Oxidation

Catalysts	Preparation mode	Ruthenium (wt%)	Particle size[a] (nm)	Activities (mol h^{-1} g$_{Ru}^{-1}$)	Catalyst weight (g)
Ru/HSAG	i. e.[b]	3.4	≤1	0.16	0.6
Ru/HSAG	i. e.[b]	3.4	≤1	0.40	0.25
Ru/HSAG	i. e.[b]	2.0	≤1	0.24	0.3
Ru/Norit	i. e.[b]	1.2	≤1	0.01	0.6
Ru/Norit	i. e. + refilling[c]	4.0	2	0.09	0.6
Ru/CECA	i. e.[b]	1.5	≤1	0.01	0.6
Ru/ESCAT 40	Unknown	5	>1	0.04	0.6

Note. Reaction conditions: aqueous solutions at 5 g liter^{-1}, 473 K, autoclave pressurized at 10 MPa with air.

[a] Particle sizes measured by electron microscopy.

[b] Preparation by ion-exchange.

[c] Ru particles saturated with hydrogen and contacted with hydrochloric solutions of $RuCl_3$ ($3RuH + Ru^{3+} \rightarrow 4Ru + 3H^+$).

The particle sizes and the metal loading of the 1.2% Ru/Norit catalyst, prepared by ion exchange and reduction as described above, were increased by deposition of ruthenium on the ruthenium particles, using a surface redox process described by Menezo *et al.* (22). Catalysts were stirred at room temperature in HCl solutions (0.1 mol liter^{-1}), first under nitrogen atmosphere, then in the presence of bubbling hydrogen for 1 h, and finally under nitrogen. Solutions of $RuCl_3$ in required amounts were then added and the suspensions were stirred for 3 h. The catalysts were then filtered, washed with water, and dried at 373 K. After four treatments, the amounts of ruthenium on the Norit support increased from 1.2 to 4 wt%. The catalysts were treated under flowing hydrogen at 573 K as the parent catalysts prepared by ion exchange (vide supra).

The amounts of ruthenium present on catalysts before and after reaction, and in the waters after WAO treatment, were determined by ICP-AES. Great care was taken to avoid loss of ruthenium during the acidic dissolution of the carbon support prior to ICP-AES analysis. The sizes of ruthenium particles were measured on TEM views taken at high resolution with a Jeol 100CX microscope on thin sections of catalysts cut with a diamond-knife ultramicrotome.

Reaction Procedure

The catalytic oxidation of acetic acid was carried out in a 100-ml autoclave constructed from Hastelloy-C22 and equipped with a gas reserve and sampling outlet. Two types of stirring devices were used, one with a magnetically driven iron bar protected by a Teflon coating (500–700 rpm), the other by a Rushton turbine in Hastelloy (1500 rpm). It was verified with the most active catalyst that the kinetics was the same with the two setups. Under standard conditions, the reactor was loaded with 50 ml of permuted water containing 5 g liter^{-1} of acetic acid (0.5 wt% or 0.083 mol liter^{-1}) and 0.1 to 0.6 g of catalyst. The reactor was purged with argon and heated to the reaction temperature under continuous stirring. The reactor was then pressurized with 10 MPa of air which corresponded to time zero of the reaction. Samples of the reaction mixture were taken at various time intervals and analyzed by HPLC (Shimadzu pump and UV detector) on a Car-H column with H_2SO_4 solutions as eluent. The total organic carbon (TOC) was measured with a Shimadzu 5050 TOC meter based on catalytic combustion of the effluents at high temperatures.

RESULTS AND DISCUSSION

Preliminary Measurements

Blank experiments without catalyst or with metal-free supports were run to verify that acetic acid was not oxidized significantly after the period of time required to obtain a complete conversion with the least active catalyst. It was also verified that the adsorption of acetic acid on the supports was negligible with respect to the amount of acetic acid in solution and thus did not affect the analytical data.

