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Catalytic oxidation of organic compounds in aqueous media

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Abstract

Ru, Pt and Rh catalysts supported on titania, ceria or active carbon and a Mn/Ce composite oxide catalysts were prepared and their catalytic behavior in Wet Air Oxidation (20 bar O_2) of phenol and acetic acid were investigated. Phenol was found to be an easily oxidizable compound as 170°C, while acetic acid was a very refractory molecule, even at 200°C. Ru(5 wt.-%)/C is a very efficient catalyst for the WAO of acetic acid without any leaching of noble metal.

Keywords: Wet air oxidation; Total organic carbon removal

1. Introduction

WAO (wet air oxidation) is a process by which organic pollutant can be transformed by oxidation under oxygen pressure and high temperatures (150–300°C), into carbon dioxide and water. It is one of the most efficient processes for removing total organic carbon (TOC) such as: insoluble polymers [1], sewage sludge [2] and certain organic compounds [3]. It has been shown that acetic acid is the most refractory compound. A certain number of experiments have been carried out to try to oxidize this refractory product. A free-radical mechanism could be involved in WAO of acetic acid. The most active catalysts now in use are homogeneous copper salts [4], Mn/Ce composite oxide catalysts [5] and Cu/Zn catalysts [7]. However, these processes provoke a partial solubilisation of copper or manganese ions during the reaction. A further process is necessary to recover the toxic ions. To eliminate the latter, attempts have been made to develop stable active heterogeneous catalysts. We have investigated phenol as a compound easy to oxidize and acetic acid as a compound difficult to oxidize.

2. Experimental

The catalysts were prepared by using the following supports: cerium dioxide (Rhône-Poulenc HSA, 200 $m^2\ g^{-1}$), titanium dioxide (Rhône Poulenc DT51, 100 $m^2\ g^{-1}$), active carbon (Lurgi BA Speziale, 900 $m^2\ g^{-1}$). A given amount of metal salts, $Ru(NH_3)_6Cl_3$, $Pt(NH_3)_2(NO_2)_2$, $Rh(NO_3)_3$, was dissolved in deionized water in the presence of dispersed support and was slowly stirred at room temperature for 20 h. The metal loading was 5 wt.-%

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for all catalysts. After drying the solution in air at 120°C in a sand bath, the resulting solid was calcined at 350°C for 3 h in air and then reduced for another 3 hours in hydrogen.

A manganese-cerium composite catalyst with an equimolar composition [Mn/Ce (1/1)] was obtained by coprecipitation from a mixed aqueous solution of manganese nitrate and cerium nitrate followed by calcination in air and reduction in hydrogen, both at 350°C [5].

Wet air oxidation experiments were carried out by using a 1 l Hastelloy C22 autoclave equipped with a magnetically driven stirrer. The cold reactor was loaded with 250 ml of distilled water containing 1 g of catalyst and 5 g l^{-1} of COD. The typical operating conditions were 40 bar total pressure, 200°C and 3 h residence time. The run was started when 20 bar of oxygen was injected into the hot reactor (200°C). Aliquot samples of the gas phase and of the solution (3 ml) were analyzed at different reaction times.

The gases (oxygen and carbon dioxide) were analyzed on a catharometer gas chromatograph equipped with a Porapack Q packed column (1/4 in., 1 m). Products of phenol conversion were analyzed on a Spectra Physic HPLC equipped with a C18 column. Acetic acid and oxalic acid were analyzed on an Aminex 87H column. The mobile phase was H_2SO_4 0.004 M. The UV-Vis. detector was used with a 235 nm wavelength.

3. Results and discussion

3.1. Phenol oxidation

A Pt (1 wt.-%)/CeO_2 catalyst was selected as a model catalyst and its catalytic activity for phenol oxidation was studied at 170°C. The oxidation produced a complete removal of COD (medium pollution: 5 g l^{-1} of phenol) after 4 h. Phenol was oxidized first partially giving smaller molecules such as carboxylic acids. The oxidation selectivity is 90% carbon dioxide and 10% secondary products (Fig. 1).

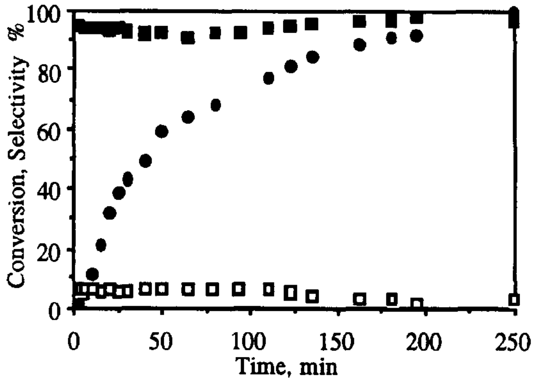

Fig. 1. Conversion (%) in the phenol oxidation and selectivity of: ■ carbon dioxide; □ byproducts.

