

Catalytic wet air oxidation of gasoline oxygenates using Rh/ γ -Al₂O₃ and Rh/ γ -Al₂O₃–CeO₂ catalysts

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Abstract

Catalytic wet air oxidation of gasoline oxygenates (ETBE and TAME) were carried out using Rh/ γ -Al₂O₃, Rh/ γ -Al₂O₃–CeO₂ catalysts in a Parr reactor at 100, 120 and 150 °C using oxygen as oxidant source at 10 bar of pressure. Aqueous solutions of ETBE and TAME were prepared using the quantities necessary to obtain 227 ppm. The quantity of catalyst used was 1 g/L. Cerium emphasizes the oxidative capacity of the rhodium catalysts at 100 °C explained by the formation of rhodium oxide sites (Rh₂O₃) at the surface, detected by TPR and XPS techniques. This capacity has been observed by the high CO₂ selectivity due to the support–metal interaction by the formation of Ce⁴⁺–O^{2–}–M⁺ bond which prevents the formation of carboxylic acids intermediate as acetic, the most refractory acid found.

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1. Introduction

In the 90's the international organisms for the environmental protection restricted up to a maximum of around 1 vol.% in benzene content in the gasoline due to its carcinogenic effects. The laws also claimed the use of gasoline with a minimum of 2.7 wt% of oxygen to reduce the formation of ozone in the air. Due to these dispositions, the use of oxygenated additives in the gasoline such as methyl *tert*-butyl ether (MTBE), ethyl *tert*-butyl ether (ETBE) and *tert*-amyl methyl ether (TAME) was increased. These oxygenates have an octane number between 105 and 110 [1], which improved the quality of gasoline. However, these compounds are highly soluble in water, for these reasons contaminated rivers, lakes and groundwater with MTBE, ETBE and TAME have been detected [2]. Techniques for the treatment in order to remove these pollutants in liquid and gas phases have been investigated. Various methods like oxidation by fenton reagent, photocatalysis, oxidation in gaseous phase using monoliths, biodegradation, etc. have become kinetic studies as

well as the intermediaries during the oxidation process [3,4,5]. Catalytic wet air oxidation (CWAO) [6] has been used in the past times to oxidize a diversity of pollutants in water. In this process, the reaction can be carried out to pressures from 5 to 200 bar and temperatures comprises between 100 and 320 °C using a supported noble metal or oxides catalysts. CWAO is an efficient process in the treatment of a great diversity of contaminants such as carboxylic acid, phenol, polymers and ethers. Depending on the conditions (temperature and pressure), two different objectives can be reached: (i) a total mineralization of the polluting agents to CO₂, N₂, and H₂O or (ii) an increase of the biodegradability of the polluting agent when orienting the reaction towards the by-product formation is easier to biodegradable. The catalysts based on Cu, Zn, Mn, and Fe have demonstrated to have excellent activity for these reactions but a process of recovery to recycle soluble metals is necessary. Therefore, the catalysts based on supported noble metals have been developed in order to avoid the loss of the metal by washing during the treatment of the polluting agent. In this work we used the technique of CWAO for the oxidation of ETBE and TAME on the Rh/Al₂O₃ and Rh/Ce–Al₂O₃ catalysts with a content of 1 wt% of rhodium, making the content of Ce vary between 1 and 20 wt% into support. Catalysts characterization was done by

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BET surface area, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD-H₂) and temperature-programmed reduction (TPR-H₂). CWAQ tests were carried out in Parr reactor using pure oxygen like oxidant to 10 bar of pressure and different temperatures (100, 120 and 150 °C) to evaluate the catalysts. A concentration of polluting agent of 227 ppm and one load of catalyst corresponding to 1 g/L were used. Several samples were taken during the reaction and analyzed by gas chromatography (GC), total organic carbon (TOC) and pH measure in order to identify intermediates and CO₂ formation.

2. Experimental

2.1. Preparation of the supports

The γ -Al₂O₃ support was obtained by the calcination of the Boehmite Catapal-B at 650 °C under airflow (3.6 L/h) during 4 h. The γ -Al₂O₃-Ce supports were prepared by wet impregnation of the Boehmite with an aqueous solution of Ce(NO₃)₃·6H₂O containing the appropriate cerium concentration (1, 5, 10 and 20 wt% Ce). The reactants were maintained under constant stirring for 3 h, afterwards the solid was dried at 60 °C in a water bath and under vacuum until dryness. The samples were placed in an oven at 120 °C for 12 h and then calcined in airflow (3.6 L/h) at 500 °C for 4 h.

