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PROCEEDINGS

126	11:00 am – 11:15 am	Selective Oxidation of Glycerol under Base-Free Condition over Supported Palladium Metal-Based Catalysts	Norfatcha h Basiron, et al.
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Selective Oxidation of Glycerol under Base-Free Condition over Supported Palladium Metal-Based Catalysts

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Abstract

Series of supported palladium metal-based catalysts with varying types of catalyst support (Hydrotalcite (HTc), activated carbon (AC), and mixture of HTc-AC) with 1% metal loading were prepared by sonication sol-gel immobilization method. The catalytic performance of the catalyst was evaluated for the oxidation of glycerol to value added chemicals that have a tremendous interest in the chemical industry. The intrinsic catalytic properties of the catalysts prior to immobilisation onto support material were characterized by BET surface area, XRD, TEM, TPR of H₂, TPD of CO₂ and PSD. The oxidation reactions were carried out in a batch reactor (Autoclave) for different catalyst supports under otherwise similar conditions. The catalytic performance clearly showed increase in conversion of glycerol increased up to 6.0 wt% accompanied by selectivity to glyceric acid of 90%, with increase in the basicity of the catalysts. The intrinsic basicity of the catalyst originates from the basicity of the support used, i.e. hydrotalcite (Mg, Al), and also activated being mildly polar. The basicity of the support helps in the desorption of polar products formed, particularly glyceric acid. The presence of active Pd sites with 1% loading is instrumental in the oxidation of glycerol. It is less clear the oxidation state and the phase of Pd active phase. Further optimisation of Pd-catalysed glycerol oxidation is plausible.

1 Introduction

During the last decades, oxidation of glycerol has attracted the attention of the scientists around the world. Glycerol is considered a particularly important building block for bio-refinery because the expanding biodiesel production gives large amounts of inexpensive glycerol as a by-product[1]. Thus, the ready bio-availability of glycerol makes it a particularly attractive starting point for the synthesis of intermediates and a large number of products, which can be obtained from glycerol oxidation. However, there are two possibilities of intermediates reaction pathways for the oxidation of glycerol, which was occurred either

via primary or secondary hydroxyl group as shown in the Figure 1. The need of based catalyst in the oxidation of alcohol is a serious limitation in this catalyst system [2, 3]. Unfortunately, using of an inorganic base such as NaOH produces carboxylic acid salt as products during alcohol oxidation [4]. Neutralization of the product stream and release of the free acid increase the operating cost of the process and produce an additional salt by-product, which are of little value and may have a negative environmental impact. The selectivity of product in liquid-phase oxidation reaction of glycerol needs an intelligent choice of a support catalyst. This research is focused on the study of palladium

