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Chapter

Nonconventional Wastewater Treatment for the Degradation of Fuel Oxygenated (MTBE, ETBE, and TAME)

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Abstract

Catalytic wet air oxidation (CWAO) is a nonconventional wastewater treatment, consisting of oxygen pressure releasing inside a reactor in order to degrade organic compounds dissolved in water, using a solid catalyst in the presence of an activated O_2 species, usually at temperatures ranges of 125–250°C and pressures of 10–50 bar. CWAO can reduce operating costs of conventional treatment due to the use of ideal catalyst that is able to improve reaction conditions at temperatures and pressures as mild as possible, simultaneously setting high catalytic activity and long-term stability of heterogeneous catalysts. Oxygenated fuels are gasoline additives in reformulated gasoline and oxyfuels. In the beginning, they provided an alternative solution of environmental problems, such as greenhouse gas emissions and octane enhancement, caused by fossil fuel use. The oxygenated fuels frequently used are methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and tert-amyl methyl ether (TAME). However, there is environmental impact from oxygenated fuel hydrocarbons related to widespread contamination of groundwater and other natural waters. Our research group developed a wide study in order to evaluate several catalysts (Ru, Au, Cu, and Ag supported on Al_2O_3, Al_2O_3-CeO_2, and TiO_2-CeO_2) and to obtain the best for the efficiency of the oxidation process.

Keywords: nanoparticles, wastewater, CWAO, fuel oxygenated

1. Introduction

1.1 Oxygenated fuels

Oxygenated fuels are oxygen-rich compounds such as alcoholic and ether fuels that act as gasoline additives in reformulated gasoline and oxyfuels. Oxygenates can be

blended into gasoline in two forms: alcohols (such as methanol or ethanol) or ethers. They have potential to provide an alternative solution of environmental problems caused by fossil fuel use. The oxygenated ether fuels used more frequently are methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and tert-amyl methyl ether (TAME), although the first fuel oxygenate used in reformulation was MTBE. The use of MTBE as an octane enhancer in the United States began in 1979 [1, 2].

MTBE is a compound (chemical formula $C_5H_{12}O$) that is synthetized by the chemical reaction of methanol and isobutylene, and it is almost exclusively used as a fuel additive in motor gasoline. Although ETBE and TAME have only secondary importance in production industry, recently they have become more prevalent, and they can be used instead of MTBE. In France, MTBE has been partially replaced by the ETBE since 1990 or as part of a "binary or ternary mixture" with MTBE [3–5].

ETBE (chemical formula $C_6H_{14}O$) is considered an attractive octane enhancer as it presents a lower reid vapor pressure (RVP) mixture and lower water solubility than MTBE and ethanol. The azeotropic mixture of ETBE with ethanol takes down the volatility of ethanol making it suitable as an additive for automatic gasoline [6, 7].

Finally, TAME (chemical formula $C_6H_{14}O$) was considered as an oxygenated fuel until the 1990s despite its octane rating lower than other oxygenated fuels; besides it is very soluble with other ethers, and it is highly soluble in water (12 g/l) [8, 9].

1.2 Importance of oxygenated fuels in petroleum industry

The leading produced fuel in the world is gasoline. Because of its widespread use and the fact that it is composed of that fraction of crude oil with lower boiling points, gasoline is the single largest source of volatile hydrocarbons to the environment. Motor gasoline comes in various blends with properties that affect engine performance. All motor gasolines are made of relatively volatile components of crude oil. Other fuels include distillate fuel oil (diesel fuel and heating oil), jet fuel, residual fuel oil, kerosene, aviation gasoline, and petroleum coke. In the petroleum refining process, heat distillation is used first to separate different hydrocarbon components. The lighter products are liquefied petroleum gases and gasoline, whereas the heavier products include heavy gas oils. Liquefied petroleum gases include ethane, ethylene, propane, propylene, n-butane, butylenes, and isobutane. Internal combustion engines of high compression ratio require gasoline with octane ratings that are sufficiently high to ensure efficient combustion [2, 10, 11].

Gasolines need additives that increase their octane rating so they can decrease their self-knock capacity, increasing their resistance to compression, and finally improve the quality of gasoline. An economical way of achieving these properties has been the use of anti-knock additives, such as tetraethyl and tetramethyl lead at concentrations up to 0.84 g/l. With the phasing out of lead from gasoline because it was increasingly recognized that lead is toxic and non-biodegradable, oxygenated fuel become a better alternative for gasoline additive, instead of lead. Oxygenated fuels act as octane enhancers, bringing the additional benefit of making gasoline burn almost completely. Actually, using oxygenated fuels in internal combustion engine leads to a reduction of greenhouse gas (GHG) emissions, compared to gasoline because they burn cleaner than regular gasoline and produce lesser carbon monoxide (CO) and nitrogen oxides (NOx) and they reduce emissions of unburned hydrocarbons. Furthermore, using oxygenated fuels in an internal combustion engine (ICE) provides an alternative to conventional fuels that can solve many environmental problems [6, 12, 13].

In the United States, air quality regulations placed on automobile exhaust gases have forced dramatic changes in gasoline formulations. By 1990, the Clean Air Act Amendments (CAAA) required additives, such as MTBE at 15% and ethanol, to be

blended in gasoline in some metropolitan areas, heavily polluted by carbon monoxide, and to reduce carbon monoxide and ozone concentrations [14].

1.3 Environmental impact of oxygenated fuels

Despite providing better conditions in terms of fuel quality, an environmental impact from oxygenated fuel hydrocarbons related to widespread contamination of groundwater and other natural waters exists. The distribution and storage of crude oil and refined products result in releases of significant amounts of hydrocarbons to the atmosphere, surface waters, soils, and groundwater. Groundwater contamination by crude oil, and other petroleum-based liquids, is a particularly widespread problem. In Mexico, the agency in charge of producing and distributing fuels derived from petroleum distillation, such as gasoline, diesel, fuel oil, diesel, and LP gas, is Petróleos Mexicanos (PEMEX). The retail distribution of gasoline and diesel is carried out by service stations (gas stations). One of the environmental risks that involves the handling of these stations is spills or leaks of fuels, which cause the contamination of the sites where the storage tanks are located [15].

Unfortunately, these oxygenates have high water solubility and high volatility, causing a high concentration of oxygenated fuel in the environment, air, and water. Another important problem happens when oxygenated fuel is accumulated in the groundwater due to it not absorbing appreciably to soil and undergoing only in slow biodegradation compared to the benzene, toluene, ethylbenzene, and the xylenes (BTEX) in gasoline. The relatively recalcitrant nature of oxygenated fuel to microbial attack makes them persistent, due to them being refractory to the biological treatments. Because of the chemical structure of these, oxygenated fuel hinders their natural biodegradation, which contains a combination of two biorecalcitrant organic functional groups: the ether bond and tertiary carbon atom. These are the reasons why water supplies close to the production sites of MTBE, ETBE, and TAME or near underground petroleum storage tanks and fuelling stations are often contaminated by large amounts of these compounds [16, 17].