2.2. Catalysts preparation

The Rh/ γ -Al₂O₃ and Rh/ γ -Al₂O₃-CeO₂ catalysts were prepared by the impregnation of the supports, γ -Al₂O₃ and γ -Al₂O₃-CeO₂, with an aqueous solution of RhCl₃·3H₂O using the amount necessary to give a final concentration of 1 wt% Rh. The mixture was maintained under constant stirring in a rotavapor for 3 h, after excess water was evaporated at 60 °C under vacuum until dryness. The catalysts obtained were dried to 120 °C for 12 h, calcined in air to 500 °C for 4 h and finally reduced under hydrogen flow for 5 h. The catalysts were labeled as Rh/A in the case of Rh/ γ -Al₂O₃ and Rh/ACeX for the catalysts supported on the γ -Al₂O₃-CeO₂, where X means the cerium amount (1, 5, 10 and 20%) (see Table 1).

2.3. Specific surface areas

The determination of the specific surface area and mean pore diameter was carried out with a Quantachrome ChemBet 3000

apparatus. The data were obtained from the nitrogen adsorption isotherm. Before the measurements the samples were desorbed at 400 °C for 2 h.

2.4. X-ray diffraction analysis

A SIEMENS-D500 diffractometer with an anode of Cu K α radiation and a graphite monochromator in the secondary beam. Intensity data were measured by step scanning in the 2θ ranges between 2° and 70° with a 2θ step of 0.02° and a measuring time of 1 s per point. The determination of the compound was made with reference to correspond cards to the γ -alumina and cerium oxide (CeO₂), according to file JCPDS.

2.5. Temperature-programmed desorption (TPD-H₂)

Hydrogen TPD was carried out in a Quantachrome ChemBet 300 apparatus. The reduced sample was first reactivated in hydrogen up to 500 °C for 1 h; afterwards the temperature was continuously diminished to room conditions. The hydrogen flow was then replaced by a mixture of 20% hydrogen/He (UHP) until saturation, followed by displacement under Argon (UHP) flow. Thermal desorption was then started from room temperature up to 500 °C at a heating rate of 10 °C min⁻¹. The hydrogen accessibility of Rh catalysts was determined from the area of the TPD thermograms using a calibrated loop and assuming a stoichiometry of H/Rh = 1.

2.6. Temperature-programmed reduction (TPR-H₂)

Analyses were carried out in a Quantachrome ChemBet 3000 apparatus. 100 mg of catalyst was placed into a microreactor tube and then hydrogen (5.0 vol.% in N₂) was passed through the tube under atmospheric pressure at 0.6 L h⁻¹. The tube was heated with an electric furnace at 10 °C min⁻¹ and the amount of H₂ consumed was monitored by the TCD signal using software integrated at the system.

2.7. XPS measurements

XPS analyses were carried out in a THERMO VG ESCALAB 250 spectrometer using Al K α radiation (1486.8 eV) with a monochromator system. The X-ray beam was 15 kV and 7.5 mA. Binding energies were corrected from charge effects with reference to the C(1s) peak of carbon contamination at 284.6 eV and measured with a precision of ± 0.2 eV. The samples, previously reduced under hydrogen flow, were placed in an Indium film and then analyzed.

2.8. Catalytic activity

Catalytic wet air oxidation experiments were accomplished in a 300-mL stainless steel pressure reactor (Parr) capable of performing batch experiments at pressures up to 20 bar and temperatures up to 300 °C and equipped with a magnetically driven stirrer (set at 1000 rpm). Experiments were carried out at 100, 120 and 150 °C. 150 mL of aqueous solutions of the ETBE

Table 1
BET areas, pore diameter and metallic accessibility obtained by nitrogen physisorption and TPD-H₂ of the Rh catalysts