Figure 1 gives the conversion of 0.5 wt% acetic acid solutions at 473 K on 0.6 g of 3.4%-Ru/HSAG with the reactor pressurized with air at 10 MPa total pressure. Since at this temperature the water vapor pressure is 1.53 MPa, the partial pressure of oxygen was only ca. 1.7 MPa. After 100 min, acetic acid was converted entirely into CO_2. No other organic products were detected by HPLC during the acetic acid oxidation and the conversion monitored with TOC measurements was similar to that obtained by HPLC which indicates that there is no organic products (e.g., polymeric species) undetected. Possible intermediate products liable to form, such as oxalic or formic acids, would be oxidized into CO_2 at a very high rate under the present reaction conditions.

The initial rate measured from the slope at the origin of the conversion curve (Fig. 1) was 0.16 mol h^{-1} g$_{\mathrm{Ru}}^{-1}$. The conversion follows a linear law at least up to 80% conversion. A similar behavior was observed for all the experiments conducted on the graphite-supported catalysts. This means that the reaction is zero order with respect to the concentration of acetic acid. This has been verified by running oxidation reactions with different concentrations of acetic acid (vide infra, Fig. 4).

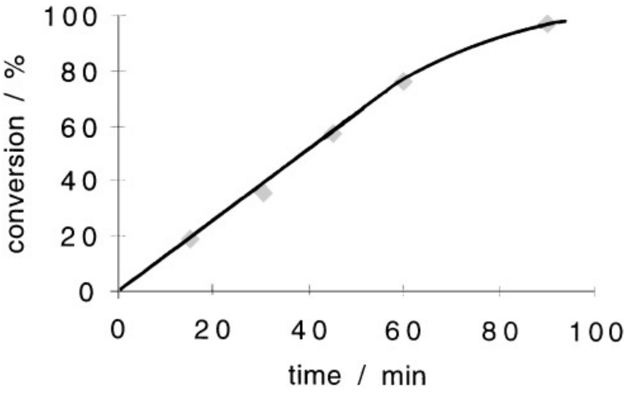

FIG. 1. Conversion of acetic acid as a function of time (catalyst, 0.6 g of 3.4%-Ru/HSAG; *T*, 473 K; reactor pressurized at 10 MPa with air).

The treated water issued from the WAO reaction was analyzed by ICP-AES. No ruthenium was present within the limit of detection, i.e., ca. 0.05 ppm. This type of analysis was repeated in several WAO experiments conducted in this investigation, and it was always confirmed that there was no ruthenium leaching from the catalyst.

Since ruthenium catalysts supported on HSAG graphite were the most active among those tested (Table 2), the influence of external mass transfer on the rate was studied with this catalyst. The initial specific rates measured as a function of the mass of 3.4%-Ru/HSAG (Fig. 2) are almost similar at about 0.4 mol h^{-1} g$_{\mathrm{Ru}}^{-1}$ up to ca. 0.4 g of catalyst and then decrease because of external mass transfer control.

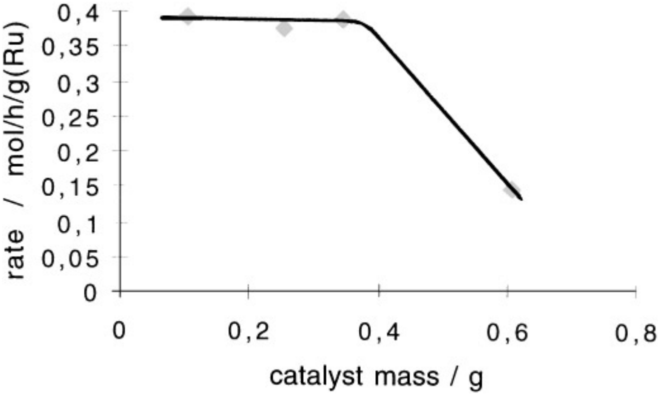

FIG. 2. Influence of catalyst mass on specific rate (catalyst, 3.4%-Ru/HSAG; *T*, 473 K; reactor pressurized at 10 MPa with air).