There have been extensive occurrences of groundwater contamination by MTBE in the United States because of its prevailing use. In a sampling study of 1208 domestic wells in the United States, MTBE was the most frequently detected fuel oxygenate and the eighth most commonly detected VOC. Perhaps the most publicized case of MTBE contamination of groundwater is the one involving public water supply wells in Santa Monica, California. In August 1995, the city of Santa Monica discovered MTBE in wells used for drinking water supply through routine analytical testing of well water [18, 19].

MTBE has been detected in snow, storm water, surface water (streams, rivers, and reservoirs), groundwater, and drinking water, based on limited surveillance operations conducted in the United States. MTBE concentrations found in storm water ranged from 0.02 to 8.7 μg/l, with a median value of less than 1.0 μg/l. In streams, rivers, and reservoirs, the detection range was 0.2–30 μg/l, and the range of median values in several studies was from 0.24 to 7.75 μg/l [5, 19].

In fact, the US Environmental Protection Agency (USEPA) included MTBE in its Contaminant Candidate List. MTBE in drinking water is carcinogenic for humans and animals. USEPA established a drinking water health advisory of 20–40 μg/l MTBE in December 1997, because it is hazardous to human health (US Environmental Protection Agency, 1997).

Although alternative ether oxygenates are detected less frequently than MTBE, these alternative oxygenates show future groundwater contaminations similar to MTBE if they are not under control.

The toxicokinetic data on MTBE in people come mainly from controlled studies of healthy adult volunteers and in a population exposed to oxygenated gasoline. MTBE quickly passes into circulation after inhalation exposure. In healthy volunteers exposed to inhalation, MTBE kinetics was linear up to concentrations of 268 mg/m^3 (75 ppm). It was measured in the blood and urine of people exposed to tertiary butyl alcohol, metabolic MTBE. The maximum blood concentrations of tertiary butyl alcohol were 17.2–1144 μg/m^3 and 7.8–925 μg/m^3, respectively, in people exposed between 5.0 and 178.5 mg/m^3 (1.4–50 ppm) of MTBE. Based on a single-behavior model, rapid (36–90 min) and slow (19 h) components of MTBE half-life were identified (41). Following the introduction of two separate fuel programs in the United States, which require the use of gasoline oxygenation products, consumers in some areas have complained of acute health disorders, such as headaches, irritation of the eyes and nose, cough, nausea, dizziness, and disorientation. The acute experimental toxicity (CL_{50}) of MTBE in fish, amphibians, and crustaceans is greater than 100 mg/l.

WAO consists of an oxidation in aqueous medium at high temperatures using pure oxygen or high pressure air as an oxidant to maintain the liquid phase. The pressures used and reported in the literature range from 20 to 200 bar and temperature between 150 and 350°C, making this process highly expensive for industrial application. The use of catalysts allows reducing the temperature and pressure conditions for oxidation and even increasing the selectivity toward CO_2. That is why we employ catalytic wet air oxidation, instead of WAO. CWAO of MTBE and oxygenated fuels of gasoline as ETBE and TAME is a nonconventional treatment for degradation of organic compounds in aqueous medium. Our research group developed a wide study in order to evaluate several catalysts and to know what the best are for the efficiency of oxidation process and the total mineralization of pollutants into CO_2 and H_2O.

2. Synthesis, characterization, and catalytic activity of noble (Ru, Au, Ag) and based (Cu) metal nanoparticles supported applied in the CWAO of fuel oxygenated

2.1 Synthesis of Al_2O_3 and Al_2O_3-CeO_2 by wet impregnation and precursor calcination

The synthesis methods occupied for the production of supported catalysts include different techniques or procedures based on a phenomenon of precipitation, chemical adsorption, hydrolysis-polymerization, etc. These methods can synthesize supported catalysts in a single step, or in two steps, that is, both the precursor salt of the support and the active phase are added in the reaction mixture in a single step; otherwise, in sequential or two steps, first the support is synthesized, usually an oxide, and then the active phase, usually a metal, is prepared by some other specific method, expecting all the metal to be added and adsorbed on the support, without metal loss and with a high metal dispersion [20, 21].

These methods determine important properties such as homogeneous metal dispersion, high specific surface area, adequate acidity/basicity ratio, metal-support interaction, and generation of structural defects, for example, oxygen vacancies and reducibility; an improvement in the catalytic performance is concluded owing to the development of these properties in the synthesized catalysts [22, 23]. So in this, study we evaluated different synthesis methods for the catalysts tested in CWAO from oxygenated fuels.

The γ-alumina was obtained by the calcination of boehmite Catapal-B (AIO(OH)), in this process an amount of boehmite (AIO(OH)) is deposited in a

fixed-bed quartz reactor in which a continuous flow of air of 1 cm^3/s is passed, and then the calcination is carried out, at a temperature of 650°C for 4 h.

Wet impregnation method was used to prepare the Al_2O_3-CeO_2 support. Ceria is incorporated into the boehmite (AIO(OH)) with an aqueous solution of $Ce(NO_3)_3.6H_2O$ (necessary amount of salt to obtain 1, 3, 5, 7.5, and 10% weight) in 100 ml of distilled water. The precursor solution of ceria is previously deposited in a ball flask, the boehmite is added to this solution and left to stir for 3 h in a rotary evaporator, and then the solution is dried with constant agitation at 60°C to evaporate the water excess. After impregnation, the obtained solid sample was dried at 120°C for about 16 h and calcined at a temperature of 650°C in air flow of 1 cm^3/s for 4 h. The CeO_2 support was obtained commercially.

2.2 Synthesis of noble and base metal catalysts by wet impregnation

The solid catalysts reported in the literature that are used in the oxidation of water pollutants can be classified into four groups: supported metal oxides, unsupported metal oxides, supported metals, and mixtures of noble metals and metal oxides. The type of supported metal is composed mainly of noble and base metals. These are also very important to influence catalyst activity. Noble metals such as Ag, Au, Ru, Pd, Rh, and Pt are very active elements for oxidation reactions; they reveal high activities and excellence stability; however, their high cost and limited availability can decrease their applicability. Base catalysts such as Ni and Cu are more interesting systems, and a lot of research is being done to improve their stability because by having a lower cost, compared to noble metals, they are an economical option; they are also active, but less stable, and suffer from carbon deposit and metal leaching [24, 25].

