

Supporting Information

Aerobic oxidation of 5-hydroxymethylfurfural with homogeneous and nanoparticulate catalysts

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1. Experimental

Materials:

5-hydroxymethylfurfural, 2,5-furandicarboxylic acid, $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, trifluoroacetic acid, glacial acetic acid, NaBr and methanol were purchased from Sigma-Aldrich and used as received. 5-formyl-2-furancarboxylic acid and 2,5-diformylfuran were purchased from TCI and used for calibration without further purification. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were obtained from Thomas Baker, India and Sigma-Aldrich, respectively.

HMF oxidation

HMF oxidation under atmospheric oxygen pressure was carried out in a three neck round bottom flask equipped with a condenser, oil bath and a stirrer-cum-hot plate. After the temperature of the oil bath reached to the desired temperature, all reagents were added into the flask and start the reaction at constant flow rate of oxygen and stirring rate. After the reaction for the desired time,

100 μL of aliquot was diluted to 1 mL in methanol. The diluted solution was then analyzed using a GC (Agilent Technology, model 6890N) equipped with a FID detector and DB-5 column of dimension 30m x 250 μm x 0.25 μm . The oxidation products were identified by their retention times in comparison with authentic samples. Each peak of the GC chromatogram was properly integrated and the actual concentration of each component was obtained from the pre-calibrated plot of peak area against concentration. The oxidation reaction under high oxygen pressure and high temperature was carried out using a Parr reactor (model 5000 multi reactor heating/stirrer system). For the oxidation reaction in Parr reactor, the reactor was loaded with all reagents, sealed and pressurized with pure oxygen. After the reaction for the desired time, the reactor was cooled to room temperature, diluted aliquot in methanol by 10 times and analyzed by GC.

Preparation of Au-CeO₂

The nanosized CeO₂ support was prepared by precipitation method from a basic solution of cerium nitrate hexahydrate, Ce(NO₃)₃.6H₂O (Thomas Baker, India). The solution was prepared by dissolving the nitrate salt in distilled water and adding 25% aqueous NH₃ solution under vigorous stirring until the pH of the solution reached to 10. The precipitated Ce(OH)₃ was filtered out, washed with distilled water, dried at 110 °C for 8 h and finally calcined at 500 °C for 4 h in air.

Au was deposited on the nanoparticulate cerium oxide by the following procedure: a solution of 80 mg of HAuCl₄.3H₂O in 10 ml of deionized water was brought to pH 10 by adding 0.2 M NaOH solution. After stabilizing the pH, the solution was added to a slurry containing colloidal CeO₂ (1.0 g) in H₂O (10 ml). After readjusting the pH to 10, the slurry was vigorously stirred for 10 h at room temperature. The Au-CeO₂ solid was then centrifuged and washed with distilled water until no traces of chlorides were detected by the AgNO₃ test. The material was dried at

room temperature for overnight and calcined at 300 °C for 4 h. The total Au content of the final catalyst was 1.90% as determined by EDX analysis.

Preparation of Au-TiO₂

Self-assembled TiO₂ nanoparticles were synthesized using salicylic acid as a template according to the method described in reference: Astam K. Patra, Swapan K. Das, Asim Bhaumik, *J. Mater. Chem.*, 2011, 21, 3925-3930.

Au was deposited on the nanoparticulate TiO₂ by the following procedure: a solution of 60 mg of HAuCl₄·3H₂O in 10 ml of deionized water was brought to pH 7 by adding 0.2 M NaOH solution. After stabilizing the pH, the solution was added to a slurry containing colloidal TiO₂ (1.0 g) in H₂O (10 ml). After readjusting the pH to 7 with NaOH, the slurry was vigorously stirred for 10 h at room temperature. The Au-TiO₂ solid was then centrifuged and properly washed with distilled water until no traces of chlorides were detected by the AgNO₃ test. The catalyst was dried at room temperature for overnight and calcined at 300 °C for 4 h. The total Au content of the final catalyst was 1.42% as determined by EDX analysis.

BET Surface area measurement:

BET surface area of the metal oxide supports were measured by nitrogen sorption isotherms using a Beckmann Coulter SA3100 surface area analyzer at 77 K. Prior to the measurement, the samples were degassed at 393 K for 12 h. The measured surface area of TiO₂ support (250 m² g⁻¹), prepared by soft-templating synthesis using salicylic acid template, was significantly higher than that of CeO₂ support (72 m² g⁻¹). CeO₂ was prepared by hydroxide precipitation method using ammonium hydroxide.

