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Base-free conversion of glycerol to methyl lactate using a multifunctional catalytic system consisting of Au-Pd nanoparticles on carbon nanotubes and Sn-MCM-41-XS

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PURPOSE OF THE ABSTRACT

1. Introduction

Glycerol, being the main side product from the biodiesel industry, is an attractive biobased platform molecule that can be used for the production of bulk and fine chemicals.1 Lactic acid and alkyl lactate are among the most promising products that can be obtained from glycerol.2 Lactic acid can be used for the production of poly-lactic acid, a biodegradable polymer with various applications in the industry.2 There is an incentive to develop efficient chemo-catalytic methodology to obtain lactic acid or alkyl lactates from glycerol in a one-pot reaction, considering the drawbacks of commercial production of lactic acid by fermentation.

To achieve the one-pot conversion of glycerol to methyl lactates (ML) without requiring a homogeneous base, a multifunctional catalytic system is needed to promote the partial oxidation of glycerol and the successive rearrangement of the trioses into ML (Scheme 1). Here, we report a novel heterogeneous system that consists of a physical mixture of bimetallic Au-Pd supported on functionalised carbon nanotubes (CNT) and Sn-MCM-41-XS. The AuPd/CNT acts as the catalyst for the initial oxidation of glycerol (Step 1, Scheme 1), whereas Sn-MCM-41-XS is a solid acid containing both Lewis and Brønsted acid sites that promotes the rearrangement of the intermediates DHA and GLAD (Step 2 and 3, Scheme 1).3 The selective conversion of glycerol to methyl lactate was investigated with emphasis on the effects of the bimetallic sites and of functionalisation of the CNT by various oxidative methods, and insights in catalyst stability were obtained by performing recycle experiments.

2. Results and Discussion

The AuPd/CNT catalysts were characterized by means of transmission electron microscopy (TEM), N2-physisorption, Energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and by Boehm titration. Both elemental analysis (ICP) and XPS confirmed the presence of Au and Pd in the bimetallic samples and XPS result further indicated they are in the form of a Au-Pd alloy.

The bimetallic AuPd/CNT were found to be more active than mono-metallic Au or Pd catalysts, while retaining the same, high selectivity to ML (Figure 1A). Functionalisation of the support CNT by various oxidative treatments (H2O2, HNO3, H2SO4 and HNO3-H2SO4) gave significantly positive effects on catalyst performance, and the yield of ML was 85% at 96% glycerol conversion (140 oC, 10 h at 30 bar air), which is the highest value reported in the literature so far (Figure 1B). The smaller size of AuPd nanoparticles (Figure 1C) and higher hydrophilicity of CNT supports, which are both caused by the functionalisation, promoted higher rate of glycerol oxidation. And the surface acidity of functionalised CNT, from the oxygenated and sulphuric groups, was beneficial to the consecutive dehydration of trioses to pyruvic aldehyde (Step 2, Scheme 1).

Insights in the reaction pathways were obtained by considering the conversion-time profiles that turned out to be a first order reaction and the initial TOF of glycerol is 180 h-1. Batch recycle experiments showed the excellent stability of the catalyst that almost no lost in terms of activity and selectivity after 5 times run.

3. Conclusion

This catalytic system reached the best performance reported so far in terms of the yield of ML. The bimetallic

nature of the Au-Pd nanoparticles, the functionalisation of CNT and the presence of Sn-MCM-41-XS proved to be crucial factors for achieving this notable results.

FIGURES

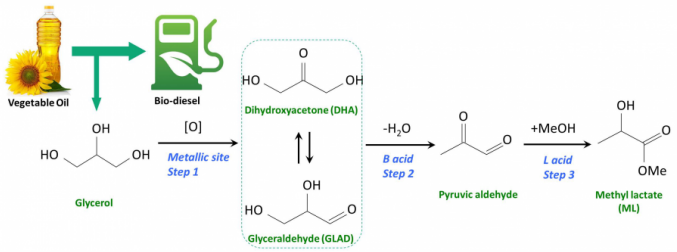

FIGURE 1

Scheme 1. Catalytic conversion of glycerol to methyl lactate.

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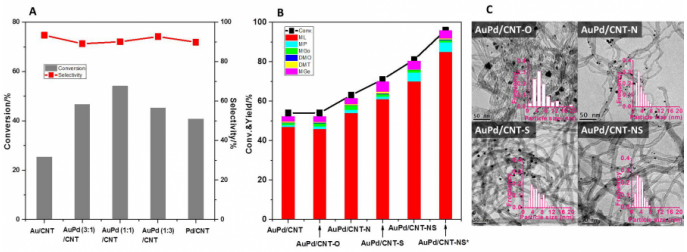

FIGURE 2

Figure 1. Catalytic performance of AuPd/CNT catalysts: (A) effects of Au/Pd molar ratio; (B) effects of functionalisation methods of CNT. (C) TEM pictures of AuPd nanoparticles supported on functionalised CNT.

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KEYWORDS

glycerol | methyl lactate | gold catalysis | CNT functionalisation

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