Synthesis of Au Nanoparticles Supported on MnO₂ Nanowires for High Performances in the Silane Oxidation

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Abstract

MnO₂ nanowires decorated with ultrasmall Au NPs showed high catalytic activities towards the green oxidation of silanes.

Introduction

Gold (Au) nanoparticles are known to be highly active towards a wide variety of heterogeneous catalytic transformations, including oxidation, reduction, C-C coupling reactions, and others. Among these transformations, silane oxidations are especially attractive as silanols are a key element in the production of silicon-containing materials. However, conventional routes for the silane oxidation generally require the presence of strong and toxic oxidants such as permanganate and dichromate. Here, we demonstrate that high catalytic performances (TOF = 590000 h⁻¹) could be achieved towards the green oxidation of silanes and H₂ production under ultralow Au loadings (0.001 – 0.0002 mol % in terms of Au) employing H₂O₂ as the oxidant, 25 °C as the reaction temperature, and MnO₂ nanowires decorated with ultrasmall Au NPs (having diameters of 3 nm or less) as catalysts.

Results and Discussion

The investigations started with the synthesis of MnO₂ nanowires (Figure 1) obtained by the hydrothermal method. The nanowires displayed well-defined shapes and uniform sizes, being 34 ± 5 nm in width and > 1 μm in length (Figure S1).

Figure 1. SEM images of MnO₂ nanowires employed as physical templates for Au deposition.

The MnO₂ nanowires could be directly employed as physical templates for the nucleation and growth of Au NPs over their surface without the need of any surface modification/functionnalization steps as depicted in Figure 2. Our approach employed AuCl₄⁻(aq) as the Au precursor, PVP as the stabilizer, BH₄⁻(aq) as the reducing agent, EG (ethylene glycol) as the solvent, and 90 °C as the reaction temperature. The uniform deposition (without agglomeration) of monodisperse, spherical, and ultrasmall (3 ± 1 nm) Au NPs over the entire surface of the MnO₂ nanowires could be clearly detected.

Figure 2. (A) Strategy for the synthesis of MnO₂ nanowires decorated with ultrasmall Au NPs. (B–E) HRTEM images of MnO₂–Au NPs.

In the next step, MnO₂ nanowires decorated with ultrasmall Au NPs were employed as heterogeneous catalysts towards the green oxidation of hydrosilanes and H₂ production. Surprisingly, high catalytic performances (TOF = 590000 h⁻¹) could be achieved towards silane oxidations. The MnO₂–Au NPs displayed good stability/recyclability, and no morphological changes or loss of activity were observed even after 10 reaction cycles.

Conclusion

We described the catalytic activity of MnO₂ nanowires decorated with ultrasmall Au NPs (towards the green oxidation of hydrosilanes, which produces silanols and hydrogen gas (H₂). Owing to their morphology comprised of ultrasmall Au NPs (3 nm), we found that the MnO₂–Au NPs displayed high catalytic performances under ultralow Au loadings (0.001 – 0.0002 mol %).

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