Effect of Catalyst Supports

All the catalysts employed in this investigation were able to oxidize totally acetic acid solutions into CO_2, albeit at different rates. Table 2 gives the initial specific rates measured at 473 K under 10 MPa of air. It is noteworthy that the rates on 3.4%-Ru/HSAG are 10 to 40 times higher than those on active carbon-supported catalysts, at least if we compare similar particle sizes. This large difference could be attributed to the difference of texture and structure between graphite and active carbons, viz.:

(i) All the active carbons are microporous and it was verified by high-resolution TEM on ultramicrotome sections of CECA- and Norit-based catalysts that the ruthenium particles were uniformly distributed throughout these supports. The effectiveness of ruthenium particles inside the micropores can thus be greatly reduced by internal diffusion. Although we never observed such a large difference of activity between active carbon and graphite in former studies on selective hydrogenation or oxidation reactions conducted in water, the internal diffusion limitation may be specially severe in the present case. Indeed, the CO_2 molecules formed might concentrate inside the micropores which would hamper the diffusion of acetic acid molecules. In contrast, the ruthenium particles are located on the external surface of the graphite support in Ru/HSAG catalysts and thus they are readily accessible to the reactant molecules in the liquid phase.

(ii) It has been shown that small metal particles prepared by ion exchange on graphite support strongly interact with the graphite steps via a transfer of electron from the graphite to the metal particles (18–21). Because of the higher density of states, the metal particles are less easily oxidized by oxygen or less covered by strongly bonded oxygen atoms and thus are more active than particles of the same size on active carbon supports.

The present data do not allow one to distinguish between these two causes which may both contribute to the higher activity of graphite-supported catalysts compared to catalysts based on active carbons.

Particle Size Effects

Catalysts 1.2%-Ru/Norit and 1.5%-Ru/CECA, containing 1-nm Ru particles prepared by ion exchange are both little active in acetic acid oxidation compared with the commercial catalyst Ru-ESCAT 40 also supported on active carbon (Table 2). Since, the particle sizes are larger in the latter, a possible effect of particle size can be anticipated. To verify this point, catalyst 1.2%-Ru/Norit was submitted to successive "refilling" treatments (22) which involve deposition of Ru adatoms on the surface of the parent particles via a surface redox reaction such as

$$3\text{RuH} + \text{Ru}^{3+} \rightarrow 4\text{Ru} + 3\text{H}^+,$$

thus producing a homogeneous growth of their size. After four refilling treatments, the metal loading increased from 1.2 to 4 wt%. Particle sizes were measured on these two catalysts by high-resolution TEM. Figures 3a and 3b gives

