

Glycerol Selective Oxidation Under Acidic Conditions

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Introduction

Apart from the decline of fossil fuel energy resources, there is the added problem, recognised internationally, that fossil fuels are responsible for the greenhouse effect and global warming. Therefore, new alternative ways must be developed to satisfy not only energy needs and the production of chemicals but also for more benign effects on the environment. An approach already being developed is the use of biomass [1-4], for producing renewable raw materials and their conversion to high value chemicals and materials. Glycerol is a non-toxic compound with many uses; however, if a surplus exists in the future, more uses for the produced glycerol needs to be found.

Recently the chemoselective catalytic conversion of glycerol was reviewed [5] highlighting the huge amount of useful compounds that can be produced through oxidation, hydrogenolysis, dehydration, pyrolysis, transesterification and esterification, polymerization and carbonylation. The importance of these transformations has been also highlighted by a recent report produced by the staff of the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL) [6].

In the present work our attention is focused on the selective catalytic oxidation of glycerol and the influence of the catalyst and the experimental conditions on the selectivity. In particular were focused on the opportunity to carry out the reaction in the absence of a base which would represent a big advantage from an industrial point of view.

Materials and Methods

Metal supported catalysts have been prepared by using the sol immobilization method using different supports (Activated carbon (AC), TiO₂, H-mordenite, MgAl₂O₄) [7]. The metal loading is 1% wt. Glycerol oxidation was carried out in a glass reactor pressurized at 300 kPa of O₂ and thermostated at 50-100 °C. To a 0.3M solution the catalyst was added (glycerol/metal ratio = 1000 mol/mol) and the reaction was started by stirring. The analysis of products was carried out by withdrawing samples periodically and using an HPLC system equipped by RI and UV detectors.

Results and Discussion

Hutchings et al. first reported that the selective oxidation of glycerol can be carried out using gold on carbon as the catalyst [8] under basic conditions. The role of the base is still matter of study but it appears to be involved in the first step of the oxidative process for the creation of the alkoxyde anion. Indeed, in this respect, the fundamental role of the basic strength of the alcoholic group has been evidenced.[9] Kinetic studies on glycerol oxidation revealed that the adsorption of the reaction products on the catalytic surface is important [10] and the presence of a base could be important for removing such products from the active surface and preventing metal leaching, thus prolonging the catalyst life. This latter conclusion is in line with the observation that, in the presence of bimetallic systems, alcohols can be oxidized, even in the absence of basic conditions, whereas glycerol appears to remain inactive [11]. Thus, up to now, the studies dealing with glycerol oxidation all reported experiments performed under basic conditions. Following these studies we first tried to push the reaction under neutral/acidic conditions by increasing the temperature. A series of experiment at 100°C

were performed (Table 1). Several mono and bimetallic catalysts were tested. Surprisingly, monometallic gold became active at this temperature, however, there was deactivation at quite low conversion (20-30%). Pt based catalysts appeared the most active but a large amount of C1-product (formic acid and CO₂) was formed. By using a bimetallic Au/Pt system the selectivity to C3 products has been enhanced, reducing the C-C bond cleavage leading to C1-products. Unexpectedly the Au/Pd system, did not increase the selectivity to C3-products which is different from its use under basic conditions,

Table 1. Catalytic activity and selectivity of catalysts on AC for the oxidation of glycerol.

Catalyst	Sel. % to C3	Sel. % to C1	Conversion at 2h
1% Au/AC	35	55	7
1% AuPd/AC	42	46	17
1% AuPt/AC	62	29	68
1% Pd/AC	48	47	5
1%Pt/AC	52	46	78
5% Pt-Bi /AC (JM)	8	90	92

Using the sol immobilization technique similar sized gold particles were prepared on non-carbon supports and investigated under the same conditions, Table 2. A strong influence of the supporting material was observed.

Table 2. Catalytic activity and selectivity of Au/oxides for the oxidation of glycerol.

Catalyst	Sel. % to C3	Sel. % to C1	Conversion at 2h
1% Au/TiO ₂	45	32	32
1% Au/MgAl ₂ O ₄	32	60	10
1% Au/H-mordenite	68	13	65

Significance

We show that the selective oxidation of glycerol can be performed under acidic conditions. This possibility is beneficial from an industrial point of view as glycolic acid can be obtained directly from glycerol avoiding any expensive neutralization step. Gold supported on mordenite showed an unexpected activity under acidic conditions. Reaction profiles also showed that the support plays an important role in preventing catalyst deactivation.

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