Cu catalysts supported on Al_2O_3 were synthesized by wet impregnation in a single step. A calculated amount of copper nitrate to obtain a concentration by weight of 5, 10 and 15wt% in copper plus an adequate amount of boehmite Catapal-B were dissolved in 100 ml of water; then the solution was adjusted to a pH of 1, with the addition of a drop of HNO_3, and stirred for 4 h, regulating the temperature from 70 to 90°C. After impregnation, the obtained solid sample was dried at 120°C for about 12 h and calcined at a temperature of 400°C in airflow of 1 cm^3/s for 4 h. Cu (5wt%)/Al_2O_3, Cu (10wt%)/Al_2O_3, and Cu (15wt%)/Al_2O_3 are the monometallic Cu catalysts supported in alumina, synthesized by wet impregnation method in a single step, which later we will name as Cu_5AlIH, Cu_{10}AlIH, and Cu_{15}AlIH.

Copper catalysts supported on Al_2O_3 were also synthesized by sol-gel in a single step. An aqueous solution of 10 ml of aluminum trisecbutoxide ($[C_2H_5CH(CH_3)O]_3Al$), 97% aldrich, d = 0.96 g/mol with 4 g of urea and copper nitrate adequate amount in grams for the percentages of 5, 10, and 15wt% in 1-butanol was progressively added, between 70 and 90°C to a mixture of water and butanol, under constant stirring. After 24 h reflux at 70°C, the resulting pseudo-gel was dried in in a rotating evaporator at 120°C for 12 h and then calcined at 400°C for 4 h. It is worth mentioning that a catalyst was prepared with a pyrrolidine additive instead of urea, exclusively with the same quantities of reagents as the 15wt% in Cu. The synthesized monometallic catalysts will be named as Cu_5AlSG, Cu_{10}AlSG, Cu_{15}AlSG, and Cu_{15}AlSGp.

Finally, the monometallic Cu/Al_2O_3 catalysts were synthesized by wet impregnation with urea and with a concentration by weight of 5, 10, and 15wt% of the metal. A calculated amount of boehmite Catapal-B was dissolved in 300 ml of deionized water; then the solution was adjusted to a pH of 3 with the addition of 1 ml of HNO_3 and stirred for 2 h. After that, 200 ml of a solution of cupric nitrate [$Cu(NO_3)_2$ ½H_2O] and urea is added dropwise to the solution of boehmite Catapal-B, regulating the temperature from 70 to 90°C. After impregnation, the obtained solid

sample was washed three times with hot water and dried at 120°C, and finally it was calcined at a temperature of 400°C for 4 h. It should be noted that a catalyst was prepared with a pyrrolidine additive instead of urea, exclusively with the same amounts of reagents as the 15wt% in Cu. The synthesized monometallic catalysts will be named as Cu_5AlIHU, Cu_{10}AlIHU, Cu_{15}AlIHU, and Cu_{15}AlIHp.

Ru-supported catalysts were prepared by wet impregnation method of Al_2O_3 and Al_2O_3-CeO_2 supports aggregating the appropriated amounts of an aqueous solution containing $RuCl_3$* XH_2O to obtain a nominal concentration of 2wt% of Ru, adding 100 ml of hydrochloric acid 0.1 M. First Al_2O_3 and Al_2O_3-CeO_2 (1.0, 3.0, 5.0, 7.5, and 10wt% of Ce) support was wetted by distilled water in a beaker in order to have high dispersion and to maximize the mass transfer of added metal salt ($RuCl_3$* XH_2O) on the surface and the pores of the catalyst. The resulting solution is stirred for 1 h; after that it is heated at 60°C. The samples were dried at 120°C for 24 h and then calcined under air flow (60 ml/min) at 650°C for 4 h, with a heat rate of 2°C/min. Finally, the catalysts were reduced under H_2 (60 ml/min) at 400°C for 5 h, with a heat rate of 2°C/min. The synthesized monometallic catalysts will be named as RuAlIH, RuAlCe_1IH, RuAlCe_3IH, RuAlCe_5IH, RuAl$Ce_{7.5}$IH, and RuAlCe_{10}IH.

2.3 Synthesis of noble and base metal catalysts by deposition-precipitation

Deposition of gold into the modified supports was carried out by the method of deposition-precipitation using urea according to the procedure described below. Support powder (Al_2O_3, CeO_2, Al_2O_3-CeO_2 (1wt%), Al_2O_3-CeO_2 (5wt%), Al_2O_3-CeO_2 (10wt%) was first dispersed in distilled water. The temperature of the suspension was kept constant at 80°C and agitated with a magnetic stirrer. Secondly, the requisite quantity of chloroauric acid ($HAuCl_4$) solution was added to the suspension, and the temperature was let to stabilize. Thirdly, 2.33 g of urea was added into the reactor vessel, and the suspension was stirred continuously for 16 h. The deposition was followed by centrifugation of the catalyst suspension in 50 ml tubes. The centrifugation was conducted three times. Separated water was decanted away, and the tube was refilled with distilled water after the first and the second centrifugations. Posterior the following separation and washing, the solid was collected and moved to a rotary evaporator and dried at 60°C in a water bath under vacuum. Final drying was done in an oven at 120°C overnight. All catalysts were calcined in air flow by heating them from room temperature up to 300°C for 4 h. The synthesized monometallic catalysts will be named as AuAlDPU, AuCeDPU, AuAlCe_1DPU, AuAlCe_5DPU, and AuAlCe_{10}DPU.

The supported Ag nanoparticles were synthesized by DP with NaOH. The procedure was the same as the described for the gold synthesis by DP with urea, only that, instead of urea, NaOH was occupied, regulating solution's pH to 9. The synthesized monometallic catalysts will be named as AgCeDPNa, AgAlDPNa, AgAlCe_1DPNa, AgAlCe_3DPNa, AgAlCe_5DPNa, AgAl$Ce_{7.5}$DPNa, and AgAlCe_{10}DPNa. All the catalysts prepared are mentioned in **Table 1**.

2.4 Characterization of noble (Ru, Au, Ag) and base (Cu) metal nanoparticles supported

Figure 1 shows the adsorption isotherms of the synthesized materials of RuAlIH and RuAlCe_1IH. It was observed that both isotherms are of type IV, which were associated with capillary condensation in mesoporous catalysts, where the hysteresis loops indicated that the pores are well distributed.

