Water remediation contaminated with MTBE using a catalytic oxidation process in batch reactor: influence of the cerium loading on the activity and CO₂ selectivity


ABSTRACT

Destruction of methyl tert-butyl ether (MTBE) in liquid phase and in a batch reactor was studied using ruthenium catalysts over alumina support, modified with different cerium loadings. Ce loading increment causes an increase in the particle size from 1.26 nm to 2.3 nm, enhancing the MTBE oxidation (at 150°C), and the selectivity toward CO₂. The high catalytic activity of Ru/AlCe10 is attributed to the species Ce⁴⁺−O²⁻−M that could favor the oxygen transfer between the catalyst surface and the adsorbed species by a redox mechanism. Thus, CeOₓ plays an important role in both enhancing the affinity between MTBE and catalyst during MTBE adsorption and promoting the catalytic activity for MTBE oxidation.

Key words | catalytic oxidation, CeO₂ loading, CO₂ selectivity, MTBE, Ru catalyst, water remediation

INTRODUCTION

Methyl tert-butyl ether (MTBE) is a gasoline additive used widely in the world. In Mexico, ‘Premium’ gasoline uses approximately 12% (V/V) of this additive, which has been banned in the USA by the Environmental Protection Agency since 2007 due to water pollution problems (Achten et al. 2001). Gasoline pollution can be mitigated by natural processes (Centi et al. 2002). MTBE has high water solubility and high volatility, which are a problem for aquifers and for air. The MTBE allowable limit in water is 20 µg L⁻¹ (Einarson & Mackay 2001); however, average concentrations of 5.8 and 13.3 µg m⁻³ have been found in ambient air in the nearby areas of two service stations (Vainiotalo et al. 1998) and 8.8 µg L⁻¹ in water of southern California (Brown et al. 2001). This product is also suspected to be a carcinogenic agent (Donna et al. 1999); hence, it is extremely urgent to prevent MTBE water pollution as well as to remediate the contamination it has caused.

Several techniques have been proposed for its removal, including adsorption, air stripping, sorption with granular activated carbon, chemical oxidation, ozonolysis, photolysis and catalytic wet air oxidation (CWAO). CWAO has been used in the industrial water waste treatment for degradation of a variety of dangerous molecules. The noble metals supported on Al₂O₃, TiO₂, CeO₂, and ZrO₂ offer the advantages of high activity and stability (Bhargava et al. 2006). Ceria is one of the most studied supports for preferential CO oxidation reaction (Pozdnyakova et al. 2006). As in many other catalytic applications, redox properties of ceria are considered to play a relevant role in this process (Trovarelli 2006). Ceria-based mixed oxides have been employed as promoters of alumina support.
in order to incorporate a redox active component to the preparation of catalysts and to improve the alumina’s thermal stability.

The aim of this work is to evaluate the performance of Ru catalysts in the CWAO of MTBE by modifying the cerium content in alumina. This will allow us to evaluate the performance of the catalyst in the CWAO for wastewater remediation.

**METHODOLOGY**

**Catalytic activity by CWAO process**

A CWAO reaction was carried out in a high-pressure stainless steel batch reactor (Parr Instruments). In the experiment, 150 mL of an aqueous MTBE solution (300 ppm) and catalyst (1 g L⁻¹) were poured into the reactor and then were purged with nitrogen to remove air. A glass beaker was used to avoid contact with the solution. The reactor was heated up to the desired temperature and the stirring was set at 1,000 rpm. The reaction was performed under air at 10 bar. Time zero was set after adding O₂. Samples of 1 mL were taken every 10 minutes for 1 hour. The catalysts were tested at 100, 120 and 150 °C.

The samples were analyzed by a gas chromatograph (Varian3400Cx) equipped with a flame ionization detector and a capillary column, DB-WAX 30 m × 0.53 mm id, 1.0 μm film, in order to determine the MTBE concentration. A carbon balance was calculated in order to determine the CO₂ selectivity.

**Catalytic carrier preparation**

The γ-alumina denoted as A was obtained by calcining boehmite Catapal-B. Boehmite was calcined at 650 °C under air flow (1 mL s⁻¹) for 24 h.

In addition, the γ-alumina supports modified with 1, 3, 5 and 10 wt% of CeOₓ were prepared by the impregnation method. Boehmite was added under stirring to an aqueous solution of Ce(NO₃)₃·6H₂O to form a slurry. Stirring was continued for 3 h at 30 rpm and 35 °C. After, water was removed using a rotary evaporator and the obtained solids were dried at 120 °C for 12 h. Finally they were calcined at 650 °C following the same procedure as for γ-alumina. These supports were identified as ACe1, ACe3, ACe5 and ACe10.

