

Gold on modified activated carbons: influence of the support surface chemistry on the glycerol oxidation.

Elodie Rodrigues^{1*}, Manuel Pereira¹, Xiaowei Chen², Juan Delgado² and José Órfão¹

¹ Laboratório de Catálise e Materiais (LCM), Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Porto, 4200-465, Portugal

² Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cadiz, Cadiz, 11510, Spain.

*elodie.rodrigues@fe.up.pt

Introduction

The production of biodiesel has been continuously increasing in Europe and US over the last 10 years and consequently the glycerol market is experiencing a surplus since this compound is obtained by 10 wt% of total biodiesel production. Liquid phase catalytic oxidation is a promising route to the valorisation of glycerol by its conversion into useful compounds, provided that catalysts used are sufficiently active and selective for the formation of compounds such as glyceric acid (GLYCEA) and/or dihydroxyacetone (DIHA), potentially useful as chemical intermediates in the fine chemicals industry [1-2]. Nano-sized gold particles supported on different carbon materials are active for the oxidation of glycerol but show very different performances. In spite of its well known influence on the catalyst activity, the role of the support in the mechanism of the reaction is still not clear.

The main goal of this work is the study of the relationship between the surface chemical characteristics of activated carbon and the performance of the respective gold supported catalysts in the selective oxidation of glycerol.

Experimental

A NORIT ROX 0.8 activated carbon was used as starting material for this study (sample AC₀). This sample was submitted to a liquid phase oxidation treatment with HNO₃ 6 M to increase the amount of oxygen-containing surface groups on the support (sample AC₁).

Support AC₁ was treated under nitrogen flow for 30 min at different temperatures (400, 600 or 900 °C) followed by a treatment under dry air flow at room temperature for 1 h. Therefore, the following samples are respectively prepared: AC_{1tt400}, AC_{1tt600}, AC_{1tt900}. These thermal treatments selectively remove the oxygen-containing surface groups, previously introduced in the treatment with HNO₃, by thermal degradation.

Gold on carbon catalysts were prepared by the sol immobilisation method with NaBH₄ as reducing agent.

Catalytic test reactions were carried out in an autoclave ($V_{\text{total}} = 195$ mL, $C_{\text{glycerol}} = 0.3$ mol/L, NaOH/glycerol molar ratio = 2, catalyst = 700 mg, $P_{\text{O}_2} = 3$ bar, $T = 60$ °C). Analyses of products and unconverted reactant were performed by HPLC. The supports were characterized by N₂ adsorption at -196 °C and by temperature programmed desorption (TPD). The noble metal loading of the samples was determined by inductively coupled plasma (ICP) analysis and the average metal particles size by high-resolution transmission electron microscopy (HRTEM).

Results/Discussion

Since no drastic changes were observed in the textural properties of the supports, in gold particle sizes (≈ 6 nm) and in metal loadings ($\approx 0.6\%$) of the catalysts, the discrepancies in performances observed in Figure 1 must be related almost exclusively to the differences in support chemical properties. The catalytic performance gradually increases with the removal of the oxygenated groups of the support. Basic oxygen-free supports, characterized by a high density of free π -electrons, lead to an enhancement of the gold activity. The prepared catalysts lead to a high total selectivity (about 80%) to products of commercial interest (GLYCEA + DIHA).

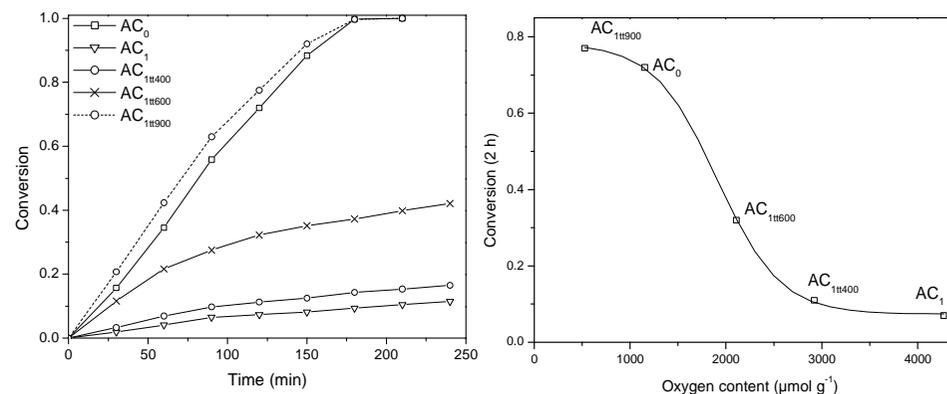


Figure 1. Influence of the modified activated carbon supports on the performance of Au/AC catalysts. Kinetic data (at left) and glycerol conversion after 2 h of reaction vs. total oxygen content (at right).

References.

1. C. Zhou, J. Beltramini, Y. Fan and G. Lu, *Chem. Soc. Rev.*, **115**, 527 (2008)
2. A. Behr, J. Eilting, K. Irawadi, J. Leschinski, and F. Lindner, *Green Chemistry*, **10**, 13 (2008)