For the catalysts of RuAlIH and RuAlCe_1IH (the other TPR analyzes the rest of the catalysts not shown), **Figure 2** which displayed a main peak of 36–52°C was

Catalyst abbreviation	Synthesis method						Target molecule		
	One step			Two step					
	Wet impregnation	Sol-gel	Wet impregnation with urea	Wet impregnation	Deposit-precipitation With urea	Deposit-precipitation With NaOH	MTBE	ETBE	TAME
Cu_5AlIH	X							x	x
$Cu_{10}AlIH$	X							x	x
$C_{15}AlIH$	X							x	x
Cu_5AlSG,		x						x	x
$Cu_{10}AlSG$		x						x	x
$Cu_{15}AlSG$		x						x	x
$Cu_{15}AlSGp$		x						x	x
Cu_5AlIHU			x					x	x
$Cu_{10}AlIHU$			x					x	x
$Cu_{15}AlIHU$			x					x	x
$Cu_{15}AlIHp$			x					x	x
RuAlIH				x			x		
$RuAlCe_1IH$				x			x		
$RuAlCe_3IH$				x			x		
$RuAlCe_5IH$				x			x		
$RuAlCe_{7.5}IH$				x			x		
$RuAlCe_{10}IH$				x			x		
AuAlDPU					x		x		x
AuCeDPU					x		x		x

Catalyst abbreviation	Synthesis method						Target molecule		
	One step			Two step					
	Wet impregnation	Sol-gel	Wet impregnation with urea	Wet impregnation	Deposit-precipitation With urea	Deposit-precipitation With NaOH	MTBE	ETBE	TAME
$AuAlCe_1DPU$					x		x		x
$AuAlCe_3DPU$					x		x		x
$AuAlCe_5DPU$					x		x		x
$AuAlCe_{10}DPU$					x		x		x
AgCeDPNa						x	x		
AgAlDPNa						x	x		
$AgAlCe_1DPNa$						x	x		
$AgAlCe_3DPNa$						x	x		
$AgAlCe_5DPNa$						x	x		
$AgAlCe_{7.5}DPNa$						x	x		
$AgAlCe_{10}DPNa$						x	x		

Table 1.
Lists the Cu, Ag, Au, and Ru catalysts supported on Al_2O_3, CeO_2, and Al_2O_3-CeO_2, tested in CWAO of fuel oxygenated (FO) with the operating conditions: T = 100°C, P(O_2) = 10 bar, VLiq = 0.25 l, CFO = 1000 mg/l, CCat = 1 g/l, and ω = 1000 rpm.

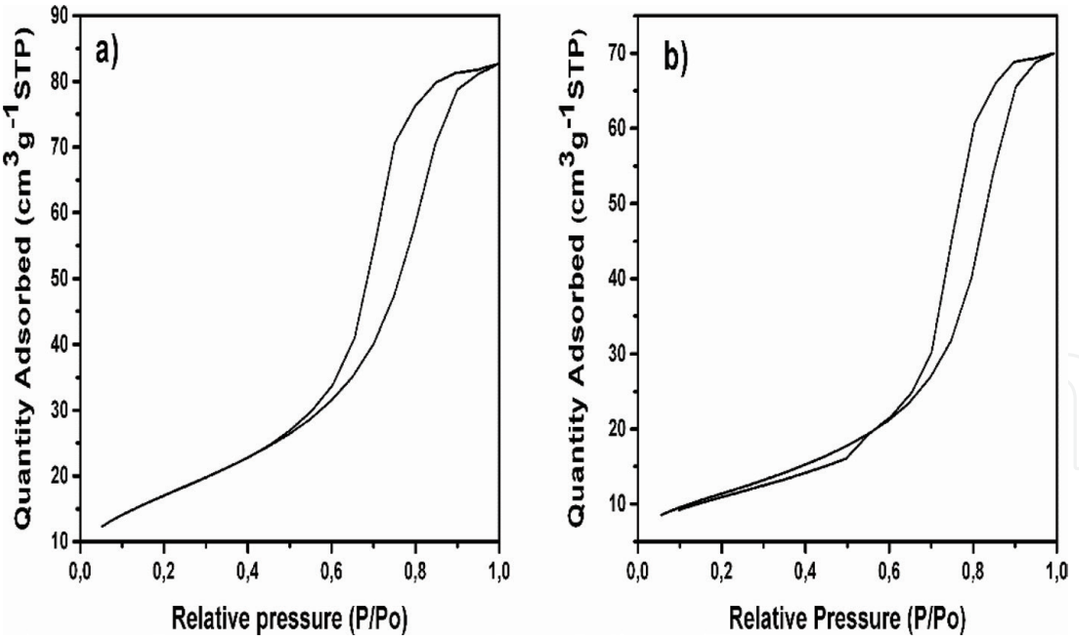


Figure 1.
Adsorption isotherms of (a) RuAlIH and (b) RuAlCe₁IH.

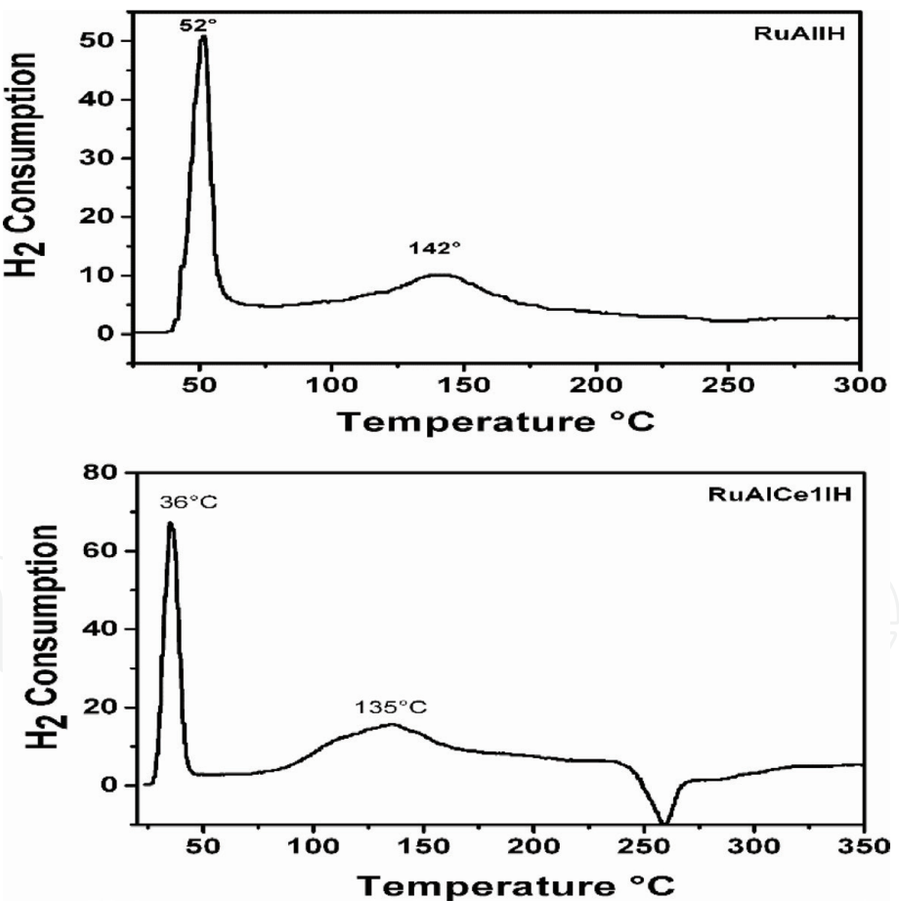


Figure 2.
H_2-TPR profiles of the catalysts RuAlIH and RuAlCe₁IH.

observed which indicates that the reduction is carried out in that first peak, and it was attributed to the oxidation change of Ru from +2 to 0 (RuO) since it was the species that was reduced first. The second signal observed at 135–142°C was attributed to ruthenium oxide (RuO_2), with an oxidation state of +4 which passes from +4 to +2 and subsequently to 0. On the other hand, the two peaks clearly observed in **Figure 2**

indicated that the ions of Ru existed in two different states to be reduced with hydrogen, meaning that at the end of the reduction, only the states +2 and 0 remain.

