#### **Electronic Supplementary Materials (ESI)**

# Ordered, Extra-Large Mesopores with Highly Loaded Gold Nanoparticles: A New Sinteringand Coking-Resistant Catalyst System

Xiaoqing Yan,<sup>a</sup> Xiaojuan Wang,<sup>a</sup> Yu Tang,<sup>a</sup> Guicen Ma,<sup>a</sup> Shihui Zou,<sup>a</sup> Renhong Li,<sup>a</sup> Xiaogang Peng,<sup>a</sup>

Sheng Dai,<sup>b</sup> and Jie Fan\*<sup>a</sup>

<sup>a</sup>Key Lab of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou, Zhejiang Province 310027, China

<sup>b</sup>Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

## **Experimental and Characterization:**

## Silica Supports:

*FDU-12(12,9)*: 0.50 g of triblock copolymers  $EO_{106}PO_{70}EO_{106}$  (Pluronic F127), 0.60 g of 1,3,5-trimethylbenzene (TMB) and 2.5 g of KCl were dissolved in 30 ml of 2 M HCl at 25 ± 0.1 °C. After 1h stirring, 2.08 g of tetraethyl orthosilicate (TEOS) was added to this solution. The synthesis composition F127/KCl/TEOS/TMB/HCl/H<sub>2</sub>O (in molars) was 0.00256/2.166/0.645/0.323/3.87/100 (Fan, J. *et. al.*, Angew. Chem.Int. Ed., 2003, 42, 3146). After stirring for 24 h at 25 ± 0.1 °C, the mixture was transferred into an autoclave and heated at 140°C for 24 h. As-made product was obtained by filtration and dried at room temperature in air. The organic templates were removed by microwave digestion as described by Tian et. al.(Tian, B. Z. *et al. Chem. Commun.*, 2002, 1186). The detailed process was conducted as follows: 0.3 g of as-made FDU-12 sample was mixed with 2mL 30% H<sub>2</sub>O<sub>2</sub> and 5mL 15M HNO<sub>3</sub> in a 30 mL Teflon sample vessel. The system was operated at approximately 800W. The operation pressure of the digestion process was maintained at 1.0 MPa for 10 minutes. The sample after microwave digestion was washed by water for three times and dried for use.

*EP-FDU-12(36,11)*: 0.50 g of Pluronic F127, 0.60 g of TMB and 1.25 g of KCl were dissolved in 50 ml of 1 M HCl at  $14 \pm 0.1$  °C.After 1 h stirring, 2.08g of TEOS was added to this solution. The synthesis composition (in molars) F127/KCl/TEOS/TMB/HCl/H<sub>2</sub>O was 0.00147/0.62/0.37/0.185/1.85/100. After stirring at 14 °C for 24 h, the mixture was transferred into an autoclave and heated at 140 °C for 24 h. Then the products was obtained by filtration and dried at room temperature in air. The organic templates were removed by microwave digestion.

*SBA-15*: 2 g of P123 and 1.5 g of KCl were dissolved in 60 mL of 2.0 M HCl at 40 °C. To this solution, 4.35 mL of TEOS was added under vigorous stirring. After 1 h, the mixture stood statically

and was aged for 24 h, and then transferred into an autoclave and heated at 140 °C for another 24 h. The solid products were collected by filtration, washed with water, and dried at room temperature in air. The organic templates were removed by microwave digestion.

# Synthesis of AuNPs:

100 mg of AuPPh<sub>3</sub>Cl was mixed with 400  $\mu$ L of dodecanethiol in 20 mL of benzene to form a clear solution, to which 84 mg of NaBH<sub>4</sub> was then added in one portion. The mixture was heated with stirring at 55 °C for 7 h before the reaction system was cooled to room temperature. AuNPs were precipitated out from the reaction mixture as black solid powder by addition of 20 mL of ethanol. The precipitate was separated by centrifuge, washed with ethanol. Finally, the precipitate was dried naturally.

#### AuNPs/SiO<sub>2</sub>:

AuNPs was loaded into SiO<sub>2</sub> supports by a colloid deposition method. Desired amount of AuNPs were dissolved in 25 mL of chloroform. To this solution, desired amount of SiO<sub>2</sub> was added. After 30 min stirring, the solid product was centrifuged and dried in air. The AuNPs/SiO<sub>2</sub> was calcined at 350  $^{\circ}$ C~650  $^{\circ}$ C for 5 h (in air) to evaluate their anti-sintering properties and catalytic performance.

