Supporting Information for

Selective aerobic oxidation of cyclic ethers to lactones over Au/CeO_2 without any additives

Shulin Liu[a,b], Shaopeng Li[a,b], Xiaojun Shen[a,b], Yanyan Wang[a,b], Juan Du[a,b], Bingfeng Chen*[a], Buxing Han[a,b] and Huizhen Liu* [a,b]

[a]Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Colloid and Interface and Thermodynamics Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. Email: chenbf@iccas.ac.cn, liuhz@iccas.ac.cn
[b]University of Chinese Academy of Sciences, Beijing 100149, P. R. China.

1. Experimental

1.1 Chemicals

Material: The reagents tetrahydrofuran (99.8%, HPLC grade, unstabilized, Acros chemicals), Tetrahydrofuran-D8 (99.5atom%D, NMR grade, Acros chemicals), $HAuCl_4 \cdot 4H_2O$ (99.999%, Across chemicals), 2-methyltetrahydrofuran (99%), phthalide (99%) were purchased from Innochem Chemical Reagent Company. tetrahydropyran (98%), δ-valerolactone (98%), isochromanone (98%) were bought from TCI. 2-Hydroxytetrahydrofuran (>95%) was purchased from Accela. γ-valerolactone (98%), $Ce(NO_3)_3 \cdot 6H_2O$ (99.5%), D_2O (99.8%) and n-decane (98.5%) were purchased from J&K Company. γ-butyrolactone (≥99%, AR grade) was obtained from Aladdin. Propyl formate (97%) and phthalan (98%) was brought from Alfa Aesar. Butylated hydroxytoluene (BHT) (99.8%) and isochroman (99%) was purchased from Acros. NaOH (99.9%, AR grade), ethanol (99.8%, AR grade) were bought from Beijing Chemical Reagent Factory. H_2 (>99.99%) was supplied by hydrogen generator (HG-1000). All the chemicals were used as received without any further purification.

1.2 Preparation of the catalysts

Synthesis of CeO_2 nanorods

CeO_2 nanorods were prepared by the hydrothermal method as reported before with some modifications.[1] In a typical experimental, 0.868g $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in 5 mL deionized water, and then 35 mL of 11M NaOH aqueous was added dropwise into the solution. After vigorously stirred at room temperature, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave, followed by hydrothermal treatment at 100°C for 24 h. After being cooled to room temperature, the white precipitate was separated by centrifugation, washed with ethanol and deionized water for several times, and then dried in an oven at 60°C over-night. Finally, the pale-yellow solid was grinded into powder.

Synthesis of Au/CeO_2

The Au/CeO_2 catalyst was prepared by impregnation method. 200 mg above-prepared CeO_2 powders was dispersed into 20 mL of deionized water, which was mixed with appropriate amount of $HAuCl_4$ solution. After being vigorously stirred at room temperature under the condition of avoiding light for 10 h, the deionized water was removed from the dispersion by vacuum-rotary evaporation at 80°C. The obtained pale-yellow powder was calcined at 300°C for 2 h under pure H_2 flow.

1.3 Catalytic activity tests

The reaction was carried out in a Teflon-lined stainless-steel reactor of 16 mL with a magnetic stirrer. In a typical experiment, 2 mL THF and the desired amount of catalyst were added into the reactor. The air in the reactor was replacement with O_2 for 3 times and then the reactor was pressurized with O_2 to certain pressure. The reactor was put into an air bath at desired temperature. After a certain reaction time, the autoclave was placed into an ice-water mixture, cooled to room temperature, and a known amount of internal standard n-decane was then added to the reactor. Then the reaction solution was centrifuged for GC analysis. The reaction experiments of other substrates are exactly the same as those mentioned above.

Reusability of the catalyst

After the reaction, the reaction mixture was centrifuged and the solid Au/CeO_2 catalyst was recovered, followed by rinsing with THF (3 × 30 mL). The Au/CeO_2 catalyst was reused directly for the next run after drying at 60 °C for 12 h in a vacuum oven.

