Pyrrolidone-modified SBA-15 supported Au nanoparticles with superior catalytic properties in aerobic oxidation of alcohols

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Preparation of SBA-15: As a typical run, 0.8 g of copolymer surfactant P123 was dissolved in 25 mL of water with 3mL HCl (10M/L), followed by the addition of 2.4 mL TEOS. After stirring at 40 °C for 20 h, the mixture was transferred into an autoclave for further condensation at 100 °C for 24 h. The as-synthesized samples were collected by filtration and treated in ethanol containing HCl to remove the surfactants.

Preparation of SBA-15-N: 1g of SBA-15 was dried at 120 ºC under vacuum for 3 h, followed by the addition of 50 mL of pretreated toluene containing 1g of N-[3-(trimethoxysilyl)-propyl]diethylenetriamine. The mixtures were refluxed overnight and collected by rotary evaporation, followed by washing with a large amount of ethanol. The sample obtained was designated as SBA-15-N. The experiments above were carried out in anhydrous conditions to avoid the reaction between amine ligands and H_2O.

Preparation of Au/SBA-15-Py: To prepare pyrrolidinone-modified SBA-15, 3.16 g of (s)-(-)-2-Pyrrolidinone-5-carboxylic acid (Py) was dissolved in the mixture of dichloromethane and DMF (molar ratio of dichloromethane/DMF is 10). Then, EDC·HCl and Et_3N (molar ratio of Py/EDC·HCl/Et_3N at 1/1.5/1.5) was added into the solution. After stirring for 20 min, 1g of SBA-15-N and catalyst amount of DMAP were added into the mixture, stirring at room temperature overnight. The above processes were carried out in anhydrous conditions. The sample was collected by filtration and washing with a large amount of ethanol and water. The obtained sample, designated as SBA-15-Py, was stirred in $HAuCl_4$ solution overnight. The product was collected, dried at 100 °C under vacuum, and reduced by $NaBH_4$ in anhydrous toluene. Au/SBA-15-Py was collected by filtration and washing with a large amount of ethanol and water.

Preparation of Au/SBA-15-N: SBA-15-N was stirred in $HAuCl_4$ solution overnight. The product was collected, dried at 100 °C under vacuum, and reduced by $NaBH_4$ in anhydrous toluene. Au/SBA-15-N was collected by filtration and washing with a large amount of ethanol and water.

Oxidation of alcohols: Catalytic tests were performed in a 100-mL high-pressure autoclave with a magnetic stirrer. The substrate and catalyst were mixed in the reactor and oxygen was introduced, Then the reaction system was heated to a given temperature. (The O_2 pressure was detected at the reaction temperature). After the reaction, the product was taken out from the system and analysed by gas chromatography (GC-17A, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17).

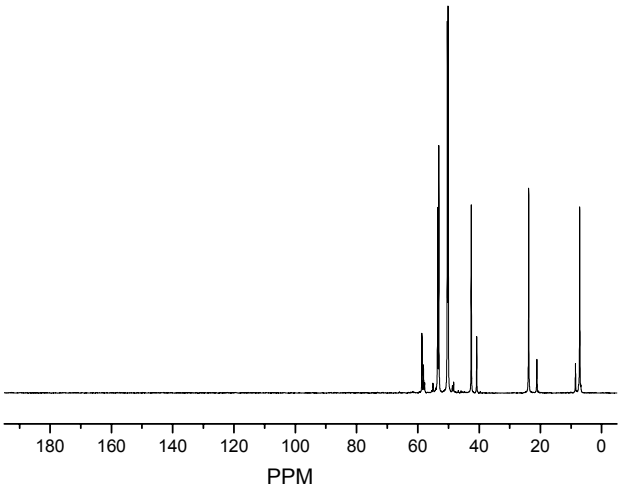


Fig. S1 ^{13}C NMR spectrum of N-[3-(trimethoxysilyl)-propyl]diethylenetriamine (DETA).