Table S1 Aerobic oxidation of HMF with Au/TiO₂ and Au/CeO₂ catalysts in the presence and absence of HTFA additive under the reaction conditions of $p_{\text{oxygen}} = 10$ bar, $T = 130$ °C and reaction time = 3 h.

Expt #	Catalyst	HMF/Catalyst	HTFA, %	HMF Conv. %	FFCA yield, %
1	Au-TiO ₂	20	0	62	45
2	Au-TiO ₂	21	1	84	79
3	Au-CeO ₂	18	0	29	17
4	Au-CeO ₂	20	1	83	71

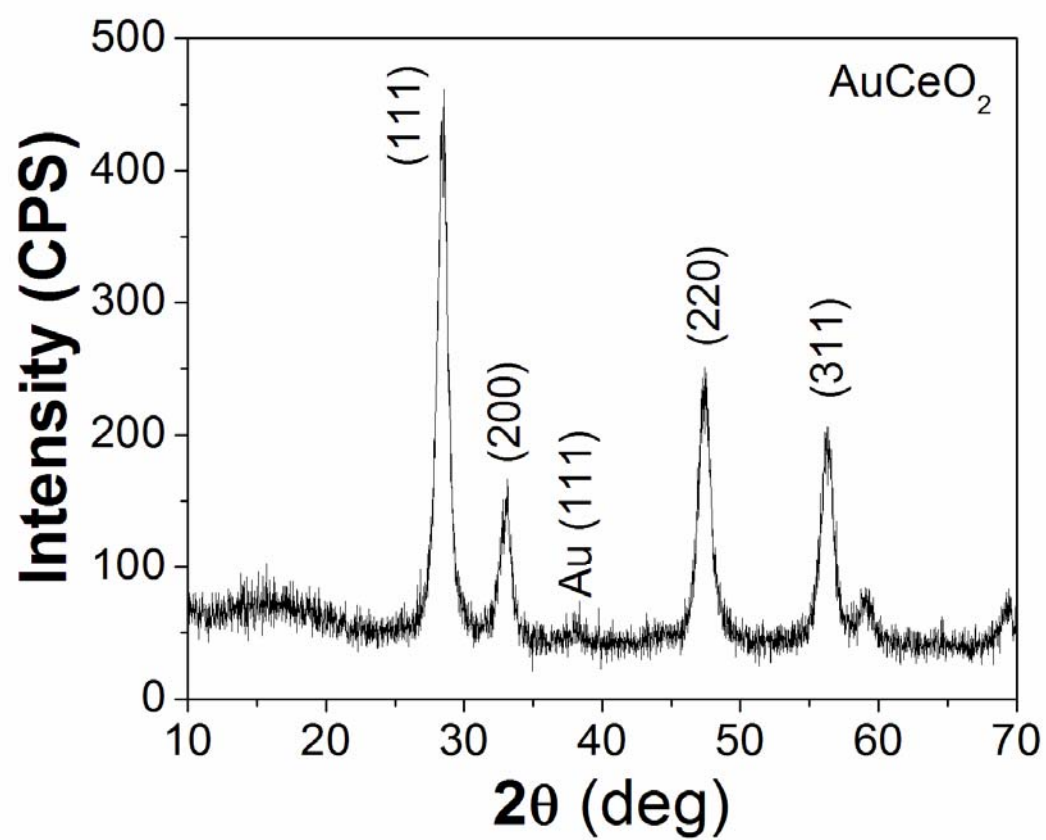


Figure S1 Powder X-ray diffraction of Au-TiO₂ nanoparticulate material.