**Catalyst preparation**

The catalysts were prepared by the impregnation method. The support was added under stirring to a solution of n-heptane containing Ru acetylacetonate. This mixture was stirred for 3 h at 30 rpm and 35 °C. Then it was evaporated under vacuum to eliminate heptane. Finally, the solids were reduced in hydrogen flow (1 mL s⁻¹) for 4 h at 400 °C. Ru content was set to 2.5 wt%.

**Characterization of the catalytic materials**

The specific surface area (SₐBET), diameter and pore volume of the supports were determined by the BET (Brunauer-Emmett-Teller) method using a Micromeritics ASAP-2000. In order to realize the analysis a 100 mg sample was used. The support crystalline phase was determined by X-ray diffraction (XRD) using a Siemens D500 diffractometer with Cu anode and secondary beam monochromator. The compound identification was made according to the reference cards 10-0425 and 431-1002 for γ-alumina and cerianite (CeO₂), respectively.

H₂-TPR (temperature programmed reduction), H₂-TPD (temperature programmed desorption) and O₂-TPO (temperature programmed oxidation) analyses were performed on a CHEMBET-3000, using 100 mg of catalyst. The samples were degassed under nitrogen flow at 300 °C for 1 hour, then the system was cooled to 35 °C. At this temperature a 5%/H₂ balance N₂ mixture was passed through the sample. The temperature was raised at a rate of 10 °C min⁻¹. On O₂-TPO experiments, the flow rate of the 5%O₂/balance He mixture was 10 mL min⁻¹ and the heating rate was as mentioned above. Finally, the profile was recorded from room temperature to 500 °C. For the H₂-TPD analysis, H₂ chemisorption was first performed at 35 °C for 45 minutes. After, temperature was increased from 35 °C to 500 °C under nitrogen flow and TPD profile was recorded.

**RESULTS AND DISCUSSION**

**CWAO of MTBE**

CWAO of MTBE was carried out in a batch reactor to obtain more information about the behavior of the activity and the percentage selectivity toward CO₂ of the ruthenium supported catalysts. The MTBE conversion as a function of content and temperature was evaluated, as well as chemical oxygen demand (COD) conversion. The temperature effect
was investigated for 100, 120 and 150 °C under 10 bar of oxygen partial pressure in the presence of the noble metal catalyst. Figure 1 shows the MTBE conversion as a function of ceria loading and temperature, and Figure 2 shows COD as a function of previous parameters. It is seen that cerium content and temperature strongly affect MTBE conversion and the COD abatement. MTBE destruction occurs either by direct oxidation (combustion) to CO2 and water, or by catalytic decomposition to form tert-butyl alcohol, isopropyl alcohol and methanol, the latter oxidized to CO2 and water. It should be noticed that no organic products from the decomposition of MTBE were detected, neither isopropyl alcohol nor methanol. According to the published results of the work team, these typical by-products of MTBE degradation have been identified (Cervantes et al.

The modified Ru/ACe1 catalyst showed the best catalytic performance at 100 °C, while catalysts with higher CeOx content showed slightly lower conversions. This active catalyst was prepared by modifying the surface of Ru/A with CeOx in a CeOx:Ru weight ratio of 1:1. A likely explanation is that these small Ru particles keep a close connection with CeO2 clusters when the support contains 1% cerium.

Due to the good performance of the Ru/ACe1 in the reaction, catalytic behavior of catalysts with higher ceria content was investigated. The results are reported in Figure 1, where different catalytic behaviors can be observed. Thus, the addition of 3, 5, and 10 wt% of CeOx under our operating conditions (100 °C, 10 bar O2) led to similar catalytic performance as Ru/ACe1. The results showed that increasing the ceria loading above 1% reduced the activity as compared to ceria loading lower than 1%. Their low conversion is attributed to their low specific surface area and dispersion, which are shown in Table 1.

There seems to be a correlation between the catalytic activity and the ability of the metal to remain in its reduced form. Although Ce3+ and Ce4+ ions can exhibit a significant activity for CWAO in Ru/ACe1, these results showed that the catalyst activity with higher ceria contents is negligible. Cerium incorporation plays an important role in the oxidation reaction. The relation between the abundances of the oxidation states (calculated with XPS analysis) is key in the efficiency of MTBE degradation, providing superficial oxygen. This fact has been demonstrated in previous works regarding CWAO of phenol and gasoline oxygenates (MTBE, tert-amyl methyl ether, ethyl tert-butyl ether) (Cuauhtémoc et al. 2008, 2009, 2011; Monteros et al. 2015; Rocha et al. 2015).