Catalyst	Ce (wt%)	Rh (wt%)	BET area (m ² /g)	Pore diameter (Å)	H/Rh
Rh/A	0	0.70	266.4	68.1	0.98
Rh/ACe1	1	0.74	232.4	69.1	0.99
Rh/ACe5	5	0.78	205.5	66.7	0.72
Rh/ACe10	10	0.89	171.7	70.2	0.46
Rh/ACe20	20	0.99	139.2	68.1	0.41

or the TAME was previously prepared using distilled water and the quantities necessary to have a concentration of 227 ppm of the organic compound. The solution was placed in the glass vessel in order to prevent the direct contact of the solution with the reactor. The respective catalyst concentration of 1 g/L was introduced in the aqueous solution, and then it was introduced to the reactor. It was first purged with nitrogen for 15 min to remove any traces of oxygen and then heated to the desired temperature under nitrogen. As soon as the set temperature was achieved, oxygen was fed continuously to the reactor to maintain an oxygen pressure of 10 bar throughout the test (1 h). Liquid samples of approximately 1 mL were periodically taken from the reactor, using a valve connected to a tube located inside the reactor vessel. This tube is provided with a microporous glass filter to prevent the catalyst loss.

Liquid samples were analyzed using gas chromatography which is equipped with a Flame Ionization Detector (FID) and provided with a capillary column (DB-WAX 30 m \times 0.53 mm i.d. 1.0 μ m). A temperature ramp was set up in order to separate the pollutant and their intermediates during the reaction. Analysis of total organic carbon was achieved using a 5000-TOC Shimadzu analyzer previously calibrated to obtain concentrations in the range of 0 at 300 ppm of TOC. pH was measured using a conductronic PC-45 and the CO₂ selectivity was calculated using the relationship used by Lin et al. [7]:

$$\text{SCO}_2 (\%) = \frac{X_{\text{TOC}}}{X_{\text{oxygenate}}} \times 100$$

3. Results and discussion

3.1. Catalysts characterization

Table 1 reports the results of BET area measurements, pore diameter and metallic accessibility of the Rh catalysts. A diminution on the BET specific surface area of the supports as the Ce content increases is observed, meanwhile, the pore size diameter remains constant. These results confirmed that cerium is in wide contact with the alumina, forming a mixed oxide which strongly modifies the textural properties [8].

In Table 1, the weight content of Rh determined by atomic absorption spectroscopy is reported. The values are among 0.7–0.99 wt%. The dispersion of the Rh on γ -Al₂O₃ and Al₂O₃-Ce were calculated with the amount of hydrogen chemisorbed, for the different catalysts, using the TPD technique and assuming a stoichiometry of H/Rh = 1. It can be observed a well dispersion in the catalyst free of Ce and with 1 wt% Ce, 0.98 and 0.99, respectively. As the Ce contents increase in the catalyst the dispersion decreases giving values of 72, 46 and 41% for contents of 5, 10 and 20% Ce, respectively. The diminution of the particle size with the load of cerium could be explained. Either cerium could be deposited on the metal surface or a segregation of the cerium oxide on the surface inhibiting the dispersion of rhodium on the surface by a metal-support interaction [8].

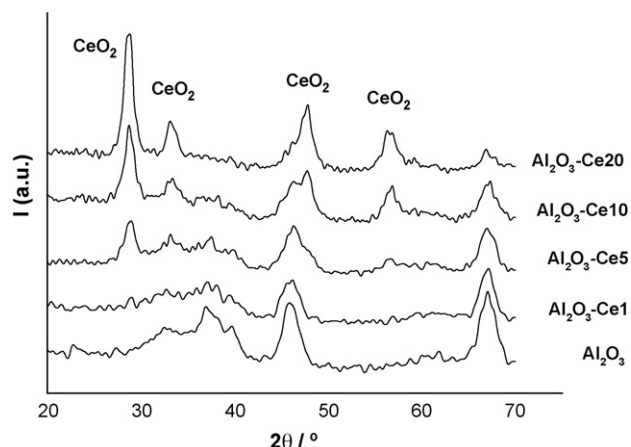


Fig. 1. X-ray spectra of the supports.

