

Catalytic Wet Air Oxidation of Ethyl Tert-Butyl Ether (ETBE) using Rh/Al₂O₃ and Rh/Ce-Al₂O₃ catalysts

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Introduction

The problem of the pollution reduction of the aqueous streams containing refractory organic chemicals dissolved is of great importance, especially in productive sectors of industry. These effluents can not be treated through conventional processes of biological oxidation, because of they have a little biodegradability and the substances contained present an inhibitor effect. The process currently used is the wet oxidation which requires high pressures and temperatures, and consequently high cost. An interesting alternative is the catalytic wet air oxidation. Catalytic wet air oxidation (CWAO) is a technique able to destroy pollutants [1]. The major advantage of this method of treatment is the high mineralisation (conversion to CO₂) of organic pollutants into effluents. The catalyst permits a significant reduction of the temperatures and the necessary pressures and improves the economy of the process. Catalysts employed are noble metals, in various supports. The aim of this work is evaluate the Rh/Al₂O₃ and Rh/Ce-Al₂O₃ catalysts performance to destroy ETBE.

Materials and Methods

Rh/γ-Al₂O₃ and Rh/γ-Al₂O₃Ce_x catalysts were prepared by impregnation method. Experiments were carried out using a Parr reactor of 300 mL. Oxygen at 10 bar of pressure was used as oxidant source. Reaction temperature was fixed at 100°C. 150 mL of ETBE solution with a concentration of 227 ppm were placed into reactor and the load of catalyst used was 1 g/L. The tests were accomplished during 1 h. These samples were analyzed by GC with a FID detector which is equipped with a capillary column (DB-WAX 30 m x 0.53 mm id, 1.0 μm). Total organic carbon (TOC) was analyzed using a 5000TOC Shimadzu analyzer. pH was measured using a Conductronic PC-45 and the selectivity of CO₂ was calculate using the follow relationship:

$$SCO_2 = \frac{X_{TOC}}{X_{ETBE}} \cdot 100\%$$

Results and Discussion

The table 1 shows the results of conversion of ETBE, TOC abatement, % Selectivity to CO₂ and Carbon balance after 1 hour of reaction in the catalytic wet air oxidation of ETBE. It can be appreciated that the best abatement in the total organic carbon (TOC) was obtained using a catalyst with 1 wt% of Ce, this catalyst showed the best conversion of ETBE, being obtaining a maximum of 85%.

The abatement of the TOC is improved with the addition of CeO₂ in the support. The abatement of the TOC diminishes with the increment in the content of CeO₂, but this it is bigger than obtains with the catalyst of Rh/A (without CeO₂).

The differences that exist between the abatement of the TOC and the conversion of ETBE indicate the production of certain intermediaries compounds that take place in the course of the oxidation of the ETBE, such as the tert-butyl alcohol (ATB), which is one of the main by-products of the degradation of the ETBE and that later it is easier of degrading.

The results obtained starting from the balance of carbon (Table 1) indicate that the addition and the increment in the content of CeO₂ contribute to the abatement of the TOC as well as to the decrease of the number of intermediaries that take place during the oxidation of ETBE, being obtained a minimum value for a content of 5% of CeO₂ and that it will be reflected in the selectivity toward CO₂ that reaches their maximum in 98%. The number of intermediaries that take place is smaller for the catalysts with 5 and 10% of CeO₂.

Table 1. ETBE Conversion, TOC abatement, Carbon balance and pH.

Catalyst	% ETBE Conversion	% TOC Abatement	# C _{TOC}	# C _{ETBE}	# C _{INT.}	CO ₂ selectivity (%)	pH
Rh/A	79	70	41.8	29.9	11.9	89	6.99
Rh/ACe1	85	79	29.8	20.6	9.2	92	6.33
Rh/ACe5	79	78	31.6	29.9	1.7	98	3.73
Rh/ACe10	78	75	35.3	30.3	4.9	96	4.50
Rh/ACe20	81	75	34.6	26.8	7.8	93	5.02

C_{TOC}: number of total carbon remain in the liquid phase [ppm]

C_{ETBE}: number of total carbon remain, associated to ETBE [ppm]

C_{INT.}: number of total carbon associated to intermediates [ppm]

The differences that exist in the pH values from one to another catalyst indicate the existence of different intermediaries which are formed during the oxidation of the organic compound. The type of intermediary will depend of the catalyst used. Among these intermediaries we can find: tert-butyl alcohol (TBA), TBF, methyl-acetate, formic acid, isobutene and carboxylic acids which give the pH variations as a result [2].

The CO₂ selectivity increase with the cerium quantity, explained by the formation of Ce⁴⁺-O²⁻-M⁺ bond[3] which emphasize the oxidation capacity of Rh/γ-Al₂O₃Ce catalysts, i.e. the major quantity of cerium promote the formation Ce⁴⁺-O²⁻-M⁺ bond. It is also known that the presence of rare earth (CeO₂) in the support of the catalysts increases the oxidation, characteristic that result of the capacity of the CeO₂ for cycle between CeO₂ and CeO_{2-x} [4,5].

The catalytic oxidation of ETBE, it has shown that these materials are catalytic promising for the catalytic wet air oxidation of organic pollutants.

Significance

This work has a basic significance concerning the development of the new catalysts whit a high selectivity to CO₂, which can be applied in the CWAO of pollutants which can not be destroyed by another technique as biological treatment.

References

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