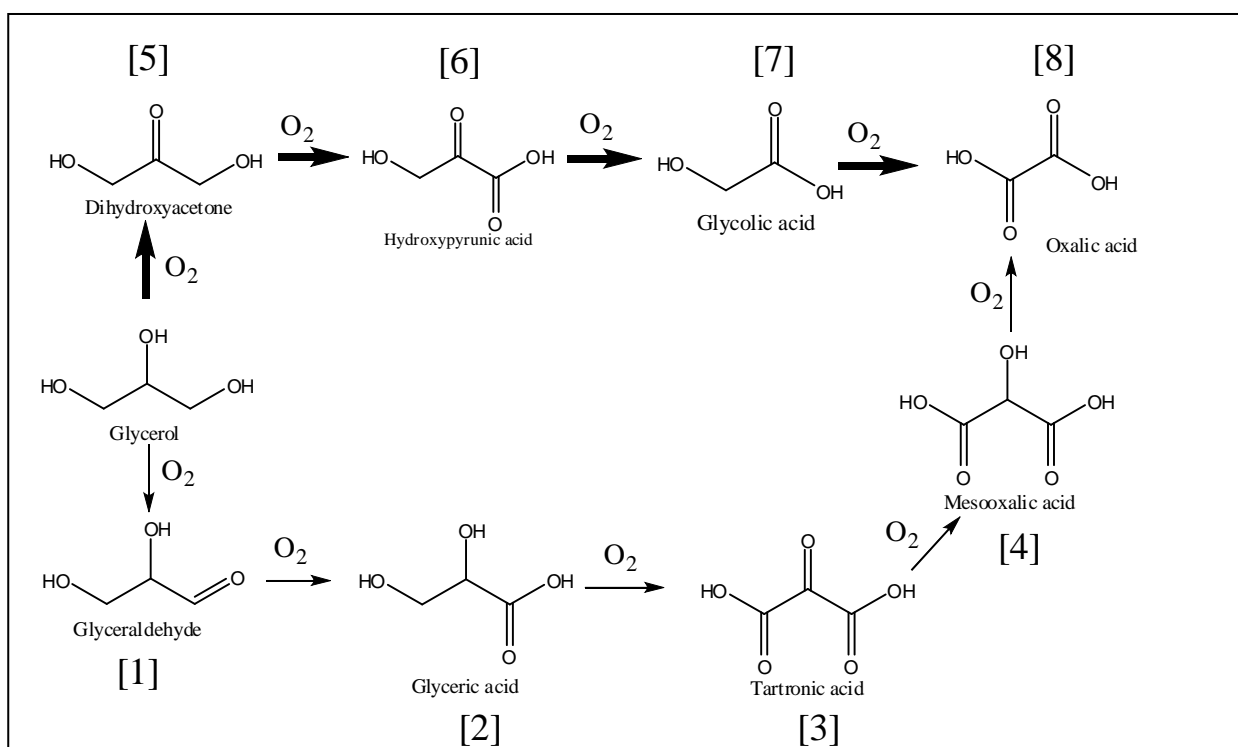


Figure 1: General reactions pathways and products of glycerol oxidation

catalysed for oxidation of glycerol in neutral condition with different catalytic support such as calcined hydrotalcite, HTc, activated carbon, AC and mixture of AC-HTc.

2 Methods

Catalyst preparation

All the synthesis was done through sol-gel immobilization method using polyvinyl alcohol (PVA) with metal loading 1%. The calcination and activation of the precursors was determined by thermogravimetric analysis (TGA) under inert gas atmosphere and temperature program reduction (TPR) in hydrogen environment.

Catalyst Characterization

Catalysts are characterized by SEM, TEM, BET and temperature program adsorption/reduction analysis technique. The crystallite size was determined by TEM analysis and the morphology of the catalyst was investigated by SEM w. The pore size distribution and surface areas were measured by BET technique. temperature program (CO-TPD) was performed to determine the support interaction and basicity,.

Oxidation of Glycerol

The batch reaction is performed in a 200 ml Top Industries batch stainless steel autoclave reactor. The standard conditions for the reactions are as follows: reaction temperature 60 °C, glycerol concentration = 0.3M, glycerol /

$\text{Pd} = 3500 \text{ mol mol}^{-1}$, pressure of O_2 is 3 bar, agitation speed 500 rpm. The products formed are analyzed using high-performance liquid chromatography (Agilent Technologies 1100 series) equipped with UV-VIS detector and refractive index detector. An Agilent Hi-Plex H, 7.7x300mm, $8\mu\text{m}$ column is used for separation. The analytical conditions were as followed, the samples are diluted with the eluent. Measuring time of 30 min, a column temperature of $60\text{ }^\circ\text{C}$ and flow of 0.4 ml/min. The peaks identification was done by the comparison with HPLC standard compounds.

3 Results and Discussion

The catalysts properties are defined from the cumulative results. The surface basic properties of the pure calcined hydrotalcite and supported palladium catalyst are studied by using TPD- CO_2 . The acid-base property of the catalyst plays an important role in the activity as well as selectivity of glycerol oxidation [5]. The CO_2 TPD profiles of palladium supported on calcined hydrotalcite and mixture of calcined hydrotalcite with activated carbon are found to exhibit similar behaviour depicted in Fig 2. The peak at lower than $200\text{ }^\circ\text{C}$ could be related to the weak basic strength (probably associated with the lattice bound OH group) [6] and maximum desorption peak at range $300\text{--}400\text{ }^\circ\text{C}$ related to the medium basic sites. The particle size of the palladium oxide was determined by TEM. The particle average sizes of PdO catalyst is about 10 nm. The dispersion in samples Pd/HTc-Ac, the crystallites structure varies from tetrahedral to octahedral and then cubic palladium particles due to agglomeration of the smaller spherical [7].