Some intermediate wet oxidation products were identified in the liquid phase, most which disappeared during the first hour. These intermediates were hydroquinone, catechol and maleic acid which oxidized into acrylic acid and into acetic acid. At the end of the experiment, only acetic acid remains in the liquid phase (selectivity: 10%). Fig. 2 shows the change of the intermediate product concentrations vs. time.

The formation of these products is in agreement with the reactional scheme proposed by Devlin and Harris [8] (Fig. 3). Phenol oxidation starts by a hydroxylation of the molecule leading to hydroquinone or catechol [6–8]. The reaction proceeds in two parallel pathways with maleic acid as a common intermediate. Maleic acid is then fully oxidized into carbon dioxide

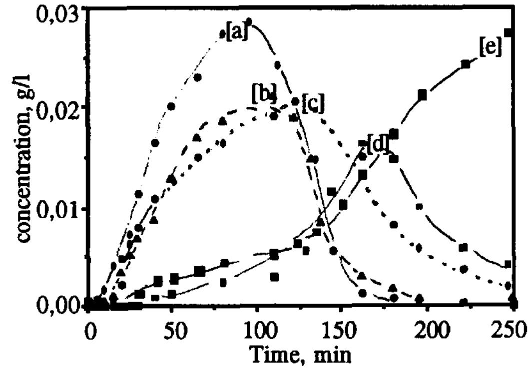

Fig. 2. Intermediary compounds of phenol oxidation: [a] hydroquinone; [b] catechol; [c] maleic acid; [d] acrylic acid; [e] acetic acid.

and water via oxalic and formic acids or partially oxidized into acetic acid which appears as a refractory product in phenol oxidation. About 90% phenol is oxidized into carbon dioxide while 10% is transformed into acetic acid.

We have tested the acetic acid oxidation on the Pt (1 wt.-%)/CeO_2 under the same conditions. The oxidation gives no conversion even after 4 h. It is clear that acetic acid is not easily converted into carbon dioxide and water.

3.2. Carboxylic acid oxidation mechanisms

Some studies carried out on the wet oxidation of various organic compounds have shown that light carboxylic acids, especially acetic acid, are the refractory degradation products of the reaction. Dubois et al. showed that for the WAO of polystyrene and polyethylene, the production of acetic acid increases with the temperature [1]. Moreover, most of the residual organic matter

