

Synthesis and characterization of Au/Al₂O₃-CeO₂ catalysts prepared by deposition-precipitation (DP) method: use on the Catalytic Wet Air Oxidation of gasoline oxygenates

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Introduction

The problem of the pollution reduction of the aqueous streams containing refractory organic chemicals dissolved is of great importance, especially in productive sectors of industry. These effluents cannot be treated through conventional processes of biological oxidation, because of they have a little biodegradability and the substances contained present an inhibitor effect. The process currently used is the wet oxidation which requires high pressures and temperatures, and consequently high cost. An interesting alternative is the catalytic wet air oxidation. Catalytic wet air oxidation (CWAO) is a technique able to destroy pollutants [1]. The major advantage of this method of treatment is the high mineralisation (conversion to CO₂) of organic pollutants into effluents. The catalyst permits a significant reduction of the temperatures and the necessary pressures and improves the economy of the process. Catalysts employed are noble metals, in various supports. The aim of this work is evaluate the Au/Al₂O₃ and Au/Al₂O₃-CeO₂ catalysts performance to destroy MTBE and TAME. MTBE and TAME are the most important additives oxygenates used in gasoline [2]. In several countries MTBE have been found in lakes, rivers, groundwater and atmosphere because this compound is highly volatile and soluble in water [3]. Recently, gasoline oxygenates (ETBE and TAME) were treated by Catalytic Wet Air Oxidation using rhodium catalysts with a high selectivity to CO₂ [4].

Materials and Methods

Au supported catalysts were prepared using DP method using Urea [5], which consists in Al₂O₃, CeO₂ and Al₂O₃-CeO₂ (between 1-10wt% of Cerium) diluted into H₂SO₄ solution (pH comprise between 7 and 8, set by Urea addition). 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]. All catalysts were characterized by BET Areas, X-ray diffraction, TEM, SEM, H₂-TPR and Uv-Vis with diffuse reflectance. Reactions of Catalytic Wet Air Oxidation of gasoline oxygenates (MTBE and TAME) were carried out in a Parr reactor. Aqueous solutions of MTBE and TAME (1000 ppm) were 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 temperature used was 100°C and the Oxygen pressure was set at 10 bar.

Results and Discussion

Six catalysts were tested in this case, Au/CeO₂, Au/Al₂O₃ and Au/Al₂O₃-CeO₂ with 1.5 wt%. Results showed that small particles of Au were deposited into support (1.2-10 nm). It can be

observed that Urea increase the BET area of the Al₂O₃-CeO₂ supports by cerium redistribution particles at the surface because namely when the Ce was auditioned to alumina in others works, the BET surface decreased [4]. Tests reactions showed that, in the case of CWAO of MTBE the best activity and selectivity to CO₂ was obtained using Au/Al₂O₃-CeO₂ with 5%wt of cerium. In the case of TAME the best conversion was obtained using Au/Al₂O₃-CeO₂(10) catalyst ,but the best selectivity was obtained with Au/Al₂O₃-CeO₂(3) and Au/Al₂O₃ catalysts. In both cases Ce additions to support increase the conversion, explained by the oxidation/reduction capacity of Ce which improved the oxidation phenomena in the catalytic oxidation reactions. The results showed in the table 1, revealed that small particles improve the CO₂ selectivity in both cases consequence of the oxidation state of gold. In the case of CO gas oxidation many authors suggest that both Au⁰ and Au⁺⁺ and the oxide support all have a role to playing the catalysis of CO oxidation. It is also well established that the presence of small gold nanoparticles interacting with the support is particularly important, since it dictates the nature of the interface at which the reaction is assumed to take place [7]. In our case after TPR analysis, it was found that the interaction of metal-support increase whit the quantity of cerium. The oxidation state was completely Au⁰ on the alumina support in the H₂ presence and for the other catalysts the oxidation states were Au⁰ and Au⁺⁺. In conclusion, the catalytic activity of gold, in liquid phase increase when a mixture of oxidation Au/Au⁺⁺ state are present on the surface, same case found by CO oxidation. Gold catalysts prepared by DP are good alternative to be used in CWAO of gasoline oxygenates.

Table 1. BET surface area, pore diameter, particle size, oxygenate conversion and CO₂ selectivity of gold catalysts at 100°C and 10 bar of oxygen pressure, [oxygenate]=1000 ppm.

Catalysts	% Ce	BET surface m ² /g	Pore diameter (nm)	Particle size by TEM (nm)	MTBE Conversion (%)	CO ₂ selectivity (%)	TAME Conversion (%)	CO ₂ selectivity (%)
Au/Al ₂ O ₃ -CeO ₂ (1)	1	110.9	20	3.18	65	83	72	98
Au/Al ₂ O ₃ -CeO ₂ (3)	3	108.6	20	6.89	62	87	75	99
Au/Al ₂ O ₃ -CeO ₂ (5)	5	103.7	20	1.38	75	98	72	88
Au/Al ₂ O ₃ -CeO ₂ (10)	10	97.0	19	4.74	60	93	80	87
Au/Al ₂ O ₃	0	106.0	20	2.50	55	94	60	99
Au/CeO ₂	100	61.0	---	4.52	61	85	78	97

Significance

This work has a basic significance concerning the development of the new gold catalysts whit a high activity and selectivity to CO₂, which can be applied in the catalytic wet air oxidation of pollutants as gasoline oxygenates.

References

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