Figure 3 corresponds to the diffraction patterns of the catalysts containing Au. It showed only signals corresponding to Al_2O_3 and CeO_2, and only a decrease of the alumina signal was observed when the content of Al_2O_3-CeO_2 increases by 10%. The corresponding Au signals were not shown in this diffractogram due to the weight % in which the catalysts were prepared, and in XRD only the metal was observed at concentrations higher than 2 and sometimes 3%.

In **Figure 4**, the H_2-TPR profiles of the Au-supported catalysts revealed that the first reduction peaks (around 50°C) appearing for all Au-supported catalysts corresponded to the highly dispersed Au peaks on the catalyst surface. This signal increased to values higher than 50°C in the case of the Au catalyst deposited in Ce which indicates a difference in the size of the particles (observed by TEM). The second peak (around 100°C) was attributed to a second oxidation state of Au that interacts with Ce. This signal increased with the Ce content. This can be supported since in the AuAlDPU catalyst, this signal did not appear; however, it appeared in the AuCeDPU catalyst.

Figure 5 shows the XRD for the copper catalysts prepared by wet impregnation method, in which γ-Al_2O_3 phase was seen as well as the intense signals that indicated the presence of CuO, and the boehmite, indicating that the metal was correctly dispersed in the three synthesized catalysts.

2.5. Catalytic evaluation (MTBE, ETBE, TAME)

2.5.1 Reaction conditions

The activity level tests of the catalysts synthesized in this study were carried out in a Parr batch 300 ml batch reactor, under the conditions of 100°C, 10 bar, and 1000 ppm of fuel oxygenated. In the standard procedure for a CWAO experiment,

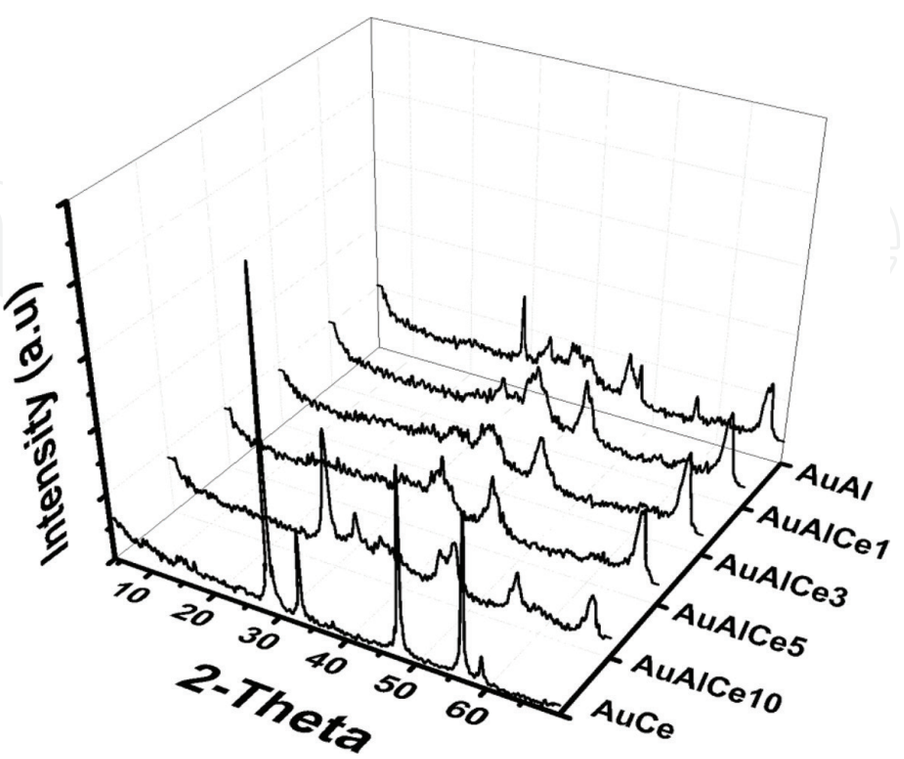


Figure 3.
X-ray diffraction patterns of Au-supported catalysts.