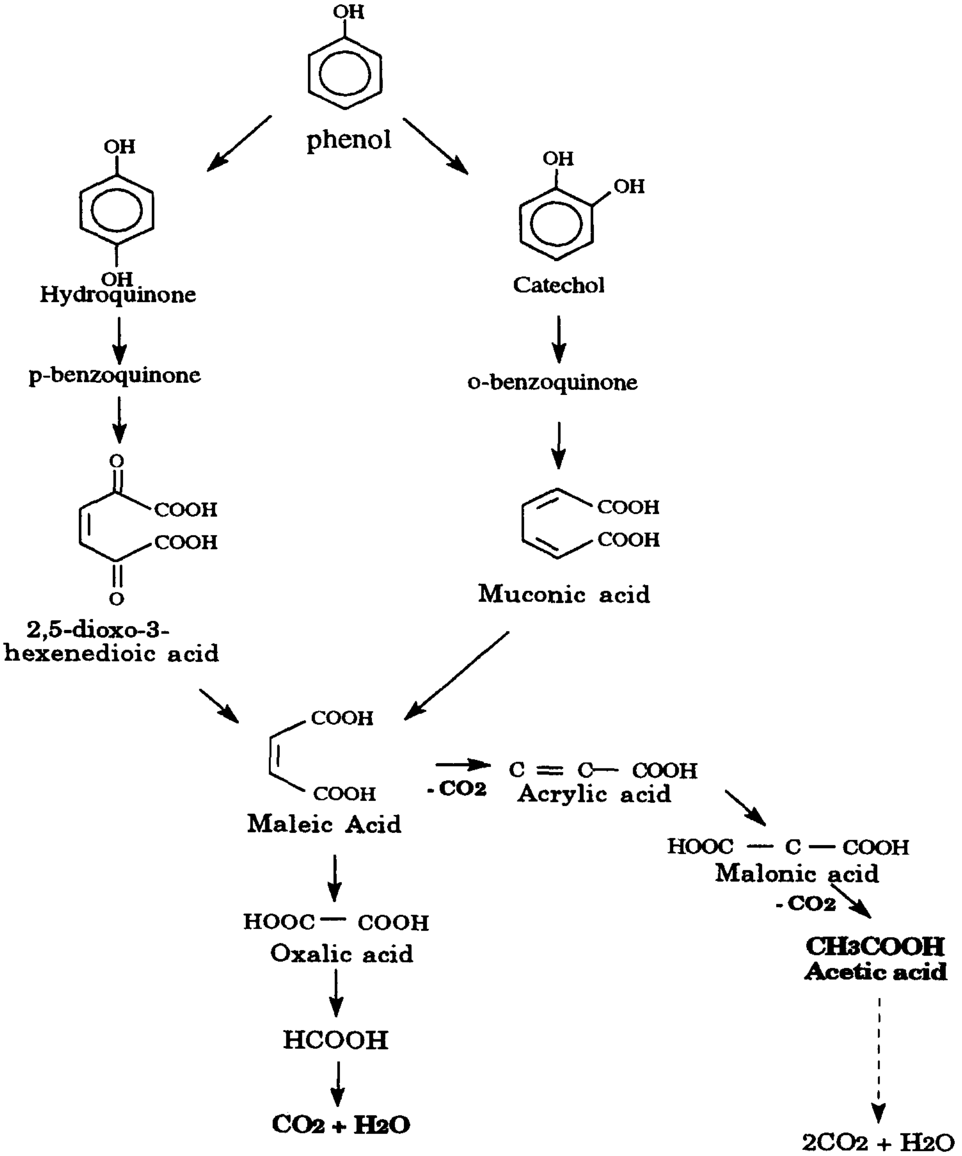

Fig. 3. Simplified scheme for phenol oxidation, after Devlin and Harris [8].

of the oxidation of sludge [2] and of alcohol distillery waste [9] is constituted of acetic acid. As acetic acid is refractory to oxidation, the decomposition of this carboxylic acid is one of the rate determining steps of the wet oxidation of various organic compounds.

Many attempts to study reaction mechanisms for WAO of organic compounds have been made. They conclude that the free-radical mechanism is involved in WAO of poly(ethylene glycol) [10], glyoxalic acid, oxalic acid [11], propionaldehyde [12], propionic and butyric acids [13], alcohol and acetic acid [14], phenol, succinic acid [15] and sludge [16]. Oxidation of these products is thought to be a free-radical mechanism.

The general scheme of the reaction is an initial cleavage of the C–H bond with formation of free radical $R\cdot$. This $R\cdot$ may react with oxygen to form an alkylperoxyl radical ($ROO\cdot$). Since the organic hydroperoxides formed are relatively unstable, decomposition of such intermediates often leads to molecular splitting and formation of subsequent intermediates with lower carbon numbers. These scission reactions continue rapidly until the formation of acetic acid, further converted into carbon dioxide and water (see Fig. 4).

In the case of acetic acid, it seems that the initiation reaction ($CH_3COOH \rightarrow CH_3COO\cdot + H\cdot$) occurs necessarily at the catalyst surface or at the metal/support interface [10]. The radicals can be stabilized by an electron transfer between the substrate and the catalyst. The attack on the a-position of COOH being excluded, four possibilities have been proposed for the propagation reactions: the radical acetate is produced at the surface of the catalyst by attack of CH_3COOH molecule with (I) a hydrogen atom [10], (II) a hydroxyl radical $OH\cdot$ [11–16], (III) an oxygen molecule [13–15] and (IV) a perhydroxyl radical $HO_2\cdot$ [14,15]. Reaction (II) with