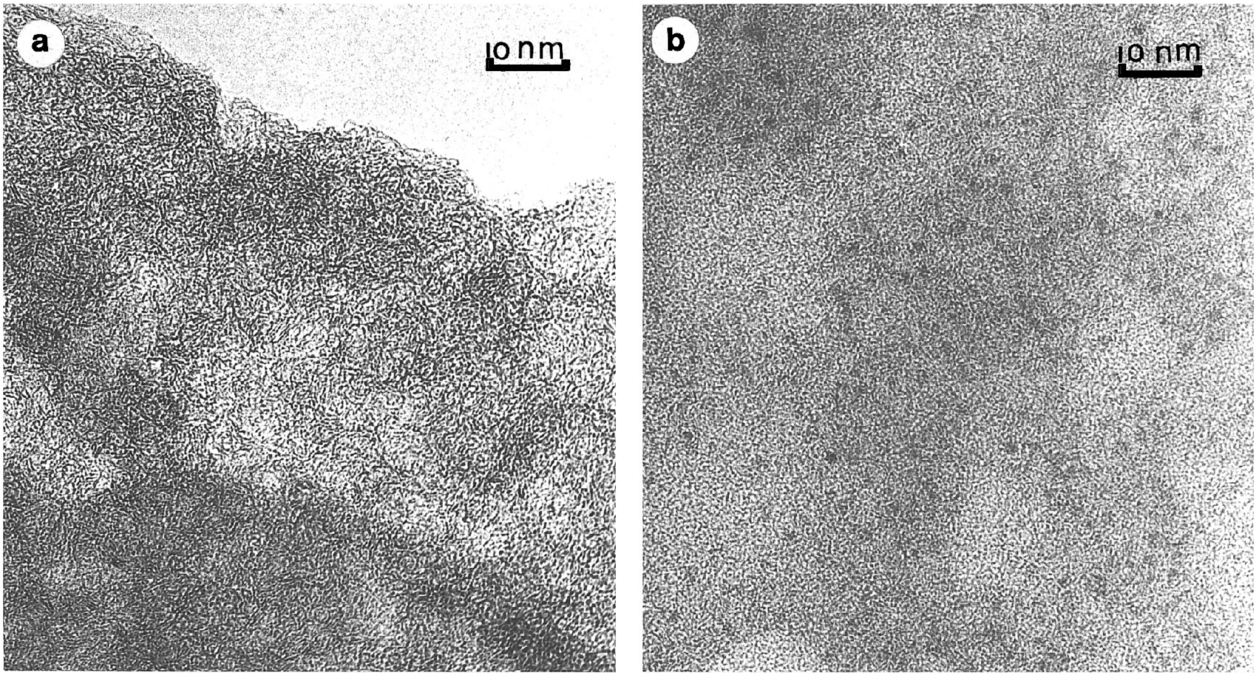

FIG. 3. TEM views taken through ultramicrotome thin sections of catalysts. (a) 1.2%-Ru/Norit; (b) 4%-Ru/Norit.

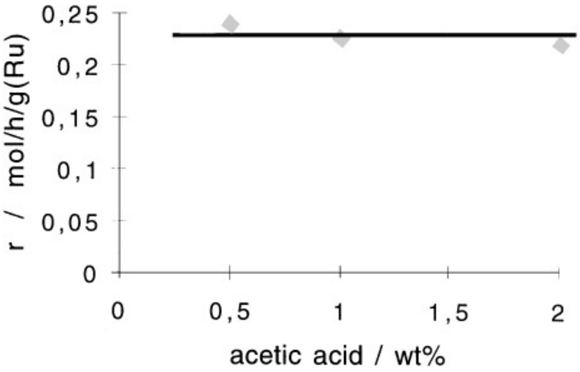

FIG. 4. Initial rate of acetic acid oxidation as a function of acetic acid concentration ($T = 473$ K; $P = 10$ MPa; 0.3 g of 2%-Ru/HSAG).

two micrographs taken through ultramicrotome sections of catalysts 1.2%-Ru/Norit and 4%-Ru/Norit, respectively. In 1.2%-Ru/Norit, the particles were at the limit of detection, i.e., $\leq$1 nm, while an average size of ca. 2 nm was measured on the micrograph of 4%-Ru/Norit. In both samples the distribution of particles was very homogeneous in the catalyst grains. Under the same reaction conditions, the specific rate measured on 4%-Ru/Norit was nine times higher than on the parent catalyst (Table 2). This experiment clearly demonstrates the effect of particle size on catalyst activity, the smallest ruthenium particles being the less active. This can be due to the high enthalpies of oxygen adsorption on small metal particles, particularly under 2 nm, resulting in a high surface coverage by strongly bonded oxygen which poisons the metal surface. Similar examples of particle size-dependent oxygen poisoning of metals have been observed in the case of glucose oxidation on carbon-supported palladium particles (9) and in the case of fuel cell oxygen electrodes involving platinum particles (23).

Similar experiments carried out with the Ru/HSAG catalysts showed that 1-nm particles prepared by ion-exchange were only 1.5 times less active than the larger ones prepared by refilling, compared to 9 times for Ru/Norit. This is in agreement with the electronic support effect discussed in the preceeding section whereby the electron transfer from graphite to the 1 nm particles decreases their affinity for oxygen.

