

CO oxidation over dumbbell like Au@Fe_xO_y nanoparticles: catalytic activity, thermal stability and effect of gold domain size

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Introduction

Catalysis by gold has been extensively studied since the pioneering work of Haruta¹ and CO oxidation has often been referred as a target reaction for gold catalysis.

Among different Au based materials, Fe_xO_y-supported gold catalyst represent one of the most active systems for low-temperature CO oxidation and dumbbell like Au@Fe_xO_y NCs represents an interesting example of Au based nanostructured materials. Indeed, in the dumbbells the epitaxial interface should enable a greater degree of charge transfer across the metal-metal oxide interface than in the case of metal oxide-supported metal NCs of more traditional catalysts, enhancing the catalytic activity². Additionally, the fact that the metal domain is typically nested in the oxide domain ensures structural stability and a high resistance to sintering of the metal domains, which is one of the main causes of deactivation in traditional catalysts. Sun et al.² pioneered the synthesis of dumbbell NCs and the exploitation of Au-Fe₃O₄ dumbbells as catalysts in the low-temperature CO oxidation in 2005. However, a deeper understanding of the properties of the dumbbell structure in CO oxidation was not yet fully exploited, as well as the effect of the gold domain size in this class of nanostructured materials.

The present contribution deals with a systematic study of the CO oxidation catalytic activity over dumbbell like Au@Fe_xO_y heterostructures as a function of the gold domain size.

Materials and Methods

Au@Fe_xO_y dumbbell nanocrystals with tunable Au domain size were prepared according to the method proposed by Sun et al.². First, Au NCs with different average diameter (namely 3, 6 and 12 nm) were synthesized by reduction of HAuCl₄ at different temperatures. Then, the Au NCs were reacted with Fe(CO)₅ in octadecene, oleylamine and oleic acid to grow dumbbell like Au@Fe_xO_y NC. The dimension of the iron oxide domain was kept constant for the three samples and equal to about 20 nm. The obtained heterostructures were deposited on gamma alumina (1% w/w Au) and loaded in a quartz flow microreactor. Catalytic activity tests in CO oxidation were carried out with 1% v/v CO, 6% v/v O₂ and balance helium at a GHSV of 3E+6 Ncc/h/g_{Au}. Catalytic tests were carried out in the 25-300°C temperature range according to a Temperature Programmed Reaction protocol (heating and cooling rate 2°C/min). Before each test the catalyst was treated in 6% v/v O₂ at 350°C for 1h.

Results and Discussion

CO oxidation catalytic activity for the 3nm Au@Fe_xO_y dumbbell NCs are presented in Figure 1A. In a typical test the temperature was first linearly increased from 25 to 300°C at a rate of 2°C/min, then the systems was cooled back to 100°C with the same rate. The linear increase of catalyst temperature resulted in a monotonically increase of the CO conversion, starting from 10% at ambient temperature and approaching complete conversion

around 200°C. During the cooling phase the conversion decreased with temperature, but higher values were recorder compared to the heating phase of the experiment. Such an hysteresis behavior is likely related to the formation of surface carbonates, in line with what reported in the literature for different gold based catalysts³. The same qualitative trend was observed independently from the Au domain size.

The performance of the three materials resulted to be extremely stable with time on stream. Both the dumbbell morphology and the gold domain size were unchanged upon multiple activation and catalytic tests, highlighting the excellent thermal stability of Au@Fe_xO_y dumbbells.

The effect of gold domain size on the CO conversion rate is shown Figure 1B. The highest rates were measured in the case of 6nm Au domain size, while no significant differences were measured between the 3 and 12 nm Au@Fe_xO_y dumbbells. The reasons of this trends are currently under investigation.

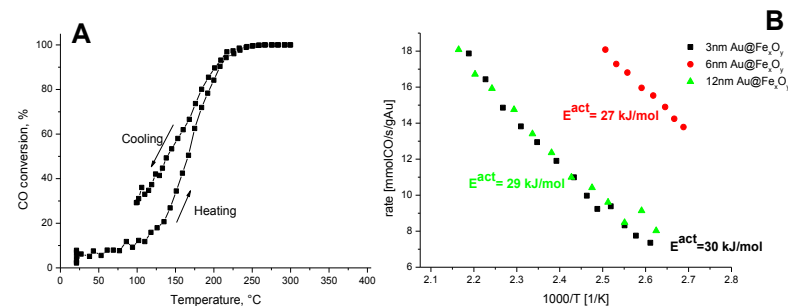


Figure 1. A: CO conversion as a function of temperature during TPR test for 3nm Au@FeO_x dumbbells. B: Arrhenius plot and apparent activation energy for Au@FeO_x dumbbells with different gold domain size. Data obtained during cooling phase.

Significance

Au@Fe_xO_y dumbbell nanocrystals exhibited good catalytic activity and excellent thermal stability for CO oxidation. The catalytic activity was Au size dependent, with an optimum performance for a gold domain size of 6nm.

References

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