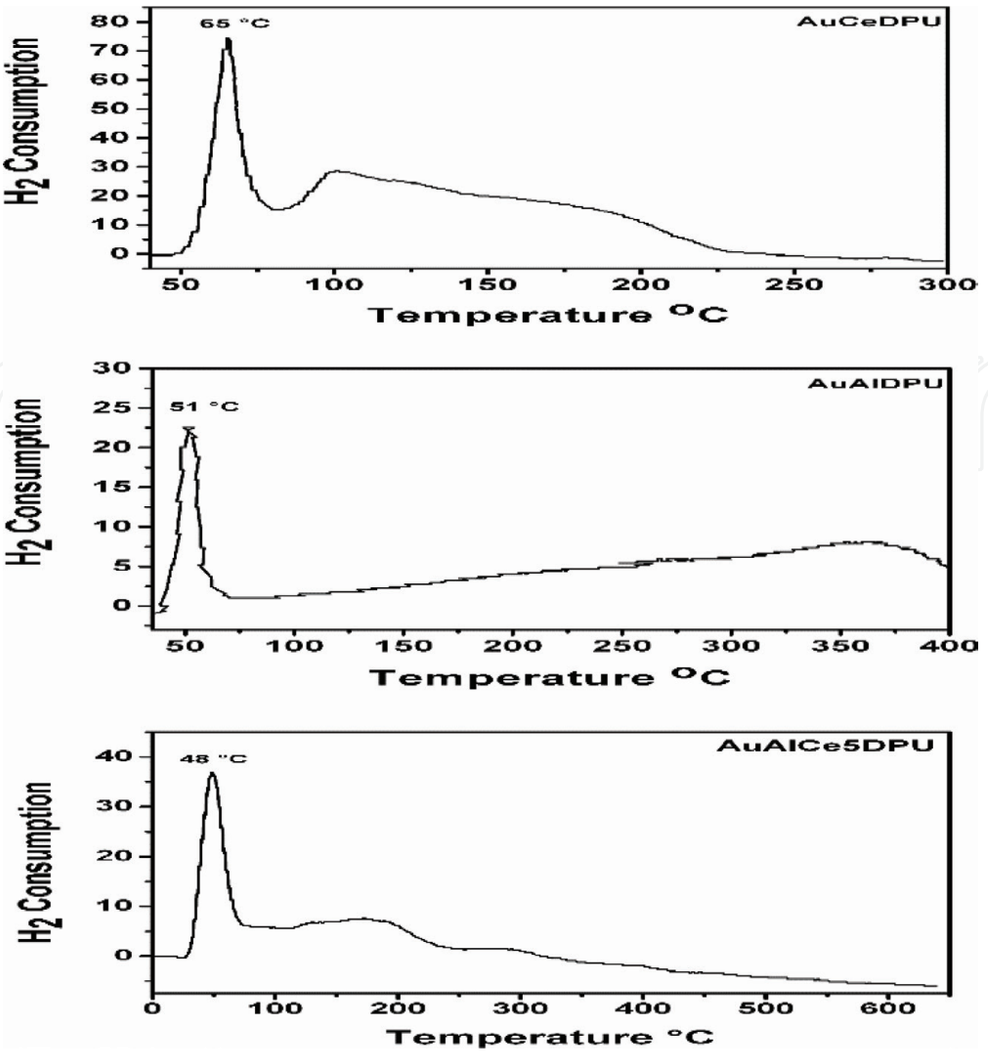


Figure 4.
H_2-TPR of Au-supported catalysts.

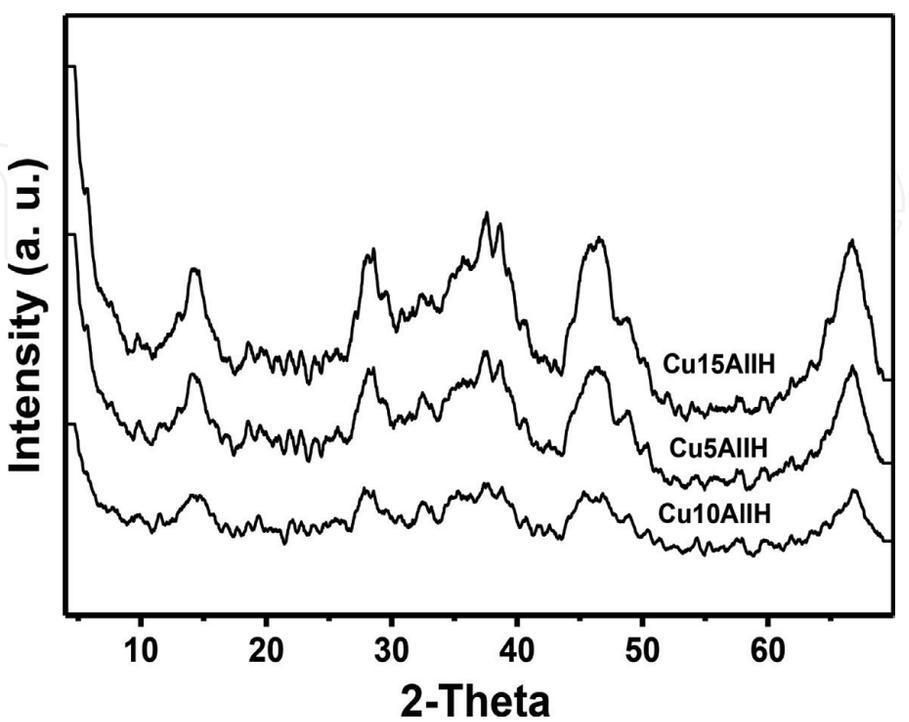


Figure 5.
X-ray diffraction patterns for the Cu-supported catalysts synthesized by wet impregnation in a single step.

250 ml of fuel oxygenated solution were poured, and 0.25 g of catalyst were placed in the 300 ml reactor. When the selected temperature was reached, stirring was started at a maximum speed of 1000 rpm. This time was taken as the zero reaction time and the reaction duration was 60 min. These conditions were the same for all synthesized materials. The liquid samples were periodically removed from the reactor, then filtered to remove any catalyst particles, and finally analyzed by gas chromatography and total organic carbon (TOC).

With the following equation, the conversion values for total organic carbon and FO were determined at different times with intervals of 30 min up to 180 min of reaction:

$$X_{TOC} = \frac{TOC^0 - TOC^{60}}{TOC^0} \times 100 \quad (1)$$

$$X_{FO} = \frac{C_0 - C_{60}}{C_0} \times 100\% \quad (2)$$

where TOC^0 is *TOC* at t = 0 (ppm), C_0 is *FO* concentration at t = 0 (ppm), C_{60} is *FO* concentration at t = 1 h of reaction (ppm), and TOC^{60} is *TOC* at t = 1 h of reaction (ppm).

The initial rate (*ri*) was calculated from *FO* conversion depending on time, using the following equation:

$$r_i = \left(\frac{\Delta_{FO}(\%)}{\Delta t\, m_{cat}}\right)([contaminant]_i) \quad (3)$$

where $\frac{\Delta_{FO}(\%)}{\Delta t}$ is the initial slope of the conversion curve, $[contaminant]_i$ = initial *FO* concentration, and m_{cat} = catalyst mass (g_{cat}/l).

So the selectivity was calculated according to the following equation:

$$S_{CO_2} = \frac{X_{TOC}}{X_{FO}} \times 100 \quad (4)$$

2.5.2. Degradation of MTBE by catalytic wet air oxidation over noble and base metals

This research studied the degradation of the fuel oxygenated MTBE through CWAO occupying Ru, Au, and Ag as the catalysts, which will be responsible for mineralizing the pollutant.

Figure 6 shows the results of the catalytic activity for CWAO of MTBE with the sets of catalysts Ru, Au, and Ag. The best activity for the set of ruthenium-supported catalysts was for the one named $RuAlCe_1IH$, since it presented a 68% conversion of MTBE and a 63% degradation of TOC; the most favorable results for this particular catalyst were attributed to a particle size of 9 nm measured by TEM, and to the contribution of ceria, due to the oxygen storage capacity phenomenon. Ceria is known for having the capacity to exchange oxygen, through its vacancies of oxygen, which promotes the increase of selectivity in all cases with the Ru-synthesized catalysts from a chlorinated salt, by the formation of a species of type $Ce^{4+} - O^{2-} - M^{+}$, contributing to improve the reducibility of ruthenium.

With respect to the Au-supported catalysts, $AuAlCe_5DPU$ was the one that stood out for its catalytic performance in comparison to the rest of its counterparts. $AuAlCe_5DPU$ reached a maximum of 73% MTBE conversion and a TOC degradation of 72%, indicating that this catalyst was efficient both to have a good

conversion and to transform to CO_2. This behavior was explained by the fact of presenting the best distribution of particles on the surface of the catalyst, according to the TEM analysis, and confirmed by TPR. The largest amount of active particles for this catalyst was below 2 nm. It was observed that the other catalysts had a similar activity attributable to the distribution of particle sizes ranging between 2 and 10 nm. According to the performed analysis, well-dispersed Au nanoparticles and the oxidation state of Au play an important role in this type of oxide-reduction reactions. The excess of CeO_2 does not allow a good selectivity toward CO_2 since it interferes in the exchange of O_2 at the time of oxidation, giving an excess of oxygen that causes the metal particle to change its oxidation state on the surface of the catalyst and confirming the theory made by Imamura et al. [26] that a balance of metal particles in oxidized and reduced state is needed to obtain satisfactory results in terms of activity and selectivity; this theory is fulfilled in molecules that are strongly adsorbed on the surface of the catalyst such as acetic acid, and according to this study, this principle can be also applied with MTBE.