1.4 Mechanism investigation

H-D exchange experiment

The reaction was carried out in a Teflon-lined stainless steel reactor of 16 mL. 24 mmol (2 mL) THF and 10 mmol D_2O were added into three reactors. And then, the air in the first reactor was replacement with O_2 for 3 times and then pressurized with O_2 to certain pressure, and appropriate amount of CeO_2 and Au/CeO_2 was added into the other two reactors respectively under the nitrogen atmosphere. Then the reactor was put into an air bath at desired temperature. After a certain reaction time, the autoclave was placed into an ice-water mixture, cooled to room temperature. The products were conducted GC/MS analysis finally.

Deuterium dynamics experiment

The procedure of deuterium dynamics experiment was similar to that of catalytic activity test. The only difference is that THF was replaced by THF-D8 in the reaction.

1.5 Characterization

The powder X-ray diffraction spectra (Power XRD) measurements were performed on a Philips X' pert MPD instrument using Cu Kα radiation (50 kV). Transmission electron microscopy (TEM) images were obtained on using a JEOL-7700 electron microscope at an acceleration voltage of 100 kV. The high resolution TEM images of the catalysts were obtained using a JEOL-2100F electron microscope operated at 120 kV. The contents of different elements in the Au/CeO_2 catalysts were analyzed by ICP-AES (PROFILE. SPEC, Leeman). X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromatic Al Kα radiation. The hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. The electron paramagnetic resonance was carried on the JES-FA-200 EPR spectrometer equipped with a high-pressure mercury lamp USH-500SC as light source. The products were analyzed quantitatively by gas chromatograph (Agilent 7890B) equipped with a flame ionization detector (FID).

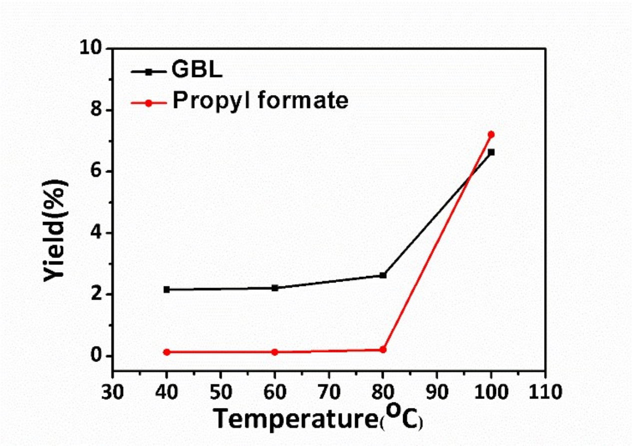


Fig. S1 Temperature curve without catalyst.

