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Sonocatalytic degradation of oxalic acid in the presence of oxygen and Pt/TiO$_2$

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ABSTRACT

In order to treat aqueous effluents containing organic pollutants, several techniques can be considered depending on the organic compound concentration. Sonochemistry appears to be a promising solution to answer water remediation issue. In fact, when submitted into a liquid, ultrasound can induce the nucleation, growth, and violent collapse of vapor/gas filled bubbles. However, despite the extreme local conditions observed during acoustic cavitation, using ultrasound alone is efficient only at low concentration in organic pollutants. In the present study, 0.05 M oxalic acid degradation kinetics were followed at 40 °C under various conditions, in presence or not of Pt/TiO$_2$ catalyst under silent conditions or ultrasound at 20 and 360 kHz. Experiments were achieved under controlled atmosphere and comparison between argon, Ar/O$_2$ (20 vol% O$_2$) and pure O$_2$ conditions was performed. Oxidation rate increase of oxalic acid was measured under Ar/O$_2$ atmosphere in presence of Pt/TiO$_2$ catalyst due to strong dispersion effect of both low and high ultrasonic frequency and formation of chemically active species by sonolysis. High frequency ultrasonic irradiation under Ar/O$_2$ atmosphere gives the highest kinetic increase compared to silent conditions with oxalic acid degradation rate around 13 μmol min^{-1} at 40 °C with 2 g L^{-1} of 3 wt% Pt on P25 TiO$_2$ catalyst.

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1. Introduction

Water remediation and treatment of industrial wastewaters containing organic compounds are today's topics. Depending on the pollutant concentration several techniques can be considered for the treatment of aqueous effluents containing pesticides, carboxylic acids, chlorinated organic compounds, drugs or dyes [1–3]. For instance, advanced oxidation processes are one possible approach and involve the oxidation of the organic matter by hydroxyl radicals which are very reactive species [4,5]. OH$^\bullet$ radicals can be in situ generated at near room-temperature by various routes involving ozone, hydrogen peroxide, homogeneous or heterogeneous catalyst with or without UV irradiation namely Fenton process, photocatalysis or ozone related systems [4,6]. The main advantage of such processes is the ability of OH$^\bullet$ radicals to non-selectively react with organic compound until total mineralization. Nevertheless, this approach can be used only for low amount of aqueous pollutants within the range of μmol L^{-1} to few mmol L^{-1}. For higher concentrations of organic compounds other techniques should be considered such as wet air oxidation or catalytic wet air oxidation [2,3,7]. Organic matter oxidation in that case is achieved in the presence of oxygen at temperatures from 130 to 320 °C and under very high pressures between 20 and 200 bars. These techniques are able to treat wastewaters with pollutant concentrations up to 0.1 mol L^{-1}; however, the drastic conditions needed can constitute a major drawback.

Sonochemistry is another promising approach that can be considered for water treatment [1,6]. In fact, when submitted into a liquid, power ultrasound induces the nucleation, growth, and violent collapse of vapor/gas filled bubbles. This phenomenon known as acoustic cavitation produces a nonequilibrium plasma inside the cavitation bubbles which is responsible for in situ radical formation and possible organic degradation at the bubble–liquid interface [8]. Thus, the degradation of carboxylic acid such as oxalic or butyric acid was studied under high frequency ultrasonic irradiation in various conditions starting from few millimolar concentrations

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[9,10]. However it appears that despite the extreme local conditions observed during acoustic cavitation and bubble collapse, ultrasound alone is efficient only at low concentration in organic pollutants [1,11]. Coupling ultrasound with catalysts can be considered as one possibility to overcome these limitations and was actually employed for the degradation of various organic compounds such as phenol, detergents, dyes or drugs [1,11–16]. For instance, zero valent metals, such as copper or iron, were shown to enhance the degradation of phenol under ultrasonic irradiation [17]. In the same way, many efforts were focused on the understanding of the interaction between ultrasound and TiO_2 catalysts using low and high ultrasonic frequency irradiation [12,13,18–21]. Under such conditions, oxidation of the organic matter is explained by the reaction with in situ generated $OH^\bullet$ radicals [13]. The use of noble metal based catalysts like Au/TiO_2 or platinum based under ultrasonic irradiation was also reported however the involved concentrations of pollutants still remain quite low and typically around 1 mM [22,23].

In the present study, the coupling of ultrasound, 3 wt% of Pt on P25 TiO_2 catalysts and oxygen was considered and investigations on the degradation of 0.05 M oxalic acid were carried out. Oxalic acid was chosen since it is a quite refractory acid that can be formed during degradation of larger molecule and can be found in various industrial effluents [24]. Our main objective is to provide new insights on the sonocatalytic mechanism under near ambient conditions and the ability of such technique to treat organic compounds in higher concentration than considered in previously reported studies.

2. Experimental

2.1. Materials

Oxalic acid (98%), $Pt(NO_3)_4(NH_3)_2$ and other analytical grade chemicals were purchased from Aldrich and Alfa Aesar and were used without further purification. Deionized water (Milli-Q 18.2 MΩ cm at 25 °C) was used to prepare all aqueous solutions. Ar/O_2 gas mixture with 20 vol% of O_2, Ar of 99.999% purity and O_2 99.999% purity were provided by Air Liquide.