The results of the catalytic activity for CWAO of MTBE for the set of silver catalysts indicated that the best conversion obtained corresponds to the AgCeDPNa catalyst with 66%, due to the presence of CeO_2. In this case, we can only mention an effect of CeO_2 because the particle sizes obtained by HRTEM and TPD-CO revealed different distributions but did not significantly impact the catalytic activity. This effect has been explained by several researchers as the formation of a bridge M-O-Ce where M means silver metal. The AgCeDPNa catalyst was the one that has a better behavior toward mineralizing CO_2 due to the oxide-reducing properties of this support. However, it was observed that the catalyst with 5% of CeO_2 has a very close TOC value with respect to the AgCeDPNa catalyst. In this case, the effect between the particle size, the activity, and the selectivity toward CO_2 was not possible to distinguish because, as the HRTEM histograms showed, the range of sizes was

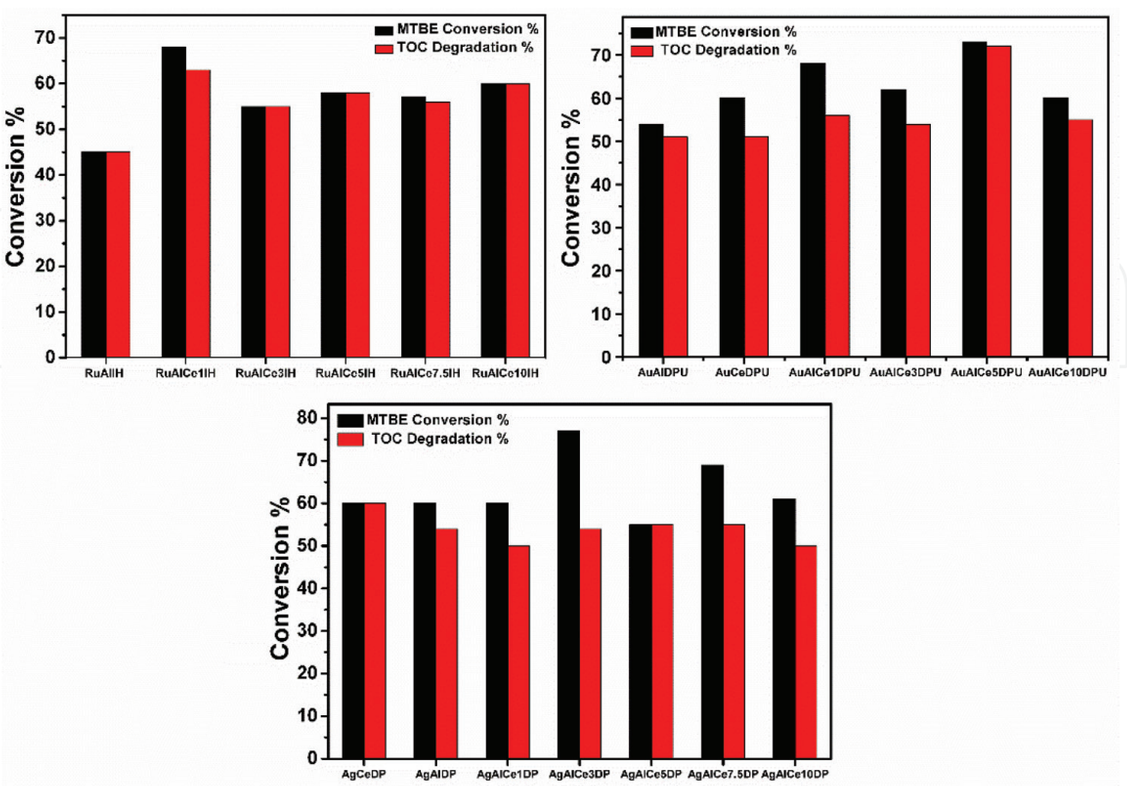


Figure 6.
MTBE conversion and TOC degradation, at 100°C and 10 oxygen bar over Ru-, Au-, and Ag-supported catalysts.

very broad in all cases; nonetheless, the effect of CeO_2 appeared in the activity and also in the selectivity. Imamura proposed a theory stating that a balance of metal particles in oxidized and reduced state is needed to obtain satisfactory results in terms of activity and selectivity, which is observed here by TPR of H_2 in the case of AgCeDPNa catalyst; Ag particles remain oxidized even with the passage of H_2 which makes them more selective toward CO_2. It is not possible in this case to account for the proportion of Ag^+/AgO particles because this can only be done by XPS, a very expensive technique and not available in this case; however, it can be concluded that, in terms of activity, the optimal catalyst is the one that only contains ceria.

2.5.3. Degradation of ETBE by catalytic wet air oxidation over noble and base metals

We also analyzed the degradation process of the ETBE molecule through CWAO using Cu synthesized by three different synthesis methods, with the main characteristic of being carried out in a single step. The aim of the application of these methods is to avoid the leaching of the metal, which has occurred in other previous experiments by different investigators, after having passed a certain time of the reaction.

The analysis results of the ETBE-treated solutions by CWAO are presented in **Table 2**; for each of the three synthesis methods of the Cu catalysts, Cu_{10}AlSG and Cu_{10}AlIHU catalysts were more active, obtaining 88 and 89% ETBE conversion, respectively, after 1 h of oxidation. But the highest values for TOC degradation were obtained with the catalysts prepared by sol-gel method, as Cu_5AlSG reached 84% and Cu_{10}AlSG 89%. This last result confirmed that Cu catalysts synthesized by sol-gel are more effective catalysts for the mineralization process, which allows to degrade the organic matter, coming from the contaminant present, by almost 90% until obtaining CO_2 in the treated solutions. In addition, we can affirm that the optimum percentage of Cu was 10%, as well as the commercial catalyst used for this type of reactions and reported in the literature.

Another discovery in this study with copper nanoparticles was realized by measuring copper concentration through atomic absorption in the ETBE-treated solutions, since no copper concentrations were obtained, particularly in the catalysts prepared by sol-gel method, opposite situation for the other catalysts prepared

Catalyst	ETBE conversion %	% TOC	SCO_2
Cu_5AlIH	76	81	100
Cu_{10}AlIH	66	82	100
C_{15}AlIH	72	80	100
Cu_5AlSG	82	84	100
Cu_{10}AlSG	88	89	100
Cu_{15}AlSG	80	78	97
Cu_{15}AlSGp	78	74	95
Cu_5AlIHU	71	59	83
Cu_{10}AlIHU	89	79	89
Cu_{15}AlIHU	86	81	94
Cu_{15}AlIHp	80	69	86

Table 2.
ETBE conversion, TOC and SCO_2 at 100°C and 10 bar of pressure during 1 h of reaction with one of $[ETBE]_o$ = 1000 ppm.

by wet impregnation and wet impregnation with urea. Therefore, we can encapsulate the copper in the alumina, by sol-gel method, thus avoiding contamination by the metal, leaching, and, in turn, obtaining an improvement in the catalytic performance of the metal.

