

Supporting Information

Ex-post Size Control of High-Temperature-Stable Yolk-Shell Au, @ZrO₂ Catalysts

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Chemicals

In all preparation steps millipore water (18.2 MΩ cm⁻²) or absolute ethanol (99.9 %, LiChrosolv®, Merck) were used as solvents. The HAuCl₄ solution was produced by dissolving gold in boiling aqua regia. Other chemical used are: sodium citrate (citric acid trisodium salt dihydrate, 99 %, ACROS organics), polyvinylpyrrolidone (K 15, Fluka), ammonia solution (28-30 % NH₃ in water, Merck), TEOS (tetraethyl orthosilicate, 98 %, ACROS organics), lutensol AO5 (BASF), zirconium butoxide (80 wt% in butanol, Aldrich), NaOH (97 %, pellets, Merck), MTBE (99.9 %, Biesterfeld), HNO₃ (65 %, J. T. Baker), HCl (37-38 %, J. T. Baker) and NaCN (> 97 %, Fluka).

Experimental Details

The standard catalyst was prepared as described in the literature.¹ The size of the gold cores was reduced by treatment of the Au@SiO₂ material with a leaching agent during step ii (Fig. 1). For this purpose, the as prepared Au@SiO₂ material was washed two times in water by centrifugation (10000 rpm, 30 min) and subsequently redispersed in water under ultrasonication for 30 minutes. For aqua regia treatment the colloid was dispersed in 15 g water and the ultrasonication bath was heated up to 80 °C. Following, fresh prepared aqua regia was added to the mixture and left under ultrasonication for 2 h. The amount of acid was 3 and 6 mL for resulting gold cores of 7 and 5 nm, respectively. After reaction the material was washed four times with water and two times with absolute ethanol by centrifugation and redispersion. Following, the SiO₂ surface was refunctionalized by redispersion in 19 g of ethanol and stirring at room temperature with 0.9 mL of ammonia solution for 1 h. For NaCN treatment, the as prepared Au@SiO₂ material was washed as described and subsequently aged in 30 g water for four days at room temperature. Afterwards, the NaCN solution (50 mg NaCN in 200 g water) was added according to the desired gold particle size. The solution was stirred at 30 °C for 60 h and following washed three times with water and twice with pure ethanol. Finally, the material was covered with a zirconia shell and the silica core was removed as described in the standard procedure.

The catalytic properties of the material were investigated in a fixed-bed reactor. Prior to catalytic measurement, the catalyst was stored under vacuum over night at 1·10⁻² mbar to remove the adsorbed water. The catalyst was introduced into a tube (5 mm internal diameter) and fixed with quartz glass wool at the bottom. The temperature was measured inside the catalyst bed by means of a thermocouple. The temperature inside the reactor was adjusted by flowing air through the reactor shell. The air is preliminary cooled by a bath of dry ice in isopropanol and subsequently electrically heated to the desired temperature. The catalytic measurements were carried out by heating the reactor from 0 °C to the final temperature with a heating rate of 2 K min⁻¹. During the temperature program, the composition of the product gas was permanently (interval of 5 s) analyzed by nondispersive IR absorption spectroscopy (EL3020, ABB). Three measurement runs were performed to activate the catalyst and reproduce the results of the activated catalyst. The first run was performed up to a temperature of 300 °C, while the following runs were stopped when a conversion close to 1 is reached.

References

1. P. M. Arnal, M. Comotti and F. Schüth, *Angew. Chem. Int. Ed.*, 2006, **45**, 8224-8227.