Kinetic Study

Graphite-supported ruthenium catalysts are the most active catalysts probably because the internal diffusion and the deactivation by strongly adsorbed oxygen are less severe than on active carbon-supported catalysts, as discussed in the two previous sections. Therefore, a more complete study of the kinetics of acetic acid oxidation with air was carried out on these catalysts.

Reaction rates were measured with 0.3 g of the 2%-Ru/HSAG catalyst as a function of temperature, pressure, and concentration of acetic acid solutions. This catalyst has a lower activity than 3.4 wt%-Ru/HSAG (0.24 vs 0.40 mol h^{-1} g_{Ru}^{-1}, Table 2). A possible cause of this lower activity could be that the particle sizes are smaller in the least metal-loaded catalyst, since, as discussed above, the smaller the particle size, the lower the activity. However, this hypothesis cannot be easily verified since in the both cases the particle sizes are smaller than 1 nm. The initial reaction rates, r_i, measured on 0.5 wt% solutions with the reactor pressurized with air at 10 MPa were 240, 127, and 57 mmol h^{-1} g_{Ru}^{-1} at 473, 463, and 448 K, respectively. The activation energy deduced from the Arrhenius plot was 100.5 kJ mol^{-1}. The rates were also measured at 473 K with the reactor pressurized with air at 5, 10, and 13 MPa. From the linear plot of ln r_i as a function of ln $P_{O(2)}$ it was shown that the initial oxidation rates vary with the pressure according to a rate law $r_i = 0.165\ P_{O(2)}^{0.65}$. The rates were also measured at constant temperature (473 K) and pressure (10 MPa) as a function of increasing acetic acid concentrations (0.5, 1, and 2 wt%). Figure 4 shows that the specific rate is governed by a zero-order rate law ($r_i = 0.23\ [\mathrm{AcOH}]^0$) with respect to the concentration. This means that acetic acid is strongly adsorbed on the ruthenium surface in agreement with the fact that carboxylic acids have high adsorption enthalpies on platinum group metals. A similar behavior was noticed for formic and oxalic acid oxidation on Pt/C catalysts (15). By combining these data, the initial rate of acetic acid oxidation (in mol h^{-1} g_{Ru}^{-1}) can be expressed according to the general rate equation

$$r_i = 1.8 \times 10^{10}\ P_{O(2)}^{0.65}\ e^{(-100500/RT)}$$

where $P_{O(2)}$ (in MPa) is the partial pressure of oxygen obtained by subtracting the water and nitrogen pressure from the total pressure.

CONCLUSION

This study highlights the following points:

(i) Complete conversion of aqueous solutions of acetic acid into CO_2 can be achieved in the temperature range 448–473 K on carbon-supported ruthenium catalysts without leaching of ruthenium which means that the WAO of one of the most refractory molecule can be conducted with a genuine heterogeneous catalytic system. Furthermore, the process was achieved with air as oxidizing agent rather than with oxygen or oxygen-rich, O_2–N_2 mixtures.

(ii) Graphite-supported catalysts are much more active than those based on active carbons. Thus, acetic acid oxidation on Ru/HSAG catalysts was completed at 448 K, and the specific rates attained up to 0.4 mol h^{-1} g_{Ru}^{-1} at 473 K.

(iii) The higher activities of 1-nm ruthenium particles supported on graphite as compared to those supported on active carbon can be attributed to the different texture and structure of the supports. On the one hand, the effectiveness of ruthenium particles in the micropores of active carbons is probably limited by internal diffusion unlike on graphite where the particles are more accessible. On the other hand, a support effect involving an electron transfer from graphite to the 1-nm Ru particles may account for a better resistance of the metal surface to oxygen poisoning and thus to a higher activity of the graphite-supported catalysts.

(iv) The oxidation activity of ruthenium is particle size dependent: the smaller the size, the lower the activity. This effect could be interpreted by the higher adsorption energy of oxygen on the small particles which leads to a high oxygen coverage and thus to a poisoning of the metal surface.

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