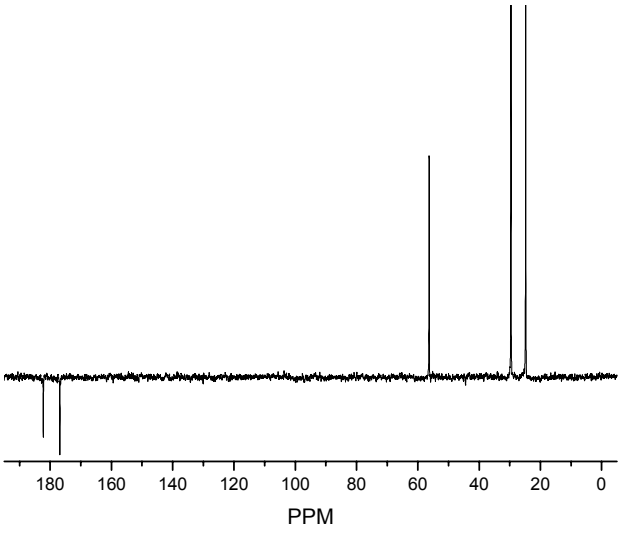


Fig. S2 ^{13}C NMR spectrum of (s)-(-)-2-Pyrrolidinone-5-carboxylic acid (Py). (The solid-state Py samples is dissolved in deuterium oxide. The signals of quaternary carbon atoms is downward.)

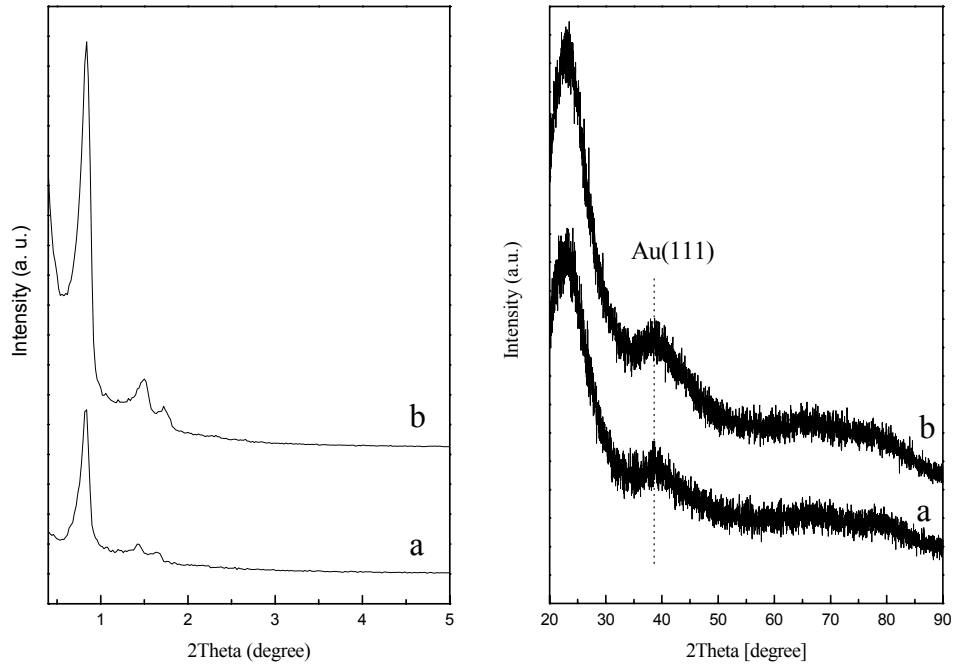


Fig. S3 XRD patterns in small (left) and wide (right) angles of (a) Au/SBA-15-Py and (b) Au/SBA-15-N.