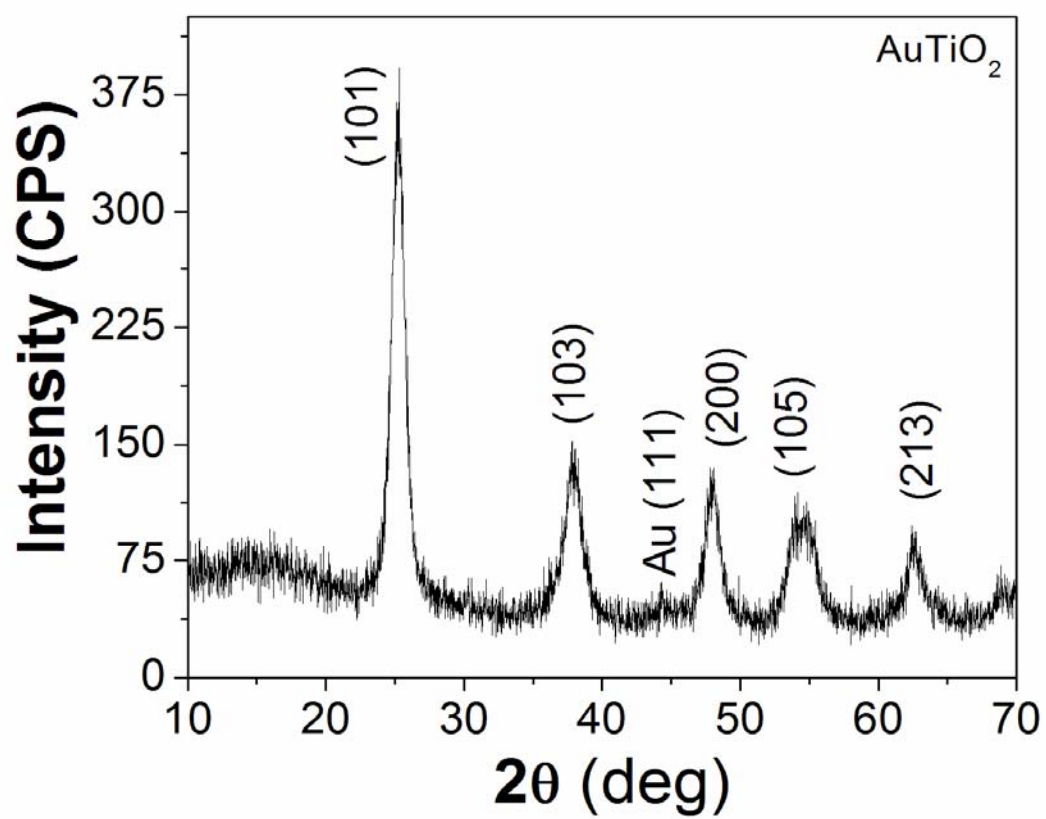


Figure S2 Powder X-ray diffraction of Au-CeO₂ nanoparticulate material.