Therefore Ru/ACe1 is an appropriate catalyst for the MTBE total oxidation. Nevertheless, ruthenium is not as noble as other VIII group metals (Pt, Pd or Rh) in oxidant environments. Ru is easily oxidized into RuO2 and into RuO3 and RuO4 at over 200 °C (Chan et al. 1997). Due to the relatively low O2 concentration in water (almost 2 g L−1 at 100 °C under 10 bar of O2), most of the Ru particles remain in their metallic form during the oxidation reaction.

Figure 1 also provides some information about the influence of temperature and CeOx wt% in the conversion. An increase in temperature leads to a higher conversion, as expected. Raising the temperature to 120 °C results in

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Ruthenium catalysts dispersion (%), particle size (nm) and BET surface area (m² g⁻¹)</th>
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<tbody>
<tr>
<td>Catalysts</td>
<td>Dispersion (%)</td>
</tr>
<tr>
<td>RuA</td>
<td>86.15</td>
</tr>
<tr>
<td>Ru/ACe1</td>
<td>93.77</td>
</tr>
<tr>
<td>Ru/ACe3</td>
<td>83.39</td>
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<tr>
<td>Ru/ACe5</td>
<td>71.95</td>
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<tr>
<td>Ru/ACe10</td>
<td>47.02</td>
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conversions higher than the ones obtained at 100 °C. The ceria content influenced the reaction as well. Conversion increased with the CeOx addition up to 80%. The optimal CeOx:Ru ratio (%wt) for this case was 5:1. When CeOx was added in a CeOx:Ru ratio of 10:1, the conversion decreased to 68%. The Ru/ACe5 catalyst is significantly more active than Ru/A. The ruthenium accessibility in the Ru/ACe5 catalyst is slightly higher than in the Ru/A catalyst. However, this small difference cannot explain the change of activity.

Moreover, ruthenium catalysts were tested in the reaction at 150 °C. Conversion is higher than the one observed with the catalyst at 120 °C. A similar but more pronounced behavior was observed at 150 °C for the Ru/ACe10 catalyst; Figure 3 shows the effect of temperature. A complete MTBE conversion was reached within 15 min of reaction. Furthermore, the conversion curves for this catalyst showed that the oxidation reaction stopped after 20 min. It is clearly demonstrated that an increase in the temperature improves the MTBE degradation considerably. In fact, MTBE completely vanished after 20 min reaction with Ru/ACe10 (150 °C), when the maximum conversion achieved for the same catalyst at 100 °C was 70% after 1 h of CWAO reaction.

The fact that all the catalysts tested for MTBE conversion were affected by temperature suggests that the CWAO reaction is highly dependent on it. Furthermore, these catalysts were highly active in the total oxidation of MTBE with molecular oxygen, and in all the reactions shown in Figure 1 the corresponding CO2 was the major detectable product. MTBE was transformed into CO2 with good yields higher than 70%. Once again, the increase in temperature led to a higher CO2 selectivity.

The liquid phase and the gas stream were evaluated by chromatography. Some organic compounds at different oxidation state were identified. However, due to the high selectivity toward CO2, the catalytic performance can be evaluated as the formation of CO2 versus time. Under the same conditions, MTBE conversion is usually higher than COD abatement because of the occurrence of intermediate compounds such as tert-butyl alcohol, isopropyl alcohol and methanol which subsequently are oxidized into CO2 and H2O (Figure 4) (Cuauhtémoc et al. 2009).

The Ce presence creates some sites that favor the formation of CO2 since it allows the ruthenium to maintain oxidation states different from zero, capable of increasing the oxidative capacity of the catalysts. It is known that the presence of rare earths (CeO2) in the support increases the oxidation property that results from the ability of CeO2 to cycle between CeO2 and CeO2-x (Zhang et al. 1996). This selectivity towards CO2 promoted by Ce is caused by species Ce4+−O2−−M+. Therefore, a greater amount of CeO2 promotes the formation of the species Ce4+−O2−−M+; then the CO2 amount is increased even more if the catalyst activity decreases (Hosokawa et al. 2005). Furthermore it has been observed that if there is a highly dispersed metal on the surface in an oxidized state, the formation of CO2 is increased, because it inhibits the formation of carboxylic acids such as acetic acid, known as the most refractory of this family of acids (Barbier et al. 1998).