Aeroxide P25 TiO_2 was provided by Evonik (Specific surface area given by the manufacturer of 50 $m^2\,g^{-1}$ with an average particle size around 30 nm) whereas mesoporous TiO_2 ($S_{BET} = 695\ m^2\,g^{-1}$) was synthetized following the procedure already published. In brief, mesoporous TiO_2 was synthesized by ultrasonically controlled hydrolysis of titanium isopropoxide in the presence of octadecylamine [25].

2.2. Catalyst synthesis

Catalysts were prepared by incipient wetness impregnation of $Pt(NH_3)_4(NO_3)_2$ solution on P25 TiO_2 with a noble metal load of 3 wt%. Samples were dried overnight under vacuum at room temperature before reduction under H_2 gas flow in temperature at 300 °C for 2 h. After reduction of the noble metal, catalysts were passivated under O_2/N_2 (1/99 vol%) gas flow prior contact with ambient air. Specific surface area of the catalyst after deposition of platinum was measured at 40 $m^2\,g^{-1}$.

For mesoporous TiO_2, platinum deposition was achieved using the sonochemical reduction of platinum ions in aqueous phase under Ar/CO atmosphere as described in the literature [26].

2.3. Preliminary study

In order to be sure that the system is not limited by diffusion of the reactive species on the catalytic sites both the mechanical stirring speed and the catalyst mass to volume ratio were studied. According to preliminary results, for catalyst mass to volume ratios below 2 $g\,L^{-1}$, the degradation rate of oxalic acid is no more limited by mass transfer and degradation rate at 40 °C under Ar/O_2 atmosphere was around 0.67 $mmol\,min^{-1}\,g_{Pt}{}^{-1}$. In the same way, oxalic acid degradation rate under mechanical stirring speed between 300 and 1500 rpm were conducted and no drastic impact on the reaction rate could be observed (Fig. S1). For practical reasons, a 400 rpm rotation speed with a glass stirrer or a 1000 rpm rotation speed with a PTFE rod were chosen for high frequency ultrasonic irradiation and silent experiments in order to insure the homogeneity of the medium. Noteworthy, due to rod geometry differences both stirring conditions give very similar results.

2.4. Ultrasonic treatment

All ultrasonic treatments were carried out within a tightly closed thermostated glass reactor insuring the control of both temperature and gas atmosphere. The kinetics under silent conditions and during ultrasonic treatment were studied at a steady temperature of 40 ± 1 °C, inside the reactor, maintained by a Hubert CC cryostat. Before starting experiments, Ar, O_2 or Ar/O_2 (80/20 vol%) gas mixture were bubbled through oxalic acid solution for 15–20 min at a 100 $mL\,min^{-1}$ rate and kept during the ultrasonic treatment. Both low and high ultrasonic frequencies were considered for the degradation of organic species leading to two different setups.

2.4.1. Low frequency ultrasonic irradiation setup

Low ultrasonic frequency treatments were carried out with a 1-cm^2 titanium probe and piezoelectric transducer supplied by a 20 kHz generator (750 W Vibra-Cell Sonics). The solution volume was 50 mL insuring that the sonotrode was reproducibly immersed below the surface of the sonicated liquid. Absorbed acoustic power within the medium was assessed by calorimetric method and was found to be around 0.35 $W\,mL^{-1}$ [27]. During silent conditions, medium homogeneity was insured by magnetic stirring with non-specified rotation speed. This magnetic stirring was actually not needed during ultrasonic treatment. In fact, even if it is known that the cavitation zone with 20 kHz ultrasonic probe with quite narrow tip of 1 cm^2 is usually focused at the end of the tip within a small cone with a length of few centimeters [28], the ultrasonic irradiation in our conditions induces a strong stirring of the solution with almost no dead volume. Picture of the 20 kHz setup is given in supplementary data (Fig. S2).

2.4.2. High frequency ultrasonic irradiation setup

The 345–360 kHz transducer with a 25-cm^2 active surface was fitted at the bottom of a 250 mL glass reactor and connected to a generator with a maximum electrical power of 125 W (L3 ELAC Nautik). The volume of sonicated solution was 200 mL and the homogeneity was insured by mechanical stirring. Absorbed acoustic power was also evaluated by calorimetric method under mechanical stirring and found to be around 0.29 $W\,mL^{-1}$. Picture of the 345–360 kHz setup is given in supplementary data (Fig. S3). Note here that with such large transducer and high ultrasonic frequency, the acoustic field is expected to be quite homogeneous within the reactor [29]. Chemiluminescence of luminol shown in Fig. S4 clearly indicates the formation of $OH^\bullet$ radicals in studied conditions and the absence of dead volume within the reactor.

2.5. Characterization techniques

2.5.1. Solid phase analyses

Low resolution TEM analyses were conducted on a Jeol JEM 3010 TEM. Samples were first dispersed in absolute ethanol or isopropanol then one drop was deposited on carbon coated grid prior analysis. Full size TEM images are given in supplementary data.

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