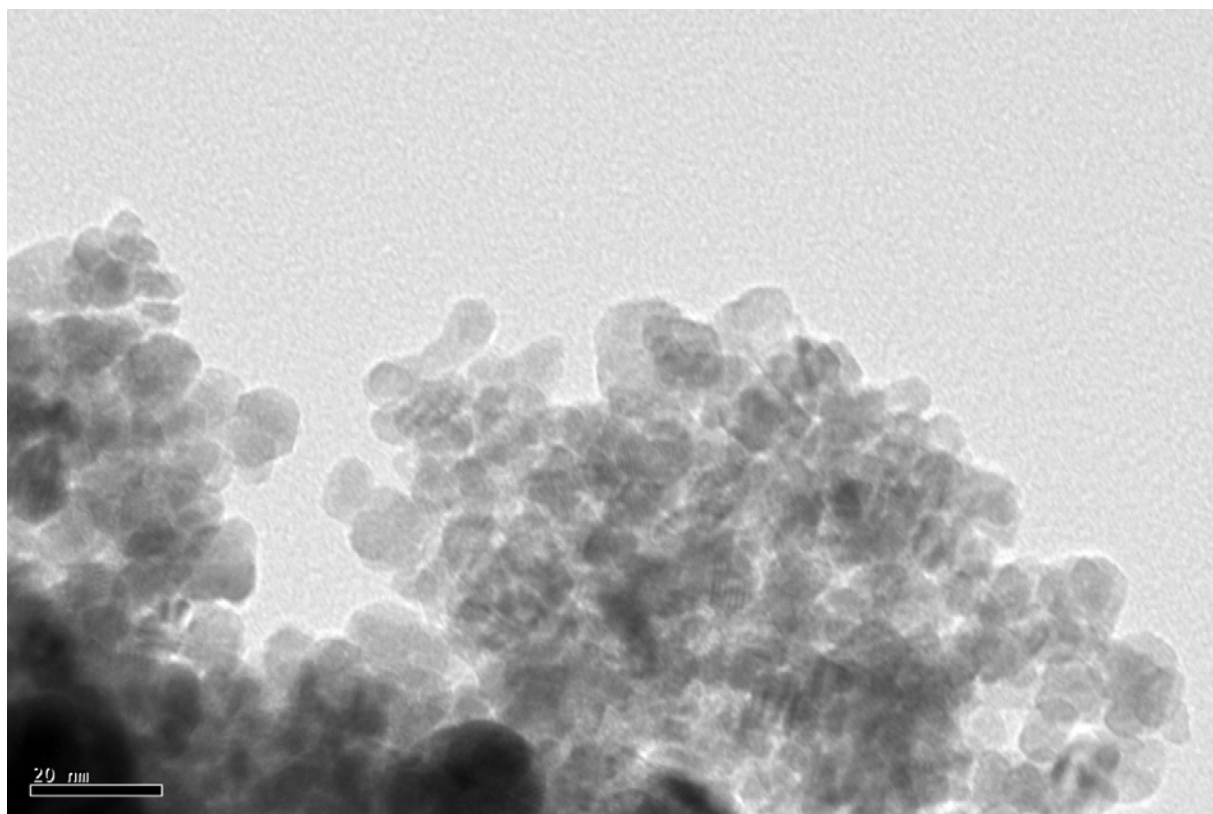


Figure S3 HR-TEM image of Au-TiO₂ material. The particle size of TiO₂ support ranges 12-20 nm size with Au loading of 1.42%.

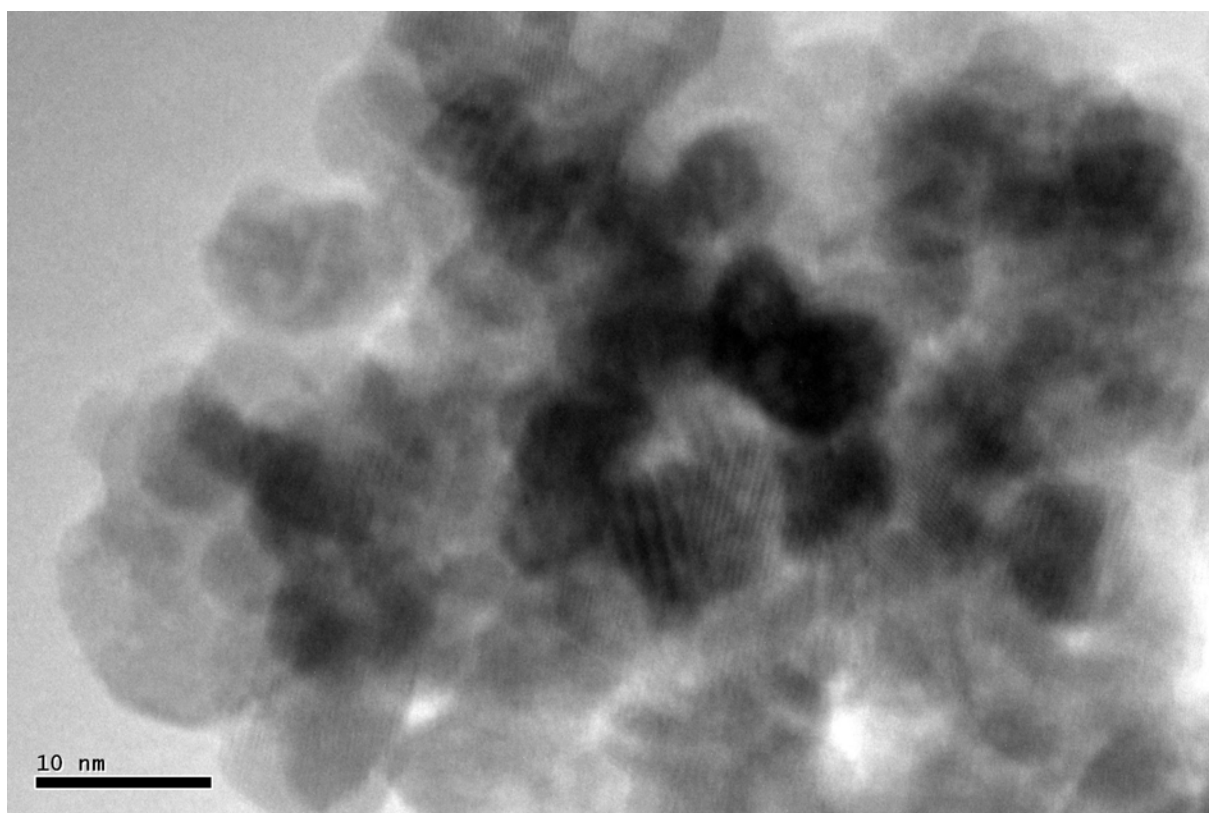


Figure S4 HR-TEM image of Au-CeO₂ material. The particle size of CeO₂ support ranges 6-10 nm size with Au loading of 1.90%.