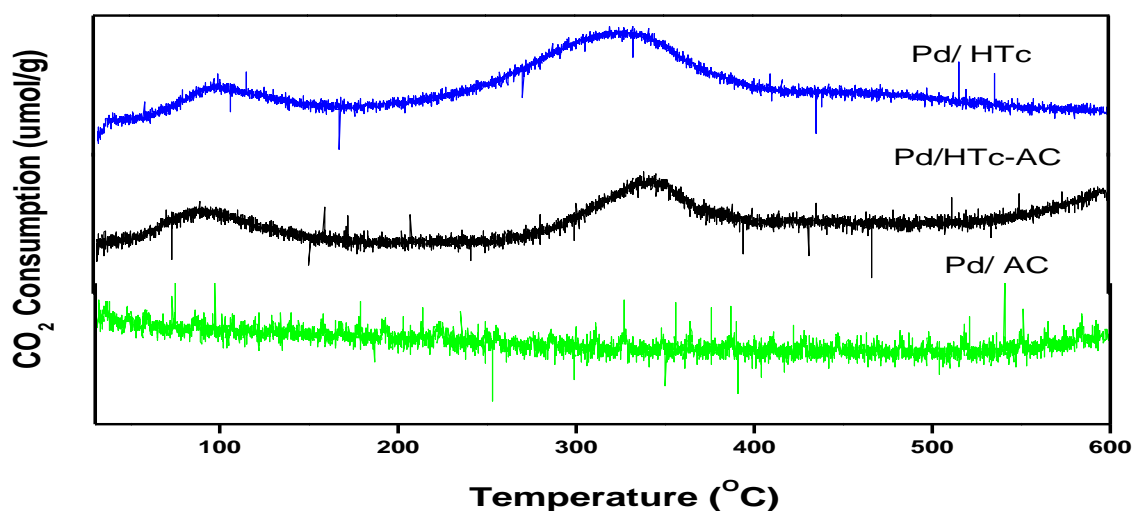
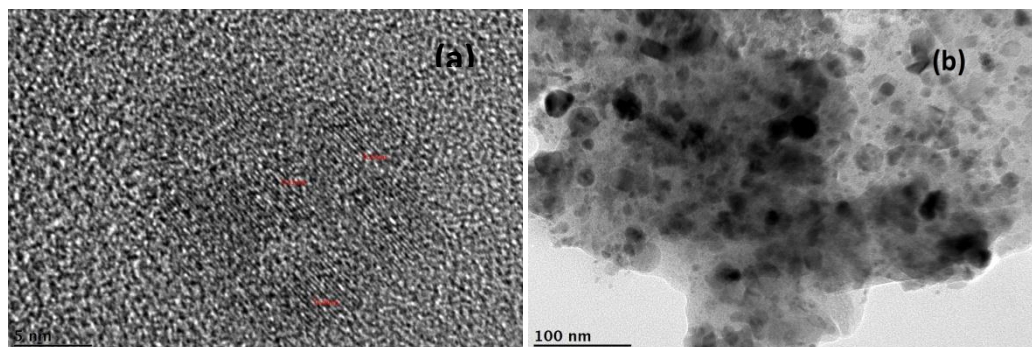


Figure 2 : Temperature programmed desorption of CO_2 profiles of various supported palladium catalysts



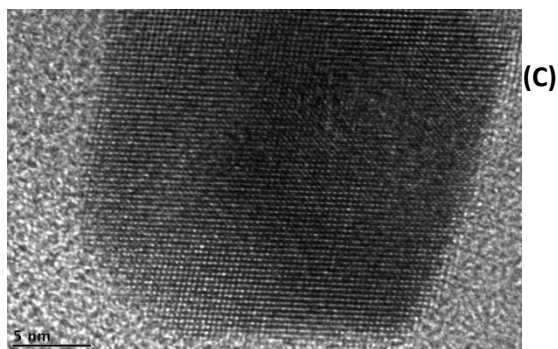


Figure 3: TEM images of (a)Pd/AC, (b)Pd/HTc-AC, and (c)Pd/HTc

Oxidation reactions were carried out for different catalyst supports. Figure 4 show that Pd/HTc offers higher activity over its competitor. The product distribution varies with the support materials.