The results of X-ray diffraction (Fig. 1) reveal that the γ -Al₂O₃ phase was formed after the heat treatment at 650 °C under airflow. With the addition of 1% of cerium to γ -Al₂O₃ only appear the signals corresponding to the γ -Al₂O₃, which can indicate that the Ce is highly dispersed in the γ -Al₂O₃. When 5% of Ce was added, the signals corresponding to the CeO₂ phase begin to show in addition to those corresponding at the γ -Al₂O₃ phase. To contents of 10 and 20 wt% of Ce, the signals of the CeO₂ phase become more important (and they overlap with those of the γ -Al₂O₃ phase) than the typical peaks of the γ -Al₂O₃ phase. This could be interpreted like a segregation of the CeO₂ or like a formation of conglomerates of CeO₂, liable to the BET area diminution.

The TPR profiles (Fig. 2) show that in the case of Rh/ γ -Al₂O₃ catalyst a major peak to 65 °C is observed and one wide and small peak among 100–175 °C. The peak corresponding to the lowest temperature (65 °C) corresponds to the reduction of the Rh³⁺ to Rh⁰ specie that reduces more easily. The second signal (100–175 °C) could correspond to an oxidized species of Rh³⁺ to Rh⁰ or to the reduction of the species in the metal-support interphase. The peak observed between 100 and 175 °C

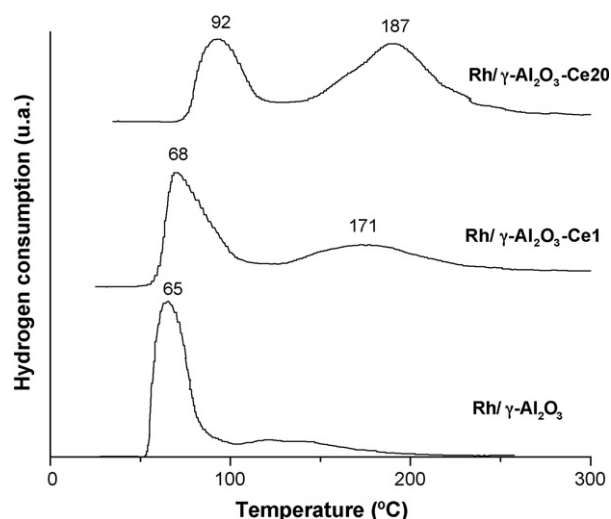


Fig. 2. TPR profiles of the Rh/A, Rh/ACe1 and Rh/ACe20 catalysts.

in Rh/ γ -Al₂O₃ in the catalyst of Rh with 1% of Ce is transformed more into a defined peak with a maximum to 171 °C and to 187 °C for the catalyst with 20% of Ce. This peak corresponds to the stabilization of a Rh^{x+} species in the oxidized state, by the effect of the presence of Ce. It has been reported that once reduced the Rh supported in CeO₂, the particles of Rh⁰ migrate in the surface of the support reoxidizing itself like Rh (3+ or x+) with surrounding cations of Ce⁴⁺ [9]. This is explained by an attended reduction of the

CeO₂ by the Rh. When the Rh is reduced to Rh⁰ a spill-over effect by the hydrogen can be produced by the metallic Rh which favors the reduction of Ce⁴⁺ at the surface of the support [10].

The Rh(3d) core level region of Rh catalysts from XPS studies are shown in Figs. 3. Accordingly, the 3d_{5/2,3/2} doublet at 307 and 313 eV for the Rh/A and Rh/ACe1 (Figs. 3a and 3b) catalysts is due to the Rh metal in the zerovalent state [11]. The second signal at the zerovalent state decays from 313 to 311 in

