Selective oxidation of propanediols

Tatyana Kotionova, Miedziak P.J., Taylor S.H., Knight D.W., Hutchings G.J.*
Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK
* kotionovat@cardiff.ac.uk

Introduction

Selective oxidation of alcohols can lead to valuable products and useful feedstock for the chemical industry [1, 2]. Noble metals catalysed oxidation in presence of oxygen is an environmentally clean option to selectively oxidise alcohols under mild conditions, in contrast to present industrial routes involving large amounts of inorganic waste or severe reaction conditions. In this work, the oxidation in liquid phase of various C_3 based diols was investigated.

Experimental

Oxidation was carried out in low pressure (up to 3 bar) glass reactor, using methanol as a solvent and reagent, and oxygen as the oxidant. The catalysts tested were 1% Au, Pd, Pt supported on titania, and combinations of these noble metals for bimetallic catalysts. Various reaction parameters were changed, and the effect on diol conversion and selectivity towards the products was measured. All the catalysts were prepared by sol-immobilization method [3]. Samples were analyzed by ^{1}H- and ^{13}C- NMR spectroscopy. Additional analysis was carried out by GC-MS. The catalysts were characterised by using X-Ray photoelectron spectroscopy (XPS).

Results/Discussion

Introducing of methyl substituents to propanediol showed to have a negative effect on the substrate reactivity to oxidation. One of the reasons may be different steric hindrance around the OH group in the different alcohols. By comparison, 1%Pd/TiO_2 gave high conversion of 1,3-propanediol and 2-methyl-1,3-propanediol, but lower selectivity for the later.
The peculiarity of 2,2-dimethyl-1,3-propanediol oxidation was that aldehydes were obtained as the reaction products.

Table 1. Oxidation of 1,3 -propanediol homologues.

Substrate	Catalyst	Conversion %	Products, selectivity %		
1,3-propanediol			3MHP	3HPA	
	1%Pd/TiO_2	69	82	7	
	1%Au/TiO_2	39	82	17	
	1%AuPd/TiO_2	45	80	19	
2-methyl-propanediol-1,3			MHB	HBA	
	1%Pd/TiO_2	62	55	45	
	1%Au/TiO_2	46	93	7	
	1%AuPd/TiO_2	37	79	20	
2,2-dimethyl-1,3-propanediol			MHP	HPA	HPAld
	1%Pd/TiO_2	15	22	16	61
	1%Au/TiO_2	30	73	26	-
	1%AuPd/TiO_2	25	60	32	7

3MHP – methyl 3-hydroxypropionate; 3HPA – 3-hydroxypropionic acid, MHB - Methyl hydroxyisobutyrate, HBA – hydroxyisobutyric acid, MHP - Methyl hydroxypivalate, HPA - 3-hydroxypivalic acid, HPAld - 3-hydroxypivalic aldehyde.

Table 2. XPS data for the catalysts synthesised by sol-immobilisation technique.

Sample	At. composition, %			
	O	Ti	Au	Pd
1%Au/TiO_2	10.8	87	23	
1%AuPd/TiO_2	12.9	84	1.1	2

The observed molar ratio of metals for the bi- and trimetallic catalysts is consistent with the absence of core-shell structures. The analysed catalysts contain predominantly metallic Au^0, and Pd^0 species. In view of this characterisation it is possible to conclude that catalysts with homogeneous distribution of metals on the surface and the metals in metallic state display catalytic activity for oxidation reactions of propanediols.

References.

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