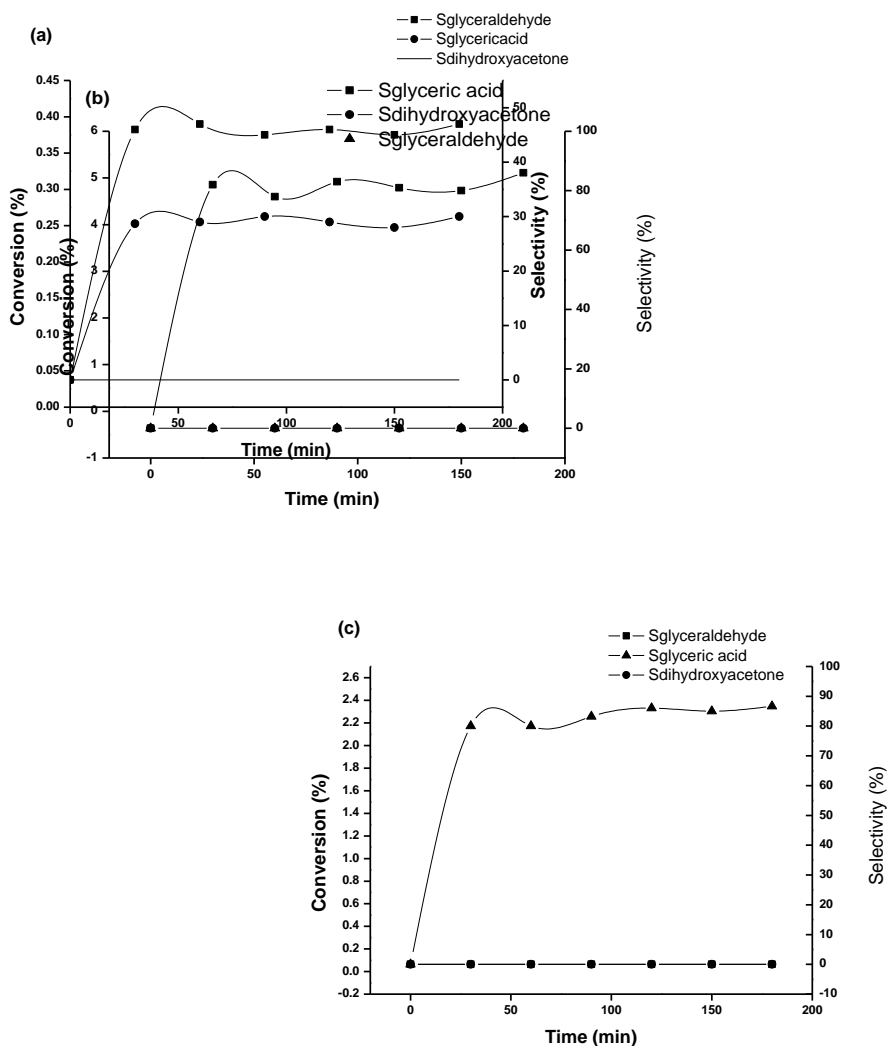


Figure 4: (a) Glycerol oxidation using catalysts (a) Pd/AC (b) Pd/HTc and (c) Pd/HTc-AC

4 Conclusion

The glycerol selective oxidation to various oxygenates was achieved using 1% Pd supported on basic supports. Glycerol was hardly activated and converted in the absence of catalyst under the reactions used. Conversion was maximum when using most basic support, i.e. hydrotalcite only. The said reaction yields glyceraldehyde, glyceric acid, dihydroxyacetone, all oxygenates being polar compounds. Modulating surface basicity has a profound effect to product selectivity whereby near 90% selectivity to glyceric acid was achieved. The orders of activity for different supports are as follows: Pd/HTc >Pd/HTc-AC> Pd/AC. This is could be due to the varying metal-support interaction, and the ease of polar products desorption. The catalytic activity of the different supporting catalysts was confirmed that the basicity of the catalyst play an important role in the activity and product selectivity. Focus should be to optimise higher glycerol actions by modification to catalyst composition, particularly that of nanoparticles of palladium.

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References

1. Petersen, J.J.B.a.G.R., "Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—the US Department of Energy's "Top 10" ". *Green Chemistry*, 2010. **12**(4): p. 15.
2. Dan, L. J.G., Junhua W., Ping C., Yanfei W., Zhaoyin H., "Bimetallic Pt-Cu Catalysts for Glycerol Oxidation with Oxygen in Base-free Aqueous Solution". *Catalysis Communication* 12, 2011: p. 4.
3. Gemma L. B., Q.H., Ceri H., Peter J. M., Nikolaos D., Meenakshishundaram S., Andrew A. H., Marco C., Jose A. L. S., Christopher J. K., David W. K., Stuart H. Taylor and Graham J. H., "Seletive Oxidation of Glycerol by Highly Active Bimetallic Catalysts at Ambient Temperature under Base-Free Conditions". *Angewandte Chemie International*. 2011(50): p. 4.
4. Xiaoli W., G.W., Fang W., Keqiang D., Fang Z., Xianfeng L., Yunbo X., Base-free Selective Oxidation of Glycerol with 3% H₂O₂ Catalyzed by Sulphonato-salen-chromium(III) Intercalated LDH. *Catalysis Communication* 2012. **28**: p. 4.
5. William C. K., Mitsuhiro M., and Robert J. D., Promotional Effect of Hydroxyl on the Aqueous Phase Oxidation of Carbon Monoxide and Glycerol over Supported Au Catalysts. *Topics in Catalysis*, 2007. **44**(1-2): p. 11.
6. Avelino. C., Sarra I., Alexandra V., Chemical Routes for the Transformation of Biomass into Chemicals. *Chemical Reviews*, 2007. **107**.
7. Viet, L.N., Duc, C.N., Hirohito, H., Michitaka, O., Tomokatsu, H. and Masayuki N., Chemical Synthesis and Characterization of Palladium Nanoparticles. *Advances in Natural Science : Nanoscience and Nanotechnology*, 2010. **1**: p. 5.