2.5.4. Degradation of TAME by catalytic wet air oxidation over noble and base metals

Another series of experiments was conducted under the same conditions described below over Cu synthetized in three different methods and Au-supported catalyst but in this experiments with TAME as a target molecule by CWAO.

Table 3 presents the analysis results of the treated solutions of TAME by CWAO; for each of the three synthesis methods of the Cu catalysts, the catalysts of Cu_{15}AlSG and Cu_{10}AlIHU were more active, obtaining 78% of TAME conversion, for both catalysts after 1 h of reaction. But the highest values for TOC degradation were obtained with the catalysts prepared by sol-gel method; Cu_{15}AlSG reached 78% and Cu_{10}AlIHU 75%. These results sustained that the Cu catalysts synthesized by sol-gel were more effective catalysts for TAME mineralization process, which allows them to degrade the organic matter, coming from the existing contaminant, by almost 80% in the treated solutions.

The results of the catalytic activity for TAME CWAO in Au-supported catalysts are shown in **Figure 7**. It was observed that the best activity happened with the catalyst at AuAlCe_{10}DPU with 80% conversion of TAME, although all the remaining catalysts showed good activity except for the catalyst with AuAlCe_1DPU; this could be explained by the fact that this molecule may not be very sensitive to particle size due to its structure.

Figure 7 also shows the abatement of TOC of the supported Au catalysts; as can be seen the best carbon transformation toward CO_2 was obtained for the AuAlCe_3DPU catalyst, with a 77% conversion, and for the AuCeDPU catalyst with 80%, although all the remaining catalysts showed a remarkable performance, without exceeding these, except for AuAlCe_1DPU.

Table 4 shows the selectivity to CO_2, and we can say that the supported Au catalysts containing Ce 5 and 10% were the least selective to CO_2. This is because there is

Catalyst	TAME conversion %	TOC	SCO_2
Cu_5AlIH	72	68	93
Cu_{10}AlIH	68	61	89
C_{15}AlIH	77	75	98
Cu_5AlSG	73	68	94
Cu_{10}AlSG	72	68	95
Cu_{15}AlSG	78	78	100
Cu_{15}AlSGp	70	41	59
Cu_5AlIHU	49	64	100
Cu_{10}AlIHU	78	75	95
Cu_{15}AlIHU	66	62	95
Cu_{15}AlIHp	69	34	50

Table 3.
TAME conversion, TOC degradation, and SCO_2 at 100°C and 10 bar of pressure during 1 h of reaction with one of $[TAME]_0$ = 1000 ppm.

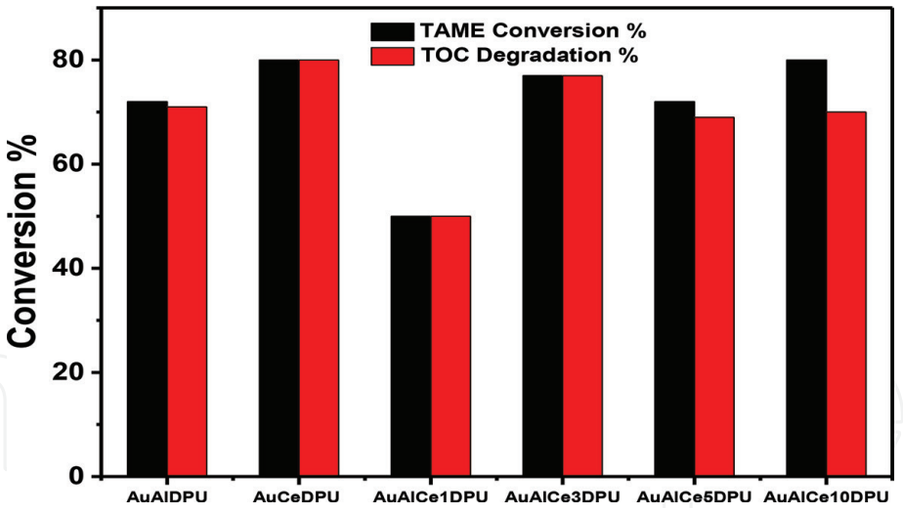


Figure 7.
TAME conversion and TOC degradation % at 100°C and 10 bar over Au-supported catalysts.

Catalysts	SCO_2
AuAlDPU	99
AuCeDPU	100
$AuAlCe_1DPU$	100
$AuAlCe_3DPU$	100
$AuAlCe_5DPU$	96
$AuAlCe_{10}DPU$	88

Table 4.
TAME selectivity at 100°C over Au-supported catalysts.

a poisoning by CeO_2 that affects the selectivity when it is in excess due to the interaction of M-Ce-O; this case shows that the optimal percentage of CeO_2 for the TAME is 3%. It is important to note that the $AuAlCe_3DPU$ catalyst is equally active and selective to the AuCeDPU catalyst, so the alumina-ceria support with low concentrations of CeO_2 is presented as an alternative for the wet oxidation process of TAME.

3. Conclusions

This study concludes that the catalytic activity for MTBE oxidation of catalysts Ru, Au, and Ag, supported on Al_2O_3, CeO_2, and Al_2O_3-CeO_2, synthesized by wet impregnation methods and DP with NaOH and urea, in two steps, is classified as follows:

$$AuAlCe_5\,DPU > RuAlCe_1\,IH > AgCeDPNa \quad (5)$$

In addition, the catalytic activity for the oxidation of target molecule ETBE on Cu catalysts supported on Al_2O_3, synthesized by three different methods in a single step, is classified as follows:

$$Cu_{10}\,AlSG > Cu_{10}\,AlIH > Cu_{15}\,AlIHU \quad (6)$$

The catalytic activity for TAME oxidation using Copper catalysts supported on Al_2O_3, synthesized by three different methods in a single step and Au supported on

Al_2O_3, CeO_2 and Al_2O_3-CeO_2 synthesized by DP with urea in two steps, is classified as follows:

$$AuCeDPU > Cu_{15}AlSG > AuAlCe_3DPU > Cu_{10}AlIHU = Cu_{15}AlIH \quad (7)$$

Acknowledgements

Authors thank the National Council for Science and Technology (CONACYT) for financing the project 132648; thanks to the Universidad Juárez Autónoma de Tabasco for PFCE-DACB project and PRODEP program.

Conflict of interest

Authors declare no conflicts of interest.

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