Supporting Information

Generation of Gold Nanoclusters Encapsulated in MCM-22 Zeolite for Aerobic Oxidation of Cyclohexane

Lichen Liu,^a Raul Arenal,^{b,c,d} Debora M. Meira^e and Avelino Corma^{a*}

^a Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Av. de los Naranjos s/n, 46022 Valencia, Spain.
^b Laboratorio de Microscopias Avanzadas, Instituto de Nanociencia de Aragon, Universidad de Zaragoza, Mariano Esquillor Edificio I+D, 50018 Zaragoza, Spain
^cARAID Foundation, 50018 Zaragoza, Spain
^d Instituto de Ciencias de Materiales de Aragon, CSIC-Universidad de Zaragoza, C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain
^e European Synchroton Radiation Facility, 6 Rue Jules Horowitz, Grenoble, BP 156, F-38042, France

* Email: acorma@itq.upv.es

Experimental Section

1. Synthesis of Au@MCM-22-S and Au@MCM-22-L

The Au@MCM-22 sample was prepared according to our previous work, with some modifications. Firstly, subnanometric Au clusters were prepared by reduction of HAuCl₄ with N,Ndimethylformamide (DMF). 0.3 mL of 0.5 mol/L HAuCl₄ solution was dissolved in 200 mL DMF and then the solution was heated at 140 °C for 48 h. After being kept at 48 h, a yellow solution was obtained and the solution was cooled to room temperature and excess DMF was removed by rotary evaporator, until the volume of the DMF solution is ca. 15 mL.

1.1 Synthesis of Au@MCM-22-S

In order to prepare the swelled purely siliceous ITQ-1 with subnanometric Au species, 1.0 g of the lamellar precursor were dispersed in 12.0 g of H₂O milliQ, and 20.0 g of a cetyltrimethylammonium hidroxide solution (50 wt.%, 50% exchanged Br⁻/OH⁻) and 6.0 g of a solution of tetrapropylammonium hidroxide (40 wt.%, 50% exchanged Br⁻/OH⁻) were added together with 15 mL of the DMF solution containing Au species. The resultant mixture was heated at 52 °C under stirring vigorously for 16 hours in order to facilitate the swelling of the layers of the precursor material. At this point, the solid was recovered by centrifugation. Finally, the solid product was dried in an oven at 60 °C. Afterwards, the swelled sample containing subnanometric Au species was calcined in air to remove the organic templates and surfactants. The calcination process was performed as following: 1) increasing the temperature from room temperature to 550 °C with a rate of 2 °C/min in N₂ atmosphere. The total time in N₂ atmosphere is about 4.5 h. 2) switching the atmosphere to air and keeping the temperature at 550 °C for 4 h. 3) Cooling down from 550 °C to room temperature in air.

1.2 Synthesis of Au@MCM-22-L

In order to prepare the swelled purely siliceous ITQ-1 with subnanometric Au species, 1.0 g of the lamellar precursor were dispersed in 12.0 g of H₂O milliQ, and 20.0 g of a cetyltrimethylammonium hidroxide solution (50 wt.%, 50% exchanged Br/OH⁻) and 6.0 g of a solution of tetrapropylammonium hidroxide (40 wt.%, 50% exchanged Br/OH⁻) and 1.0 mL of 1-octanethiol were added together with 15 mL of the DMF solution containing Au species. The resultant mixture was heated at 52 °C under

stirring vigorously for 16 hours in order to facilitate the swelling of the layers of the precursor material. At this point, the solid was recovered by centrifugation. Finally, the solid product was dried in an oven at 60 °C. Afterwards, the swelled sample containing subnanometric Au species was calcined in air to remove the organic templates and surfactants. The calcination process was performed as following: 1) increasing the temperature from room temperature to 550 °C with a rate of 2 °C/min in N₂ atmosphere. The total time in N₂ atmosphere is about 4.5 h. 2) switching the atmosphere to air and keeping the temperature at 550 °C for 4 h. 3) Cooling down from 550 °C to room temperature in air.

2. Characterizations

High-resolution STEM images were obtained using a High Angle Annular Dark Field detector (HAADF), which allows Z-contrast imaging. The powder sample was dispersed in ethanol and then dropped on Cu grid. The high-resolution STEM measurement was performed on FET Titan low-base microscope at 300 kV equipped with a Cs probe corrector, a monochromator and an ultrabright X-FEG electron source. The convergence angle was 25 mrad and the inner and outer angles for HAADF imaging were 70 and 200 mrad, respectively.

X-ray absorption near-edge structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) at Au L₃-edge (11919 eV) and Pd K-edge (24350 eV) were carried out on BM23 at European Synchrotron Radiation Facility (ESRF). A double crystal monochromator equipped with a pair of Si (111) crystals was used. Si and Pt mirrors with an angle of 2 mrad were used to reject the harmonics, for Au and Pd, respectively. Data was collected in fluorescence mode using a Si drift detector. The samples were prepared as self-supported pellets and measured at room temperature. A corresponding metallic foil reference was collected simultaneously for energy calibration. EXAFS oscillations were extracted using Athena code and analysed using Arthemis software. The range used to transform the EXAFS oscillations ($k^2 \chi(k)$) was $\Delta k = (3-11) \text{ Å}^{-1}$ and the fits were performed in the interval $\Delta R = (1.7-3.3) \text{ Å}$. The local environment of the Au atoms was determined using the phase shift and amplitude functions for Au-Au calculated for gold foil. The photoelectron energy origin correction (ΔE_0), the passive electron amplitude reduction factor (S_0^2) were found for the Au standard and used as fixed parameters to fit the samples. For each contribution a coordination number (N_i) and a distance (R_i) were fitted independently while the mean square relative displacement (σ_i^2) were set to be the same for both samples.

