

Single phase Au-Pd catalysts

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Introduction

Bimetallic systems attract great interest due to their unique catalytic, electronic, and optical properties which differ from their corresponding monometallic components. In particular, Au/Pd systems have been extensively studied¹. The observed synergistic effect between gold and palladium lies on the presence of alloyed phases² or core-shell structures³. We recently reported on a preparation method for Au-Pd alloys on carbon, which produced a single alloy phase. The procedure avoids the segregation of metal constituents and uses preformed particles of Au stabilized by polyvinylalcohol (PVA) and immobilized on active carbon as nucleation centers for the additional metal deposition. In this work we focused our attention on the role played by the protective agent in obtaining alloyed phases.

Materials and Methods

Activated carbon is commercially available from Camel (X40S). Au/AC catalysts seeds were prepared using three different methods: the PVA/NaBH₄ system (0.73% Au_{PVA}/X40S)²; the THPC/NaOH system (0.73% Au_{THPC}/X40S)⁴; and magnetron sputtering (0.74% Au_{Mag}/X40S)⁵. Pd was subsequently deposited following the procedure reported elsewhere². The total metal loading was 1%wt and the overall atomic ratio between gold and palladium was 6:4. The catalysts were characterized by means of XRD, ICP and HRTEM/EDX. Glycerol oxidation was carried out in a glass reactor pressurized at 300 kPa of O₂ and thermostatted at 50 °C. To a 0.3M solution the catalyst and NaOH were added (glycerol/metal ratio = 1000 mol/mol and NaOH/glycerol=4 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

In order to study the role played by the protective agent on the gold nanoparticles, we prepared three different Au/C precursors: two using different molecules to stabilize gold nanoparticles (PVA and THPC) and the third involves totally unprotected gold nanoparticles prepared by magnetron sputtering. The immobilization of PVA sol has been reported to generate high metal dispersion when activated carbon is used as the support, almost maintaining the same particle dimension as in the sol². On the contrary THPC-protected sol gives some aggregation of small sized particles during the immobilisation step⁵. Magnetron sputtering technique provided an extraordinary high metal dispersion on activated carbon⁶. These metal distributions were further confirmed by the activity and selectivity results obtained for the oxidation of glycerol (Table 1) where higher activity and lower selectivity

corresponding to smaller particles. However, when Pd was deposited onto Au/AC precursors an unexpected metal distribution was found: Au(PVA)/AC precursor produced bimetallic particles of average size 3.4 nm and single alloy composition. The deposition of Pd on the Au(Mag)/AC and Au(THPC)/AC precursors resulted in a consistent increase in particle size, different alloy composition, and some segregation of both gold or palladium. The effect on catalytic activity was substantial, as shown in Table 1.

Table 1. Catalytic activity of mono and bimetallic catalysts in the glycerol oxidation

Catalyst	S90	TOF (h ⁻¹)	Size (nm)
0.73% Au _{PVA} /AC	68	900	2.4
0.74% Au _{Mag} /AC	41	3249	1.7
0.73% Au _{THPC} /AC	50	2512	2.0
1% Pd@Au _{PVA} /AC	78	3446	3.4
1% Pd@Au _{Mag} /AC	70	337	5.2
1% Pd@Au _{THPC} /AC	84	1405	3.7

As expected from previous results the Pd@Au_{PVA}/AC results in very high activities. However, in the other two cases, with metal segregation, not only were the TOF lower than the Pd@Au_{PVA}/AC, but the TOFs were also lower than the corresponding Au monometallic catalysts. Furthermore, the presence of alloys resulted in an enhanced selectivity towards the formation of glycerate over the corresponding monometallic gold catalysts and that selectivity appeared not to be correlated with metal dispersion as for monometallic catalysts

These results confirmed that the high activity showed by Pd@Au_{PVA}/AC can be attributed to the presence of alloy. In addition, the Au stabilization method also plays an important role: the Au_{PVA}/AC precursor is the only catalyst that avoided the growing and/or the reconstruction of gold nanoparticles during the deposition of Pd.

Significance

We showed that only Au nanoparticles protected by PVA are stable during the subsequent Pd deposition and efficiently provided seeds for a single phase alloy nucleation. Unprotected or THPC protected Au nanoparticles grew during the deposition and reduction of Pd producing metal segregation. The single phase Au-Pd bimetallic catalyst resulted the most active in the glycerol selective oxidation but alloy phases lead to enhanced selectivities.

References

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