**Chemical oxygen demand**

The abatement of COD obtained at 100, 120 and 150 °C is shown in Figure 2. At 100 °C it is observed that the effect of cerium on COD is negligible. This remains constant between 35 and 40%, probably because of the difficulty of
the formed products to be completely oxidized at this low temperature.

An increase of the COD abatement was observed at 120 °C and a higher activity for Ru/ACe5 is shown. After this, ceria-loading activity decreases and it is similar to that obtained with Ru/A. The cerium oxides could favor the oxygen transfer between the MTBE solution and the adsorbed species by a redox mechanism, which increases the carbon species oxidation, targeting the reaction toward the CO2 formation.

The increase in the COD abatement values is also observed at 150 °C. At this temperature the Ru/ACe5 catalyst showed 91% abatement, which is the highest. This behavior is probably due to the ability of the cerium to enhance the oxidation of pollutants, improving oxygen exchange in the catalyst surface, the conversion and selectivity toward CO2. Moreover the formation of refractory compounds is reduced.

Temperature programed oxidation of the catalysts after use in CWAO of MTBE

The results of oxygen consumption and catalytic performance showed that for fresh catalyst samples, no oxygen consumption takes place during TPO within the temperature gap 30–650 °C. Moreover the results showed that the oxidation rate (Figure 5), even when it is high at the beginning of the reaction, diminishes dramatically after a few minutes. This cannot be explained only considering the decrease of MTBE concentration nor by the by-products accumulation, more resistant to oxidation. Probably the combination of both enhances the catalyst deactivation; some by-products promote the carbonaceous deposit on the catalyst surface and cause its deactivation.

In this section, a comparative characterization of fresh and used catalysts for CWAO reaction was conducted by a technique usually employed in steam reforming catalyst deactivation: TPO. The oxygen consumption is measured by the formation of CO2. The ruthenium catalyst TPO profile showed one large CO2 peak with a maximum at 400 °C. The peak at 400 °C suggests that the most difficult carbonaceous deposit to remove is formed on the surface of catalyst with no cerium content. The overall combustion peak can be roughly broken down into two symmetrical Gaussian peaks, indicating that there are different types of carbon deposits. The first peak was assigned to carbon species oxidized by ruthenium. This is an indicator of the metallic function participation in the catalyst in the combustion process. The second peak is characteristic for carbon oxidation over the alumina support (Augustine et al. 1989).

In contrast, as indicated in Figure 5, the carbonaceous deposit formed over the Ru/ACe10 catalyst was lower, showing that these carbon species are more easily oxidized than the ones formed by Ru/A catalyst. The oxidation profiles show that in ruthenium catalysts with no cerium content, there are, at least, two kinds of carbon deposits, which are oxidized at different temperatures. The deposits were located on the Ru surface, and others on the cerium surface were found too. In fact, according to Pieck et al. (1989), even with a single reactant and one-site catalyst, different kinds of coke may be formed and can exhibit different reactivities toward gases such as hydrogen, oxygen or steam. As is shown in Figure 5, the oxygen surface concentrations suggest that most of the surface carbon species are located over alumina, which explains the TPO profile.

X-ray diffraction characterization

The crystalline phases presented in samples, calcined by air, were determined by XRD analysis. The XRD patterns of the supports are displayed in Figure 6. In this work modified γ-alumina was obtained with CeOx (denoted as ACeOx). The CeOx addition led to differences in surface area and in XRD spectra between the γ-alumina (A) and ACeOx. The diffractograms show that gamma phase is formed. (Figure 6). In cerium oxide-rich samples, the dominant diffraction peaks are cerianite, characteristic of CeO2 from ACeOx. CeOx planes overlapped with alumina, especially for RuACe10 support, where the CeOx signal is greater. A decrease in alumina peak intensity is due to the increase of cerium oxide concentration in the support, indicating that the specific surface of the alumina decreases as a
function of the cerium oxide load. After ceria oxide impregnation on boehmite, the observed main peaks at 28.6°, 33.1°, 47.5°, and 56.3° can be attributed to the cerianite single phase. The additional features at 37.3° and 66.9° are characteristic of the alumina support.

At low cerium content no cerium oxide phase was detected by XRD. This may be due either to the formation of Al–Ce oxide ‘solid solutions’ with spinel structure or to the occurrence of amorphous cerium oxide. Moreover in cerium oxide-rich catalysts, with the increase of cerium oxide, some peaks of spinel alumina move. This shift indicates that part of the cerianite species enters into the alumina lattice, promotes the contraction of its unit cell and creates solid solutions with Al-O-Ce oxide conformation with spinel alumina structure.

