

Selective oxidation of alcohols using supported gold palladium nanoparticles

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Introduction

Oxidation of alcohols to aldehydes using environmentally benign oxidants like O₂, H₂O₂ has received considerable attention in the recent past. To achieve a high selectivity for the desired product, it is important to understand the parallel and consecutive reactions, which can lead to side product and thus lower selectivity for the product of interest. Supported Au-Pd based catalysts are found to be very active for this transformation [1]. It has been also demonstrated that the combination of gold and palladium could provide a further pronounced enhancement in activity when the two metals are deposited together by sol-immobilisation [1]. In spite of vast amounts of literature on the alcohol oxidation the exact mechanism of this transformation is still unclear [2]. In an attempt to unravel the mechanism of this oxidation, kinetics of this oxidation was studied in details [3]. Also the application of the catalysts in oxidation of different alcohols was investigated [4].

Experimental

Benzyl Alcohol oxidation was carried out using Au-Pd/TiO₂ as catalyst prepared by a sol-immobilisation method in a 50 ml glass stirred reactor. Octanols oxidation was carried out using Au-Pd/TiO₂ as catalyst prepared by impregnation method in autoclave reactor (Parr). For the analysis of the products, GC-MS and GC were employed. Deuterium NMR spectra were obtained using a JEOL Eclipse 300 MHz NMR spectrometer for dilute solutions in deuteriochloroform. Analytical results over the early stages of the reaction for alcohol disappearance, aldehyde appearance and toluene formation were linear with time and were transformed into initial rates (v/mol s⁻¹)

Results/Discussion

Table 1. Solvent free aerobic oxidation of alcohols ^a

Substrate	Conversion %	Selectivity %
1-Octanol	4.4	99.6
3-Octanol	21.2	71.7

^a Reaction conditions: Catalyst : 5%(Au-Pd)/TiO₂ Alcohol 20 ml, catalyst 3.5 mg, 160 °C, pO₂: 2 bar, stirring 1500 rpm, time: 3h

Au-Pd/TiO₂ catalysts were found to be very active and selective for the aerobic oxidation of alcohols to corresponding aldehydes including aromatic and aliphatic alcohols. A representative

data for the aliphatic alcohols are given in Table-1. A detailed mechanistic investigation on this type of oxidation was carried out for the aerobic oxidation of benzyl alcohol. Kinetic studies using α, α-dideuteriobenzyl alcohol and protonated benzyl alcohol gave a kinetic isotopic effect of approximately 2.5 as shown in Figure-1. Based on this, we have proposed that breaking of β-H in benzyl alcohol is involved in the rate determining step.

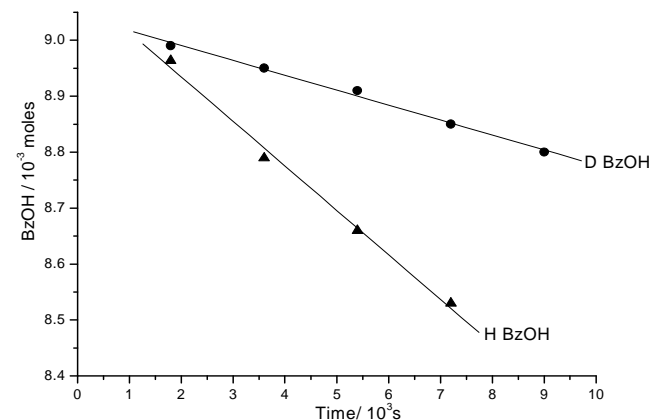


Figure 1. Rate of disappearance of benzyl alcohol (▲ proton; ● deuterated) under 1 bar He reaction with 1% AuPd/TiO₂ catalyst (0.02 g).

We also propose that there are two reactions that are active in the overall oxidation of benzyl alcohol to benzaldehyde; oxidation and disproportionation reactions [3]. The oxidation reaction yields only benzaldehyde and the disproportionation reaction results in an equimolar mixture of benzaldehyde and toluene. This disproportionation reaction is thermodynamically feasible because of the formation of water as shown in the following equation.



References

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