Glucose oxidation over activated carbon-supported gold clusters

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Abstract: The catalytic performance of gold clusters (Au_{25}, Au_{38}, Au_{144}) immobilized on activated carbon was investigated for the aerobic oxidation of glucose. The Au cluster catalysts annealed at 120 ^{O}C in air exhibited significantly better catalytic performance than those treated at 150 ^{O}C and 300^{O}C, and also than the commercial Pd/AC, Pd-Bi/AC, and Au/AC. The excellent catalytic activity of the robust Au cluster catalysts was a result of the partial ligand removal, providing catalytically active sites. We observed a distinct size dependence of gold clusters in the aerobic oxidation of glucose, which follows as Au_{144}/AC> Au_{38}/AC> Au_{25}/AC.

Keywords: Glucose oxidation, gold clusters, activated carbon, Au size dependence.

1. Introduction

The transformation of renewable biomass-derived glucose into valuable gluconic acid has resulted in interesting sustainable developments.[1-2] Recently, Au clusters (size <2 nm) with atomic monodispersity were developed and documented as new and robust catalysts.[3] These Au clusters exhibited good performance in selective oxidation reactions such as CO oxidation, sulfoxidation, and oxidation of alcohols.[4] The catalytic activity of Au clusters was significantly enhanced if the protecting organic ligands were partially removed. Herein, we investigated the catalytic performance of Au clusters immobilized on activated carbon (AC) in the aerobic oxidation glucose. It was found that Au clusters annealed at 120 ^{O}C in air to partially remove surface ligands exhibited excellent catalytic activity and very high selectivity to gluconic acid.

2. Experimental

Au_{25}, Au_{38} and Au_{144} clusters were synthesized according to literature methods. Then the as-prepared Au clusters were immobilized on AC support. Typically, 10 mg Au clusters were dissolved in 25 mL CH_2Cl_2 and then 1.0 g AC supports were added. After stirring for 12 h at room temperature, the Au_n/AC catalysts were collected by centrifugation and were dried in a vacuum oven. The as-preapred Au catalyst was further annealed at 120 °C, 150 °C and 300 °C for 2 h in the presence of air to prepare Au_n/AC-120, Au_n/AC-150 and Au_n/AC-300 catalysts, respectively.

3. Results and discussion

The aerobic oxidation of glucose to gluconic acid catalyzed by AC-supported Au clusters was performed at 60 ^{O}C in the presence of NaOH under O_2 flow. First, we investigated the catalytic performance of Au_{38}/AC catalysts in the oxidation of glucose, which were pretreated at different temperature. It was found that the Au_{38}/AC-120 catalyst, exhibited significantly better catalytic performance than Au_{38}/AC-150 and Au_{38}/AC-300 catalysts under same reaction conditions (**Figure 1a**), and also than the commercial Pd/AC, Pd-Bi/AC and Au/AC (**Figure 1b**). Thermogravimetric analysis (TGA) and FT-IR spectroscopy clearly showed that some of the surface ligands were removed to provide catalytically active sites for the aerobic oxidation of glucose after thermal pretreatment. When the annealing temperature was raised to 150 ^{O}C and 300 ^{O}C, the sintering of Au clusters was observed (**Figure 2a-c**), which led to the decrease of catalytic activity. Interesingly, we observed a distinct size dependence of Au cluster in the aerobic oxidation of glucose, which follows as Au_{144}/AC>Au_{38}/AC>Au_{25}/AC (**Figure 2b**).

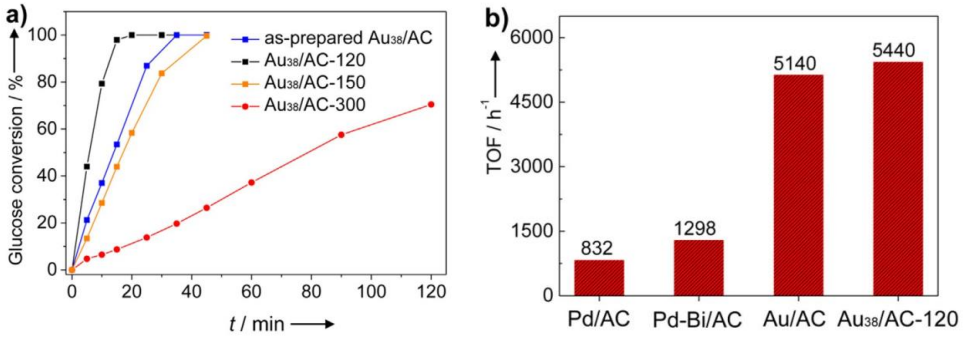

Figure 1. a) Glucose conversion versus time over as-prepared Au_{38}/AC, Au_{38}/AC-120, Au_{38}/AC-150, and Au_{38}/AC-300. b) TOF values of Pd/AC, Pd-Bi/AC, Au/AC, Au_{38}/AC-120.

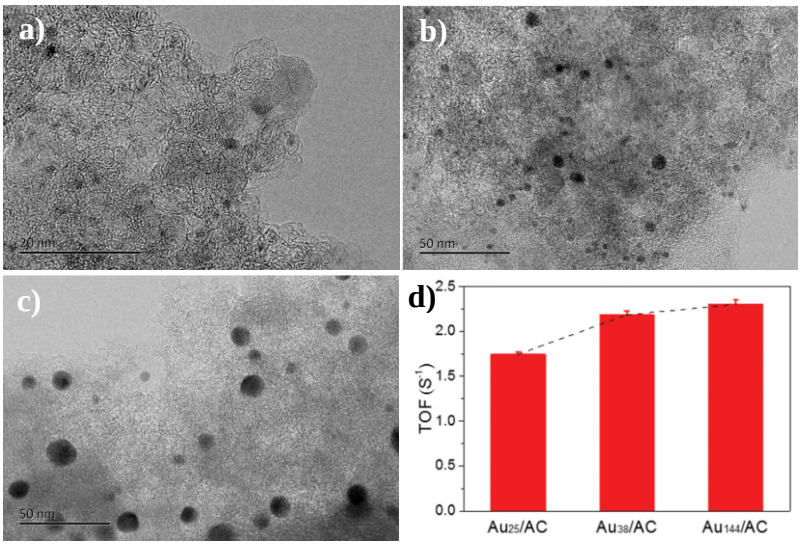

Figure 2. a-c) TEM image of the Au_{38}/AC-120, Au_{38}/AC-150, Au_{38}/AC-300. d) TOF values of Au_{25}/AC, Au_{38}/AC, and Au_{144}/AC.

4. Conclusions

We prepared Au_n/AC catalysts through a simple impregnation of Au clusters on AC and then investigated their catalytic activity in the aerobic oxidation of glucose to gluconic acid. The annealing of Au_n/AC catalysts at 120 ^{O}C was found to remove some ligands on the surface, which provided catalytically active sites for glucose oxidation. Au_n/AC-120 (n=25, 38, 144) exhibited higher catalytic activity than as-prepared Au_n/AC, Au_n/AC-150 and Au_n/AC-300 catalysts. Interestingly, it is found that the catalytic activity of Au_n/AC increased with the increase in core size and surface area of Au clusters in the following order: Au_{25}/AC < Au_{38}/AC< Au_{144}/AC. These well-defined Au clusters might be used to catalyze other aerobic oxidations under mild conditions.

References

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