

# Catalytic Wet Air Oxidation of Methyl tert-Butyl Ether (MTBE) using Gold supported catalysts prepared by deposition-precipitation method

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## Introduction

Methyl tert-Butyl Ether is the most important additive oxygenates used in gasoline [1]. Actually in Mexico, Premium gasoline use 12v/v% of MTBE. In several countries MTBE have been found in lakes, rivers, groundwater and atmosphere because this compound is highly volatile and soluble in water [2]. It have been established that ether gasoline oxygenates are very resistant to be oxidized by biological process. Recently, this pollutant was treated by Catalytic Wet Air Oxidation using rhodium catalysts with a high selectivity to CO<sub>2</sub> [3]. Consequently, another catalysts have been tested on the CWAO of gasoline oxygenates. Among of these catalysts the gold supported prepared by deposition-precipitation (DP) method which have been used previously on the CWAO of the succinic acid [4]. Two catalysts were tested in this case, Au/TiO<sub>2</sub> with 5 wt% and 8 wt% respectively. A series of news Au catalysts with 2 wt% metal amount were synthesized and characterized in order to be used in this reaction.

## Materials and Methods

Au catalysts were prepared using DP method using Urea [5], which consists in TiO<sub>2</sub> (Degussa P25, BET area approximately of 40 m<sup>2</sup>/g) diluted into HAuCl<sub>4</sub> solution (pH comprise between 7 and 8, set by Urea addition). Normally, the temperature of work is fixed at 80°C and the time contact of this suspension diverges between 1 and 16 hours. After, the precipitate is separated by centrifugation and then washed with distilled water preheated at 50°C during various periods in order to eliminate the impurities. Subsequently, the catalysts obtained were calcinated under air flow heating slowly at 2 °C/min until 300°C during 4 hours, in order to obtain well dispersed particles, associated with a good activity in oxidation reactions [6]. Firstly two catalysts were prepared, as mentioned above, and tested on the CWAO of MTBE. An aqueous solution of MTBE (1000 ppm) was prepared and put in a glass recipient in order to prevent the corrosion problems caused by the formation of carboxylic acids during the reaction. The temperatures used were 100, 120 and 150°C and the Oxygen pressure was set at 10 bar. After results obtained, a new series of 6 catalysts with a 2 wt% metal amount, were prepared using TiO<sub>2</sub>, TiO<sub>2</sub>-CeO<sub>2</sub> and CeO<sub>2</sub> supports prepared by sol-gel method in order to be used in the CWAO of MTBE; only results characterization are presented here.

## Results and Discussion

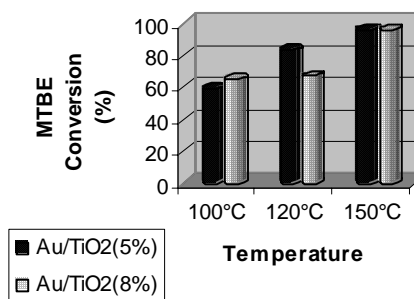
Au catalysts showed a good performance on the CWAO of MTBE. It can be seen in the fig 1 that only temperature effects were found because both catalysts showed practically the same behavior after 1 hour of test. The only difference observed was the CO<sub>2</sub> selectivity which diminish when the temperature increase. This phenomenon can be explained by the well dispersion particles on the TiO<sub>2</sub> surface which improve a good activity and CO<sub>2</sub> selectivity of these catalysts. Small particles comprises between 1 and 2 nm were observed by HRTEM in both cases, effect of the thermal treatments. In summary the metal amount does not have an effect significant on the catalytic activity because nanoparticles were obtained in both cases. After these conclusions, another series of catalysts were prepared. The metal quantity was lowest and set at 2 wt%. Cerium was incorporated to TiO<sub>2</sub> because their oxidation capacity. It can be seen in the table 1 that the incorporation of cerium to TiO<sub>2</sub> augments the BET surface of supports awaiting around 100% in the case of the 10 wt % Ce. Analysis of ray X diffraction (see fig. 3) showed that only anatase phase was formed and Au signals were found. The quantity of metal deposited on the support was evaluated by ICP and the results obtained showed the performance of the method used because practically all the metal was placed on the support, which exemplify one more time the performance of DP Urea method.

**Table 1. BET areas of supports and gold content of catalysts after deposition-precipitation on the supports.**

Supports	Cerium wt%	BET area (m <sup>2</sup> /g)	Pore diameter (Å)	Catalysts With Au 2 wt%	% Au by ICP
TiO <sub>2</sub>	0	63.77	33.02	Au/TiO <sub>2</sub>	2.0046
TiO <sub>2</sub> -Ce2.5	2.5	71.29	53.82	Au/TiO <sub>2</sub> Ce2.5	1.9965
TiO <sub>2</sub> -Ce5	5.0	117.05	58.34	Au/TiO <sub>2</sub> Ce5	2.1704
TiO <sub>2</sub> -Ce7.5	7.5	ND	ND	Au/TiO <sub>2</sub> Ce7.5	1.9875
TiO <sub>2</sub> -Ce10	10	137.53	68.93	Au/TiO <sub>2</sub> Ce10	2.1146
CeO <sub>2</sub>	100	101.22		CeO <sub>2</sub>	ND

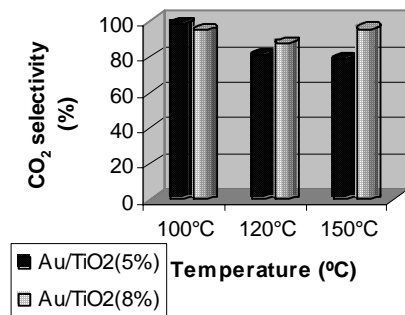
## Significance

This work has a basic significance concerning the development of the new catalysts to be applied in the CWAO of gasoline oxygenates.

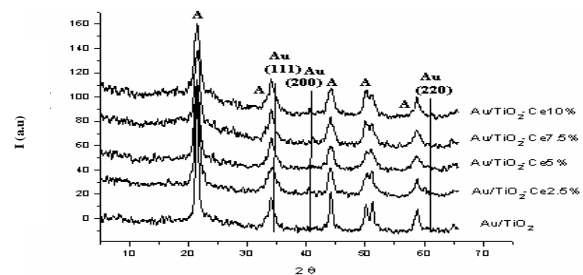


**Figure 1.** MTBE conversion after 1 hour of oxidation reaction using gold catalysts. [MTBE]=1000 ppm, PO<sub>2</sub>= 10 bar.

**Figure 2.** Selectivity's towards to CO<sub>2</sub>, after 1 hour of oxidation reaction using gold catalysts. [MTBE]=1000 ppm, PO<sub>2</sub>= 10 bar.



**Figure 3.** DRX spectrums of gold catalysts.



#### References

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