Comparison between MnO2, TiO2 and CoO for the Ozonation of oxalic acid

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Abstract: Advanced oxidation, is the main of research in ozone fields for many years. Ozone generations and uses as an oxidant and also the use of heterogeneous reactor were improve the de development of catalytic ozonation axes. The object of our project is the application of catalytic ozonation for some refractor molecules. Oxalic acid was chosen as a model of refractor molecules. In fact, it is the final product of the degradation by ozone of many organic molecules in aqueous solution. Ozonation have a significant effect on the mineralization of water charged with oxalic acid. In our experiences, the dioxide of manganese and titan and the oxide of cobalt were used as homogenous catalysts. Experiences of ozonation have been done in ambient conditions in a gas-liquid reactor with a capacity of 2 liters. Studies of ozone concentration, type and mass of catalysts and oxalic acid concentration have been done. With 1mmol/l of oxalic acid solution and 43mg/l of ozone, we obtained 50% of maximal oxidation report after 20min. the addition of 1g of MnO2 to the solution in the reactor changed the same report to 85% after 5min. a comparison between MnO2, TiO2 and CoO was done and results prove that the oxide of cobalt is more efficient than the two other catalyst. However, with the same mass added to the reactor 500 mg for each catalyst, the rate of conversion obtained with MnO2 and CoO was nearly 95% and 90% with TiO2 but the kinetic of CoO is faster than the two other catalysts.

Keywords: ozone, oxalic acid, MnO2, TiO2, CoO.

1 Introduction

The water pollution by organic matters is a world problem among which aspects and impacts are obviously different according to the level of development of countries. Thus, the searches are to face the presentation of a reliable and effective technique for the treatment and the mineralization of waters containing refractor molecule. A big interest was brought to the development of the processes of advanced oxidation (POA). Oxalic acid is usually the most dominant final products in aqueous ozonation processes and it is a typical refractory compound to conventional chemical oxidation. So that it was chosen as a model of refractor molecules. Literature reports many works where oxalic acid was treated.

Magnesium oxides are the most widely studied metal oxides as ozonation catalyst, and they are reported to be the most efficient in ozone decomposition in gaseous medium [1]. Andreozzi and al. (1996) [2] studied the ozonation of oxalic acid in aqueous solution. They found an important improvement in the ozonation of oxalic acid with MnO2 as catalyst to the non-catalytic processes. Also, titanium oxide is characterized by its extensive use in catalytic oxidation processes and by its capacity of adsorbing oxygen in the form of superoxide ion, O2-, a rich electron species [3], which in water promotes the decomposition of ozone into free radicals [4]. Fernando J. beltran and al. (2002) [5] tested the addition of TiO2 as catalyst of oxalic acid ozonation. They found that its presence significantly improved the ozonation rate of oxalic acid compared to the results from non-catalytic processes. Concerning cobalt oxide based catalysts; several authors have reported their efficiency in the mineralization of organic pollutants.

Alvarez et al. (2007) [6] investigated different Co active phases deposited on the γ-Al2O3 surface (CoO, CoAl2O4, Co3O4) and reported that the sample containing Co3O4 as the main Co phase provided the most promising results on the ozonation of pyruvic acid. Faria et al. (2009) [7] tested the addition of Cerium, manganese and cobalt oxides as catalysts for the
ozonation of selected organic compounds. They noted that the high dispersion of Co oxide on the support and the multivalence oxidation states of cobalt (Co (II) and Co (III)) was suggested to be responsible for the catalytic reactivity of the catalyst. Also the same authors noted that the catalysts containing cobalt are apparently more stable than those containing manganese, therefore being more promising as catalysts for the ozonation of organics in the aqueous phase.

In the present work, the preparation and the comparison of a series of manganese, cobalt and titanium oxides, was carried out, with the aim of evaluating their performance as homogenous ozonation catalysts for the mineralization of oxalic acid as organic pollutants in aqueous solution.

2 MATERIAL AND METHODS

Experiments were carried out in 2l glass cylindrical ractor surmounted by an engine of excitement pulling a helix in pales ten allowing a good distribution of the substances in the solution. Ozone was produced in a laboratory ozone generator from pure oxygen (Fig. 1). The aqueous slurry (1l) was prepared with a given amount of powder catalyst and oxalic acid (99%) in concentration of 1mmol/l at the natural pH (pHoxalic acid ≈3.0). Experiences have been done in ambient conditions of temperature and pH.

Concentration of oxalic was determined by HPLC with a 1100 Series Hewlett-Packard liquid chromatograph provided with an UV-VIS detector and a chemstation software package for data analysis and automatic control of chromatographic conditions. A 4.6 mm i.d.,250 mm length ODS-P column was used. The analysis was carried out isocratically with a 70/30 (v/v) water/ acetonitrile mobile phase (phosphoric acid was used to keep the water pH at 2.5). Flow rate was set at 1ml/min. At these conditions oxalic acid retention time was 2 min.