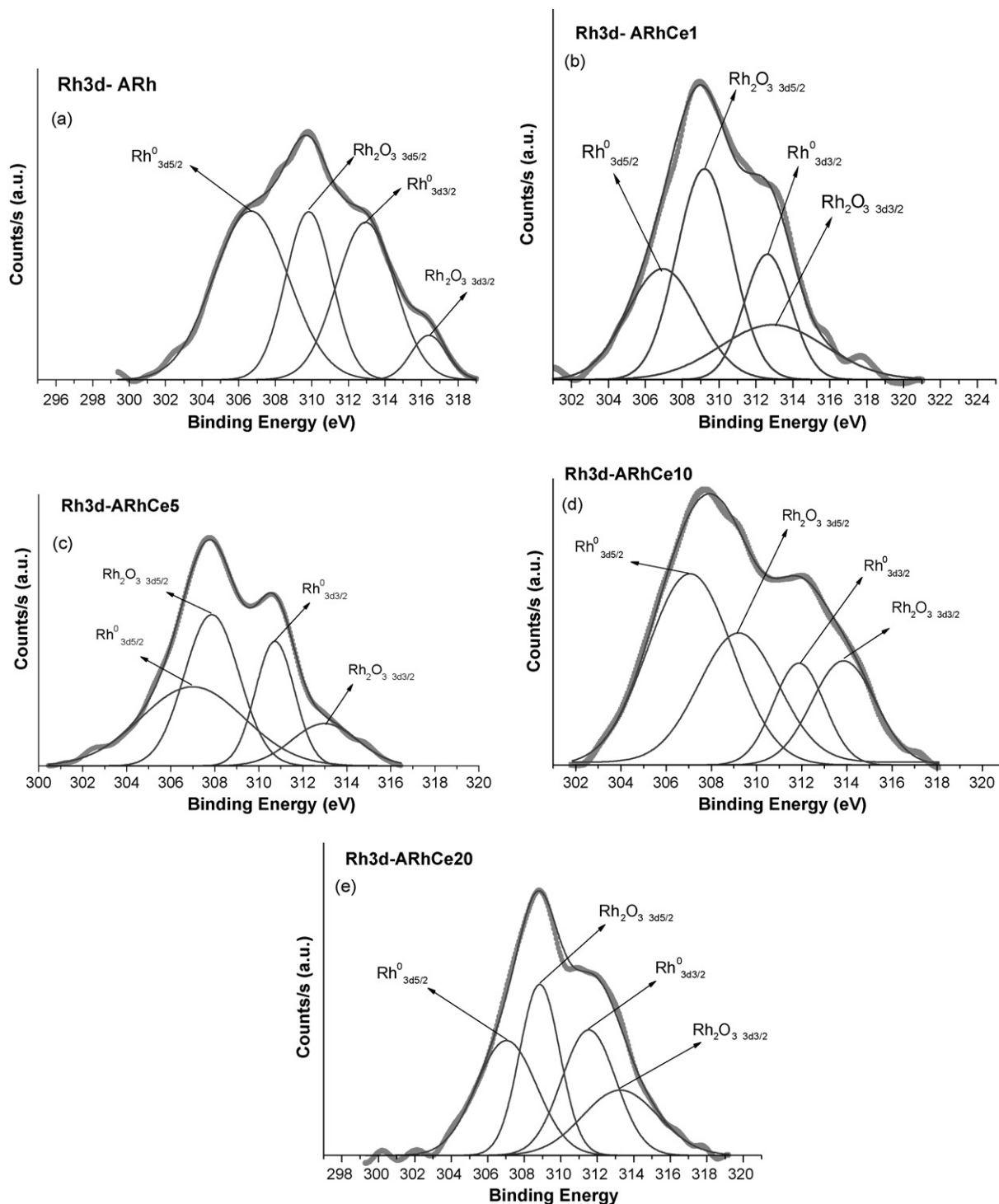


Fig. 3. Rh3d core level spectra of (a) Rh/A; (b) Rh/ACe1; (c) Rh/Ace5; (d) Rh/ACe10 and (e) Rh/Ace20.

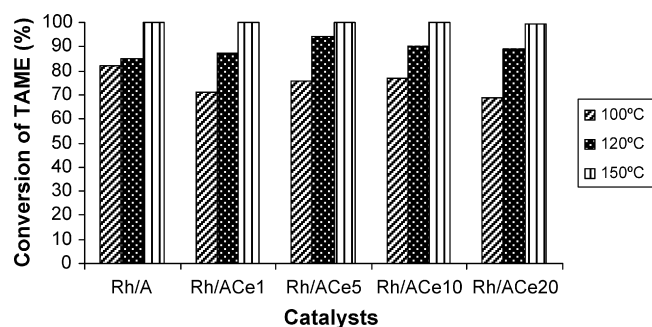


Fig. 4. CWAQ of TAME at 100, 120, 150 °C and 10 bar of oxygen pressure.