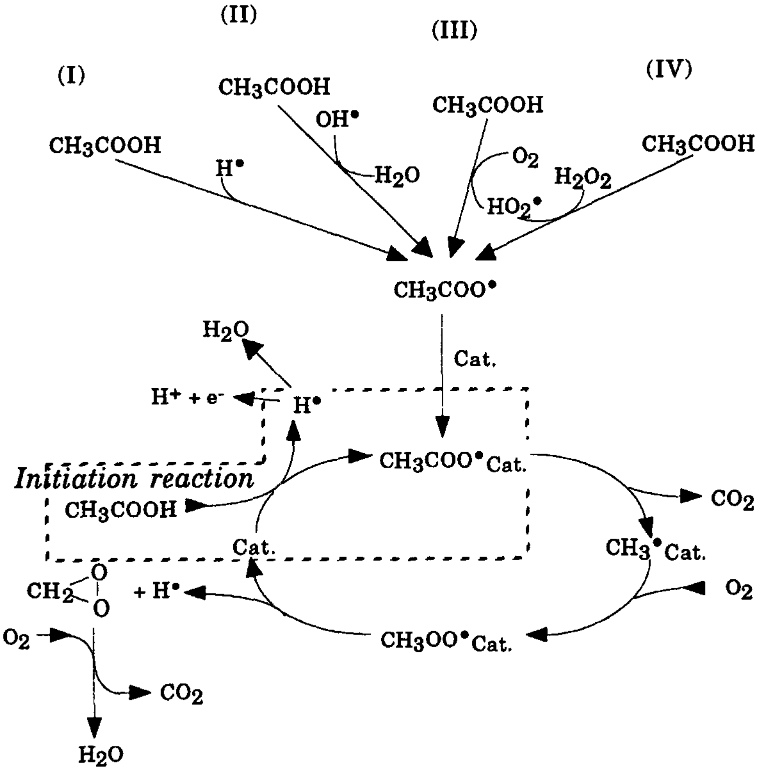

Fig. 4. Scheme for acetic acid wet air oxydation.

OH · is very rapid. Nevertheless owing to the excess of oxygen in the medium, reaction (III) is most likely to be the dominant one. A $HO_2\cdot$ radical is then produced which can react further with another molecule of acetic acid (IV). The acetate radical produced by one of the reactions (I–IV) undergoes a decarboxylation. The methyl radical is then oxidized via a peroxyl radical according to the general scheme valid for the free radicals $R\cdot$.

3.3. Acetic acid oxidation

Titania is generally used in aqueous solutions for the photocatalytic water purification [17]. It was thus interesting to investigate the activity of the titania supported catalysts in acetic acid oxidation. The results are reported in Table 1. This table shows that Ru is the best metal for the wet air oxidation of acetic acid. However, on titania, the activity remains relatively low.

The activity of Ru supported on active carbon was also investigated. The results are reported in Fig. 5 and Table 1 which give also the performance of the Mn/Ce Imamura's catalyst.

This Fig. 1 shows that active carbon is an excellent support for promoting the activity of Ru in carboxylic acid oxidation. The selectivity of the oxidation reaction was good: there was less than 2% byproduct. Moreover, a chemical analysis of the catalyst after the oxidation reaction confirmed that no ruthenium was solubilized. Nevertheless, the carbon support was partially oxidized into carbon dioxide.

Table 1
Acetic acid conversion and reaction selectivity (%) for 1 g of catalyst

Catalysts	Conversion after		Carbon dioxide
	1 h 30	3 h	Selectivity
Pt (5 wt.-%)/TiO_2	3	6	100
Rh (5 wt.-%)/TiO_2	7	9	100
Ru (5 wt.-%)/TiO_2	14	42	100
Ru (5 wt.-%)/C	62	97	98
Mn/Ce	42	76	96

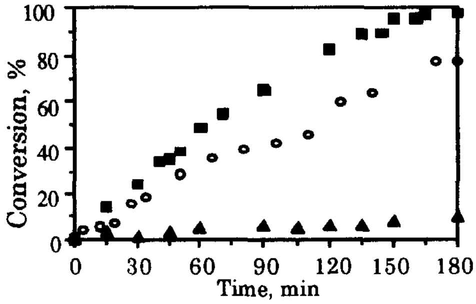

Fig. 5. Acetic acid conversion with: ▲ Ru (5 wt.-%)/TiO_2; ■ Ru (5 wt.-%)/C; ○ Mn/Ce.

Ru (5 wt.-%)/C has a better activity than Mn/Ce. Moreover, contrary to what can be observed with Ru, a significant amount of manganese ions went into solution and so it was necessary to add a process retaining toxic ions.

4. Conclusions

Ru (5 wt.-%)/C was found to be a very efficient catalyst for the wet air oxidation of carboxylic acids and specially of acetic acid. The oxidation produced a quasi complete removal of COD after 3 h (97%) and a good selectivity (98% of carbon dioxide). However, there are a few problems of stability and of safety insomuch as a part of the carbon support is oxidized during the reaction. The search for finding very active catalysts not having this drawback is in progress.

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