#### Measurement and Characterization:

Nitrogen adsorption isotherms were measured at -196 °C on a Micromeritics ASAP 2020 adsorption analyzer. Before the adsorption analysis, calcined samples were outgassed under vacuum at 200 °C in the port of the adsorption analyzer. X-ray diffraction patterns were recorded on a Ragaku Ultima IV diffractometer using CuK $\alpha$  radiation. HAADF-STEM images were recorded on the TECNAI G2 F20 operated at 200 KV. The sample was embedded in epoxy resin, and then microtomed into sub-100-nm ultra thin film at room temperature. These thin film samples floated on water or other solvents were collected by copper mesh with polymer micro grid for TEM imaging.

#### Catalytic Oxidation of Cyclohexanol:

The oxidation of cyclohexanol was carried out in a fixed bed vertical glass reactor (h = 250 mm, d = 12 mm), fitted with a glass frit carrying the catalyst mixed with quartz sand and provided with an electronically controlled furnace. The oxygen stream (8 mL/min) was controlled by a mass flow instrument and the liquid reagent (0.9 mL/h) was supplied through a syringe pump. Liquid vaporisation occurred on the reactor wall prior to the catalytic bed. The products were analyzed by GC. The selectivity was calculated as mol of produced cyclohexanone per mol of reacted cyclohexanol and the carbon mass balance > 99 % in the case of selectivity > 99.5%.



Fig. S1 Nitrogen sorption isotherms of AuNPs/EP-FDU-12 samples with different metal loadings.

Table S1 Physicochemical	properties of AuNPs/EP-FDU-12 sat	nples with different metal loadings.
<b>Lubic</b> SI i hybreochenneu		inples with anterent metal loudings

			-	
Samples	Dc <sup>a</sup> (nm)	Dw <sup>b</sup> (nm)	$Pv^{c}$ (cm <sup>3</sup> /g)	$S_{BET}^{d}(m^2/g)$
0	27.3	9.6	1.04	422
1.0%	25.6	9.7	0.98	373
6.2%	28.1	9.5	0.81	303
14.4%	32.5	8.8	0.72	278
20.8%	32.5	9.8	0.68	278

<sup>*a*</sup> Cage size, calculated from the adsorption branches of the N<sub>2</sub> sorption isotherms based on the BdB sphere model; <sup>*b*</sup> Window size, calculated from the desorption branches of the N<sub>2</sub> sorption isotherms based on the BdB sphere model; <sup>*c*</sup> pore volume. <sup>*d*</sup> BET surface area.

# **Eliminate Diffusion Effect:**

Two different mass of the gold catalysts were filled into two fixed bed vertical glass reactors with the same cross section area. The flow rate of cyclohexanol (from 0.15 to 1.2 ml/h) and the velocity of oxygen stream (from 1.2 to 18.4 mL/min) is changed to ensure the same contact time for two catalyst system during the reaction process. The tests were performed at 200 °C. The similar activities for the selected two catalysts during this test suggest that the diffusion effect has been eliminated under these reaction conditions.



**Fig. S2** The impacts of contact time on the conversion of cyclohexanol based different catalysts a) 9.1wt% AuNPs/EP-FDU-12(36,11); b) 16.7wt% AuNPs/EP-FDU-12(36,11).



**Fig. S3** TOF variations of supported AuNPs in gas-phase cyclohexanol selective oxidation carried out at different temperatures using various loading amount of AuNPs/EP-FDU-12(36,11) as the catalysts (selectivity > 99.5%).



**Fig. S4.** XPS peaks of a) Au4f, b) Cl2p, c) S2p and d) P2p of 16.7 wt% AuNPs/EP-FDU-12(36,11).



**Fig. S5.** a) XRD patterns of supported AuNPs (the average crystal size is calculated by Scherrer's equation based on the peak width of Au(111) reflection), and b) The crystallite size of AuNPs/EP-FDU-12(36,11) after thermally aging at 650  $^{\circ}$ C in air for 5 h with different Au loading amount.



**Fig. S6** TGA curves of 16.7wt% and 4.8wt% AuNPs catalysts after gas-phase cyclohexanol selective oxidation. The reaction time is listed after the comma, and the coking content is calculated based on the weight loss between 300  $^{\circ}$ C and 700  $^{\circ}$ C.