the case of the Rh/ACe5 catalyst and from 313 to 312 in the case of Rh/ACe10 and Rh/ACe20 catalysts. All catalysts showed the peak at 308.8 eV ($3d_{5/2}$) which were assigned to the rhodium 3+ oxidation state. Concerning the $3d_{3/2}$ peak, which was associated at the 3+ oxidation state of rhodium too, we can observe that in the case of the catalyst without cerium content (Rh/A) the signal was found around 316.5 eV with a small surface area. These signals decrease from 316.5 to 313.2 eV in the case of Rh/ACe1, Rh/ACe5 and Rh/ACe20 catalysts (Fig. 3b, c and e). Nevertheless in the case of Rh/ACe10 catalyst the signal $3d_{3/2}$ decreases from 316.5 to 314 eV and their surfaces increase, explained by the fact that in cerium presence at the support surface the Rh particles changed their Rh^0 state by Rh^{3+} , phenomenon already found in the TPR analysis.

3.2. Catalytic wet air oxidation of ETBE and TAME

The results of catalytic wet air oxidation of ETBE at 100 °C and 10 bar of oxygen pressure obtained after 1 h are shown in Table 2. We can observe that the most important total organic carbon (X_{TOC}) abatement was obtained by Rh/ACe1 catalyst with a 85% of ETBE conversion. In general, the abatement of total organic carbon is enhanced with the addition of the Ce in the support with respect to Rh/A without Ce. However, at higher load of Ce a low decrease in the X_{TOC} is observed. The Rh/ACe1 catalyst also showed the higher conversion of ethyl *tert*-butyl ether (X_{ETBE}). For the Rh/A, Rh/ACe5, Rh/ACe10 and Rh/ACe20 catalysts, the conversion is similar.

The differences that exist between TOC abatement and conversion of ETBE indicate the production of intermediates formed during the oxidation, such as *tert*-butyl alcohol, which

Table 2

CWAQ of ETBE at 100 °C and 10 bar of oxygen pressure

Catalyst	Ce (wt%)	X_{TOC} (%)	X_{ETBE} (%)	CO ₂ selectivity (%)
Rh/A	0	70	79	89
Rh/ACe1	1	79	85	92
Rh/ACe5	5	78	79	98
Rh/ACe10	10	75	78	96
Rh/ACe20	20	75	81	93

is one of the main by-products of the degradation of the ETBE and that it is easier to destroy.

The results obtained from the carbon balance (Table 3) indicate that the addition and the increase in the Ce content emphasize the total organic carbon abatement as well as diminish the number of intermediates formed during CWAQ of ETBE. The catalyst Rh/ACe5 showed the minimum value to the number of intermediates and the best selectivity towards CO₂ (98%). We can observe that the low values, concerning the number of intermediates formed during CWAQ, were obtained using Rh/ACe5 and Rh/ACe10 catalysts. The differences that exist in the values of pH of one to another catalyst indicate the formation of different intermediates during the oxidation of ETBE. The intermediates formed are related with the catalyst used. Among these intermediates we can find *tert*-butyl alcohol (TBA), *tert*-butyl formate (TBF), methyl-acetate, acetone, formic acid, isobutene, and carboxylic acids which give result similar to the variations of pH [12].

In Table 4 the results obtained from the CWAQ of ETBE at 120 and 150 °C are shown. Generally, ETBE conversion was increased as the temperature increased. For all the catalyst, the Ce addition does not offer improvement in the activity at these temperatures, nevertheless the conversion was higher than 90% and the selectivity showed was around 80% in all cases. We can explain this behavior by the fact that when the conversion percentage augments, the formation of intermediates like carboxylic acids also increase and then the CO₂ selectivity decreases. It has been found that carboxylic acids are the latest intermediates formed during CWAQ of pollutants and that the acetic and formic acids are the greatest refractory compounds [13]. In other words, to destroy acetic and formic acids the CWAQ conditions are more severe, around 200 °C and 20 bar of oxygen pressure [14]. In summary the best conditions to improve the selectivity to CO₂ (98%) were obtained using Rh/ACe5 at 100 °C and 10 bar of oxygen pressure because when