It must be pointed out that a progressive shift of the diffraction peaks to higher Bragg angles was observed in Ce-rich catalysts, which is due to the insertion of Ce ions into the alumina lattice, and also to Al-O-Ce ‘solid solutions’ conformation with cerianite structure.

**BET surface area**

Table 1 shows the specific area for ruthenium catalysts supported on alumina and alumina–ceria. The catalyst’s BET surface area decreases with the higher cerium content addition (Table 1). This can be explained by the introduction of cerium oxide into the alumina lattice during the impregnation process.

The Ru/γ-Al₂O₃-CeO₂ solid with the highest CeO₂ content (10 wt%) shows the lowest BET surface area (163 m² g⁻¹); at this cerium oxide content, it is probable that CeO₂ is segregated on the γ-Al₂O₃ surface, promoting the blockage of some alumina porous and therefore causing a reduction in BET surface area. Moreover some CeOₓ isolated crystals could be formed, not interacting with the rest of the support.

**Temperature programmed desorption**

Different highly dispersed 2.5 wt% Ru/ACeOₓ catalysts were prepared by the impregnation method at different cerium content and then treated in a reductor medium (H₂, 10 mL min⁻¹, 3 h) as is shown in Table 1. It was found that the dispersion of the active phase ruthenium decreases through the effect of CeOₓ content (Table 1). This Ru dispersion was between 97% and 47%. Nevertheless Ru/ACe1 dispersion is greater than that of Ru/A. For higher CeOₓ content, the dispersion is lower than the one obtained for RuA. This same behavior is observed in the size of metal particles, (Table 1), where the increase from 1.16 nm for Ru/ACe1 to 2.31 nm for Ru/ACe10 is correlated with the increase in CeOₓ content.

**Temperature programmed reduction**

The H₂-TPR profiles of the Ru/A and Ru/ACeOₓ catalysts are shown in Figure 7. Hydrogen consumption can be observed at low temperature within the range from 28 to 80 °C for all the catalysts. This peak could correspond to the reduction of Ru²⁺.

Figure 6 | XRD patterns of the supports: (a) Al₂O₃, (b) Al₂O₃-CeO₂ (1 wt%), (c) Al₂O₃-CeO₂ (3 wt%), (d) Al₂O₃-CeO₂ (5 wt%), (e) Al₂O₃-CeO₂ (10 wt%).

Figure 7 | H₂-TPR profiles of the ruthenium supported catalysts.
The catalysts containing cerium showed variations of the hydrogen consumption. There is a second reduction temperature at 140 °C attributed to the reduction of Ru\(^{3+}\). Catalysts with 3 and 5 wt% of cerium show a shift of reduction temperature probably due to strong Ru- Ce interactions. The Ru/ACe10 catalyst’s TPR profile shows a shoulder at 162 °C which could correspond to the reduction of an oxidized ruthenium species or to the interphase Ru-Ce caused by ruthenium crystallites surrounded by cerium atoms. Furthermore, CeO\(_2\) reduction in alumina changes in relation to pure cerium oxide, due to Ce-Al interactions (Kamonsuangkasem et al. 2017). This type of interaction promotes a surface oxygen increase, which is eliminated by reduction at temperatures around 300 °C (Shyu et al. 1988). In this sense, only the samples RuAlCe5 and RuAlCe5 showed a reduction close to the above-mentioned temperature; therefore, only those two samples exhibited a higher concentration of surface oxygen.

CONCLUSIONS

The Ru/ACeOx supported catalysts efficiently promote the catalytic decomposition of MTBE at a temperature range of 100–150 °C. These materials catalyze their degradation to tert-butyl alcohol and methanol, which could be fast biodegraded by microorganisms. Isopropyl alcohol, tert-butyl alcohol and methanol are the only products in this process.

At 100 °C ruthenium supported over alumina with 1 wt% of Ce (ACe1) was the best active catalyst for MTBE oxidation in aqueous media. At 120 °C the most active was Ru/ACe5 and finally at 150 °C, the Ru/ACe10 catalyst is the most efficient one, which reveals that these materials could be applied as catalysts for remediation of water contaminated with MTBE. The catalysts with 3 and 5 wt% of Ce presented a higher surface oxygen concentration, increasing the efficiency in MTBE degradation.

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