Effect of alumina on the aerobic oxidation of primary (benzyl alcohol) and secondary (hydroxymatairesinol) alcohols over gold-supported catalysts

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Introduction

Supported gold nanoparticles (Au NPs) are considered to be promising catalysts for the various reactions of fine chemistry due to their high selectivity and low prone to leaching [1]. Recently, it was found high activity of Au NPs supported on alumina in the aerobic oxidation of secondary alcohol (naturally occurring lignan hydroxymatairesinol (HMR)) to oxidomatairesinol (oxoMAT), which exhibits high superoxide scavenging activity [2]. It was shown that acidity of alumina affects significantly the oxidation of HMR.

The present work is dedicated to the comparative analysis of aerobic oxidation of alcohols with different structure (benzyl alcohol and hydroxymatairesinol) on Au NPs supported on alumina with different morphology and acidity.

![Scheme 1. Structure of benzyl alcohol and hydroxymatairesinol in two isomeric forms (HMR1 and HMR2).](image)

Materials and Methods

Gold (3 wt. % Au) was supported on alumina support by deposition-precipitation with HAuCl₄ and urea. Two types of alumina were used as support: i) commercial alumina (Al-com) from Alfa-Aesar and ii) nanostructured alumina (Al-SG) synthesized by the sol-gel method using organo-metallic precursors as in [2]. Before catalytic test catalysts were pre-reduced in hydrogen at 350°C. Obtained gold samples were studied by N₂ adsorption, XRD, TEM, XPS Au 4f, UV-vis and FTIR of pyridine adsorbed. The catalytic activity of gold catalysts was tested at 110 °C and 10 atm of oxygen in the one-pot oxidative esterification of benzyl alcohol in alkali free methanol solutions in the absence of any base additive. Aerobic selective oxidation of HMR to oxoMAT was carried out in a stirred 200 ml glass reactor at 70 °C and atmospheric pressure.

Results and Discussion

In spite of similar size of Au NPs for Au/Al-com and Au/Al-SG catalysts their activity in the studied reactions was different. In the aerobic oxidation of benzyl alcohol the highest activity was found for Au NPs supported on Al-com support, while activity of both catalysts were comparable in the aerobic oxidation of hydroxymatairesinol. The less acidic alumina favors the oxidation of primary alcohol. Alumina acidity does not affect significantly the oxidation of relatively large HMR molecule. However, in the latter reaction Au/Al-com with small pores deactivated faster than Au/Al-SG characterized with large pores.

![Fig. 1. Catalytic activity (in TON values after 1 h) in the aerobic oxidation of benzyl alcohol and hydroxymatairesinol (in TOF values after 10 min) for Au/Al-com and Au/Al-SG catalysts (left) and concentration of Lewis acid surface sites (LAS) found for Al-com and Au/Al-SG (right).](image)

Significance

The data obtained in this work may be applied for the development of new effective catalysts for aerobic oxidation of a wide variety of alcohols.

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