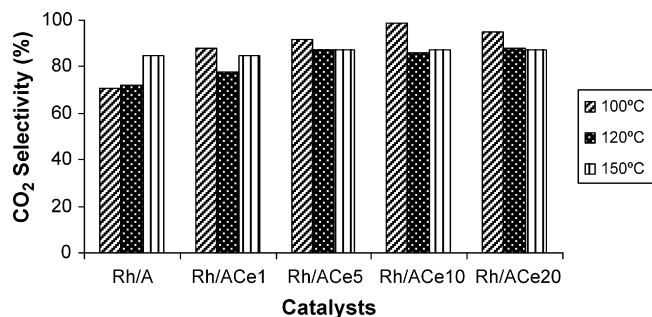


Fig. 5. Selectivity toward CO₂ after CWAQ of TAME at 100, 120, 150 °C and 10 bar of oxygen pressure.

Table 3

Carbon balance after CWAQ of ETBE at 100 °C and 10 bar of oxygen pressure

Catalyst	# C _{TOC}	# C _{ETBE}	# C _{INT.}	CO ₂ selectivity (%)	pH
Rh/A	41.8	29.9	11.9	89	6.99
Rh/ACe1	29.8	20.6	9.2	92	6.33
Rh/ACe5	31.6	29.9	1.7	98	3.73
Rh/ACe10	35.3	30.3	4.9	96	4.50
Rh/ACe20	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 at the ETBE (ppm); # C_{INT.}: number of total carbon associated at intermediates (ppm).

Table 4
CWAQ of ETBE at 120 and 150 °C and 10 bar of oxygen pressure

Catalyst	X_{ETBE} (%)		CO ₂ selectivity (%)	
	120 °C	150 °C	120 °C	150 °C
Rh/A	96	99	81	80
Rh/ACe1	92	99	83	82
Rh/ACe5	93	99	86	83
Rh/ACe10	95	99	85	85
Rh/ACe20	94	98	84	84

the temperature was increased the refractory compounds were also increased.

The conversion of CWAQ for TAME on Rh/A and Rh/ACeX catalysts with different Ce amounts after 1 h of reaction are shown in Fig. 4. The TAME conversion is increased with the temperature augment for all the catalysts. At 100 °C the conversion obtained for all the catalyst was in the range of 70–80 °C (Fig. 4). However, the selectivity toward CO₂ arises to 100% in the Rh/ACe10 catalyst at 100 °C, Fig. 5. At 120 °C, the cerium addition to the Rh catalysts the activity was improved and increased with the increase in the Ce quantity, especially for the catalyst with 5% of Ce with a percentage more than 90% was obtained. In this case the maximal CO₂ selectivity obtained was around 85% using Rh/ACe5, Rh/ACe10 and Rh/ACe20 catalysts due to the increase of the refractory intermediates compounds already explained by the CWAQ of the ETBE. At 150 °C all catalysts showed around 99% of TAME conversion with a maximal value to CO₂ selectivity around 85%.

The Ce addition creates some sites that emphasize CO₂ formation due to the fact that, this compound stabilizes Rh oxidized as Rh³⁺, the presence of this specie was observed by XPS measurements, increasing the oxidizing capacity of the catalysts. It is known that the presence of rare earth (Ce) on the support of the catalysts increases the oxidation activity, which is explained by the reoxidizing capacity of Ce between CeO₂ and CeO_{2-x} [9]. This selectivity towards CO₂ promoted by the Ce-oxidized sites is originated by the bonds (Ce⁴⁺–O²⁻–M⁺), consequently, when a greater amount of Ce promotes the formation of the Ce⁴⁺–O²⁻–M⁺ bonds [15].

The XPS results showed Rh⁰ and Rh³⁺ sites in all catalysts and that Rh³⁺ sites increase due to the cerium addition. Rh-supported catalysts can be used in the catalytic wet air oxidation process with a good activity and selectivity to CO₂.

4. Conclusions

The catalytic wet air oxidation of gasoline oxygenated additives as ETBE and TAME are favored by the Ce addition due to the formation of sites able to increase the oxidizing capacity of the Rh catalysts. Ce effect addition was explained by the Ce⁴⁺–O²⁻–M⁺ bond formation and related as the spill-over phenomena showed by TPR. By XPS technique, the presence of Rh³⁺ was detected. Rh-supported catalysts can be used in the catalytic wet air oxidation of gasoline oxygenates as ETBE and TAME which showed good activity and selectivity to CO₂.

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