Oxide of Cobalt was prepared by precipitation according to the procedure described by Imamura et al., 1985 [8] from the corresponding salt aqueous solutions Co (NO3)26H2O. In the batch, 200 mL of a sodium hydroxide 3 M solution was added drop wise to the metal salt solution (ca 15 g in 100 mL of distilled water) under continuous stirring. The resultant precipitates were thoroughly washed with distilled water, dried at 100 °C for 24 h and calcinated in air (50 cm3 min_1, measured at room T and P) at 450 °C for 3 h. The catalysts were sieved before use and a particle size of 100–300 µm was selected for the kinetic experiments in order to minimize mass transfer effects.
3 RESULTS AND DISCUSSION

3.1 WITHOUT CATALYST

3.1.1 EFFECT OF OZONE CONCENTRATION

In figure 2 we represent the variation of the ratio of conversion of oxalic acid for different concentration of ozone.

![Fig. 2 Effect of ozone concentration on oxalic acid ozonation](image)

It is clear that the augmentation of ozone concentration improve the mineralization of water charged with oxalic acid.

3.1.2 EFFECT OF OXALIC ACID CONCENTRATION

In figure 3 we represent the variation of oxalic acid concentration for two initial concentration 1mmol/l and 2mmol/l.

![Fig. 3 Ozonation of oxalic acid without catalyst, [O3]=43mg/l; DO2=21.6l/h; T=25°C; pH=4.3](image)

Oxalic acid is a refractor molecule which is difficult to eliminate without any catalyst. In fact, an aqueous solution of oxalic acid 1mmol/l take above 30min to be 50% mineralized. And if the initial concentration is 2mmol/l, mineralization can’t be superior at 37% even if time exceeds 30min.

3.2 WITH CATALYST

3.2.1 EFFECT OF MnO2 AS CATALYST

In figure 4 we represent the variation of the ratio of conversion of oxalic acid for different amount of MnO2 added to an aqueous solution of oxalic acid (1mmol/l).
The addition of MnO₂ to the oxalic acid solution has a significant effect on its ozonation. In fact, the maximal conversion ratio obtained without catalyst was 50%. Catalytic effect accelerates with the quantity of MnO₂ added. In fact, the addition of 1g of MnO₂ in the reactor improves this ratio to 85% after 5min only.

In figure 5 we represent the same variation of figure 4 with 10mg/l of ozone concentration.

3.2.2 EFFECT OF TiO₂ AS CATALYST

In figure 6 we represent the variation of the ratio of conversion of oxalic acid for different amount of TiO₂ added to an aqueous solution of oxalic acid (1mmol/l).
With 0.5g of TiO2 added in the reactor, we can obtain 80% of oxalic acid conversion after 2h of ozonation.

In figure 7 we represent the same variation that exists in figure 6 but with maximal ozone concentration (43mg/l) and maximal amount of catalyst (1g).

![Fig.7 Ozonation of oxalic acid with MnO2 and TiO2 as catalyst, [O3] =43mg/l; DO2=21.6l/h; T=25°C; pH=4.3](image)

With the same mass added to the reactor 1g for each catalyst, the conversion ratio obtained with MnO2 was 85% after 5min of ozonation and 60% with TiO2 after above 40min of ozonation.

### 3.2.3 Effect of CoO as Catalyst

In figure 8 we represent the variation of the ratio of conversion of oxalic acid for different amount of CoO added to an aqueous solution of oxalic acid (1mmol/l).

![Fig.8 Effect of Co on oxalic acid ozonation [O3]=10mg/l; DO2=21.6l/h; T=25°C,pH=4.3](image)

With 0.5g of CoO added in the reactor, we can obtain 93% of oxalic acid conversion after above 3h of ozonation.

### 3.3 Comparison between Catalysts

In figure 9 we represent the variation of the ratio of conversion of oxalic acid for the same mass of TiO2, MnO2 and CoO added to an aqueous solution of oxalic acid (1mmol/l) at the same ambient conditions to can compare between them.
Comparison between MnO$_2$, TiO$_2$ and CoO for the Ozonation of oxalic acid

With the same mass added to the reactor 500 mg for each catalyst, the conversion ratio obtained with MnO$_2$ and CoO was nearly 95% and 90% with TiO$_2$ after above 3h of ozonation. But the kinetic of cobalt is faster than the two other catalysts.

Cobalt and manganese presents both +2 and +3 valences. Thus, it could be assumed that the presence of such species has a promoting effect in ozonation reactions.

4 CONCLUSIONS

Oxides of manganese (MnO$_2$), anatase (TiO$_2$) and of cobalt (CoO) were evaluated as homogenous ozonation catalysts for the mineralization of oxalic acid.

All the prepared metal oxides catalyze the ozonation of oxalic acid, significantly increasing the extent of mineralization of the corresponding solution, compared to single ozonation. The experimental results showed that MnO$_2$ and cobalt are more efficient ozonation catalysts than TiO$_2$ which might be related both to their higher surface areas and enhanced redox properties. Oxide of Cobalt kinetic is apparently faster than those of manganese and titan.

REFERENCES