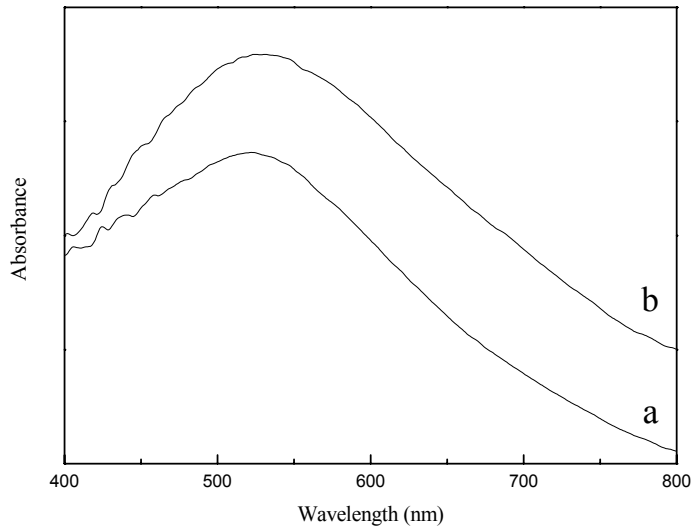


Fig. S4 UV-Vis spectra of (a) Au/SBA-15-Py and (b) Au/SBA-15-N.

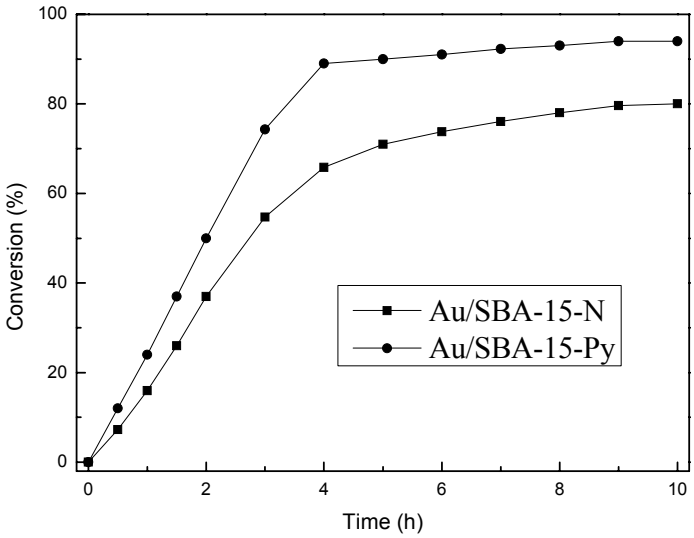
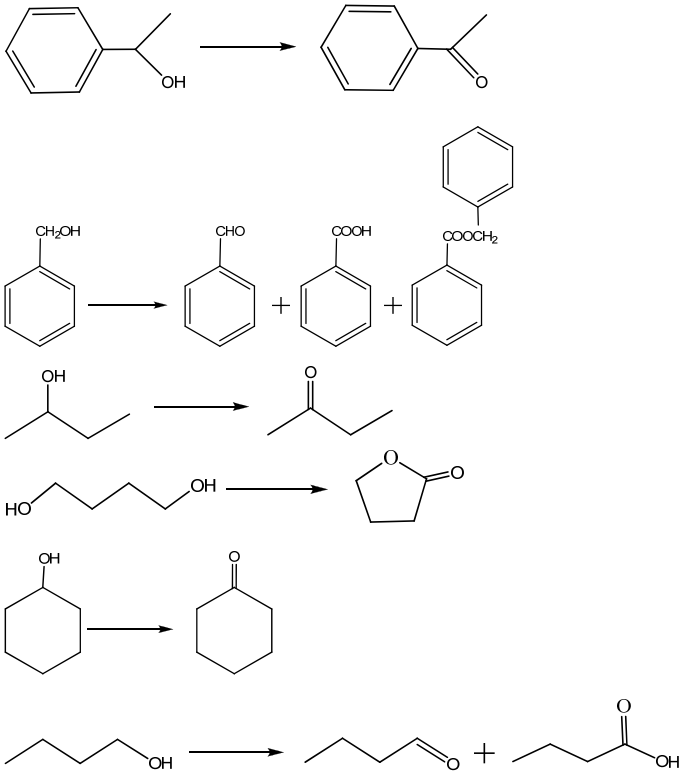


Fig. S5 Dependences of catalytic conversion on time in phenylethanol oxidation over Au/SBA-15-Py and Au/SBA-15-N catalysts.

Reaction


Scheme S1. Alcohol oxidations over Au/SBA-15-Py and Au/SBA-15-N.