3. Catalytic measurements for aerobic oxidation of cyclohexane

The aerobic oxidation of cyclohexane was carried out in batch reactor. 2 mL of cyclohexane (~1.6 g) and 25 mg solid catalyst was mixed and the reactor was flashed with O_2 several times. The reaction was performed at 150 °C with 10 bar of O_2 . 50 µL of liquid mixture was taken out of the reactor and mixed with 1 mL of acetone at different reaction time. 100 uL of triphenylphosphine solution (10 wt%) and 7.3 mg of dodecane as internal standard was then added to the acetone solution with agitation of 5 min. The reaction products were analyzed by Varian GC (CP3800) with HP-5 column with a length of 30 m and diameter of 0.25 mm. The injector temperature was 250 °C and detector temperature was 300 °C. Helium was used as carrier gas with a flow of 2 mL/min and a split ratior of 40. 1.0 µL of liquid was injected into the column.

In order to quantify the yield of adipic acid, esterification reaction with methanol was carried out to transform adipic acid into dimethyl adipate. 50 uL of the reaction mixture was mixed with 200 mg of 10% of boron trifluoride-methanol solution (~1.3 M, from Fluka) and kepted at 80 °C for 1.5 h. After the esterification reaction, 0.8 g of H₂O and 2.0 g of CH₂Cl₂ was added to the mixture. After extraction, the organic layer was injected to the GC for analysis.



Fig. S1. High-resolution STEM images of Au@MCM-22-S sample. (a, b) STEM image of a single Au atom and the corresponding contrast profile of a single Au atom. (c, d) STEM image of Au₂ cluster and the corresponding contrast profile. (e, f) STEM image of Au₁₂ cluster and the corresponding contrast profile. (g, h) STEM image two Au clusters with less than 10 atoms.



Fig. S2. STEM images of AuNP/MCM-22 sample prepared by deposition-precipitation method. The size of Au nanoparticles is mostly between 1-2 nm.



Fig. S3. UV-vis spectra of MCM-22, AuNP/MCM-22 and two Au@MCM-22 samples containing Au nanoclusters.



Fig. S4. Distributions of products in the oxidation of cyclohexane by Au@MCM-22-S sample. Reaction conditions: 2 mL cyclohexane, 25 mg solid catalyst, 150 °C, 10 bar of O₂.



Fig. S5. Recycle tests of Au@MCM-22-L sample for oxidation of cyclohexane. (a) Conversion of cyclohexane and the corresponding distributions of products in three cycles: (b) first cycle, (c) second cycle and (d) third cycle. Reaction conditions: 2 mL cyclohexane, 25 mg solid catalyst, 150 °C, 10 bar of O_2 . After each test, the solid catalyst was recycled by filtration and then washed with acetone, before being used for another catalytic test.



Fig. S6. Yields of various products at different conversion of cyclohexane when using Au@MCM-22-L as the catalyst. (a) first cycle, (b) second cycle and (c) third cycle. Reaction conditions: 2 mL cyclohexane, 25 mg solid catalyst, 150 °C, 10 bar of O_2 . After each test, the solid catalyst was recycled by filtration and then washed with acetone, before being used for another catalytic test.



Fig. S7. Catalytic test of Au@MCM-22-S and Au@MCM-22-L using the same amount of Au. The molar ratio of cyclohexane/Au was kept the same for both tests. Reaction conditions: 2 mL cyclohexane, 150 °C, 10 bar of O₂.



Fig. S8. Selectivity and yield of different products for the aerobic oxidation of cyclohexane with small amount of Au@MCM-22-L as the catalyst. The reaction conditions are the same as described in Fig. S6: 2 mL cyclohexane, 150 °C, 10 bar of O₂.



Fig. S9. Aerobic oxidation of cyclohexane by Au@MCM-22-L in the presence of initiator and the corresponding control reaction without addition of Au@MCM-22-L catalyst. As can be seen in this figure, in the presence of initiator (tert-Butyl hydroperoxide, TBHP, 0. 25 mol% to cyclohexane), the aerobic oxidation of cyclohexane can be initiated in a shorter induction period than 5 mg of Au@MCM-22-L. Furthermore, when both Au@MCM-22-L and TBHP are used as the catalyst, the aerobic oxidation of cyclohexane can occur immediately, indicating the high activity of Au@MCM-22 for initiating the radical reaction.



Fig. S10. Product distributions of the aerobic oxidation of cyclohexane in the presence of initiator. (a) ~0.25 mol% of TBHP and (b) ~0.25 mol% of TBHP and 5 mg of Au@MCM-22-L. Reaction conditions: 2 mL of cyclohexane, 150 °C and 10 bar of O_2 .



Fig. S11. STEM images of Au@MCM-22-L sample after three consecutive cycles of oxidation of cyclohexane. Au clusters with size of ~1 nm and some subnanometric Au clusters can be seen in these images.