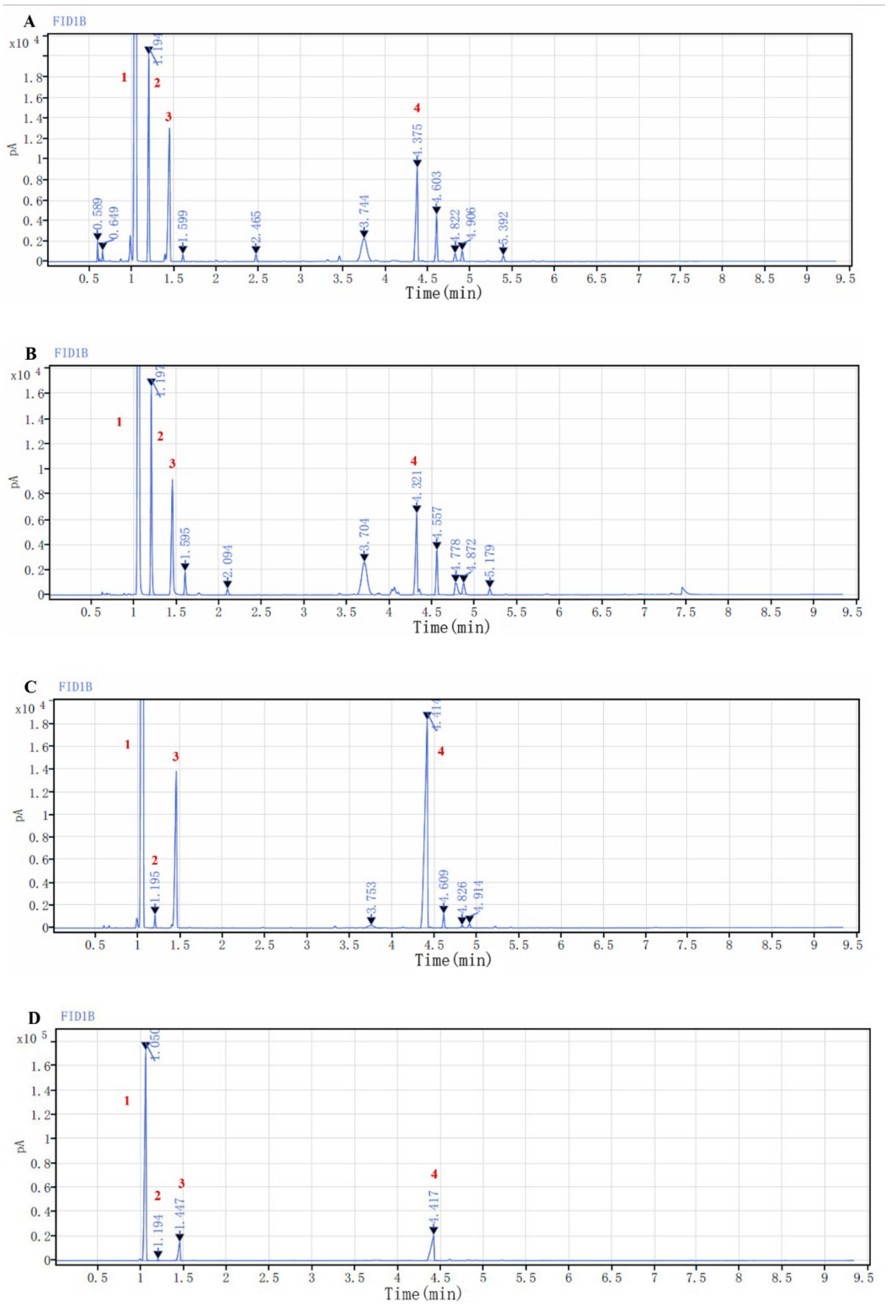
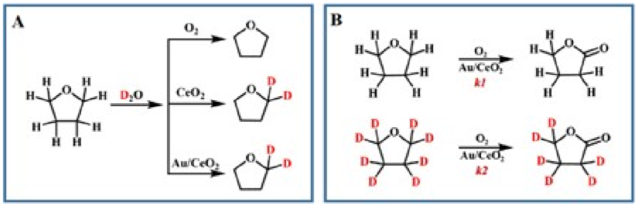


Fig. S2 The GC of liquid products after the reaction. Reaction Conditions: Reaction conditions: THF (2 mL), catalyst (20 mg), t (6 h), PO_2(1MPa) and stirring speed (600 rpm) with n-decane as internal standard. A, without any catalyst, T (100℃); B, CeO_2, T (100℃); C, Au/CeO_2, T (100℃); D, T (120℃).1-THF; 2-propylformate; 3-n-decane; 4-GBL.



Scheme S1 H-D exchange (A) and deuterium dynamics experiments (B).

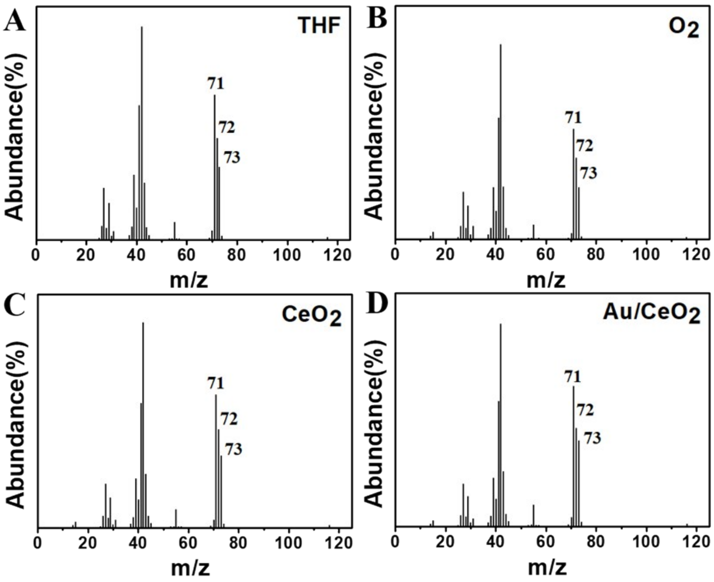
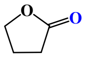
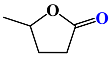
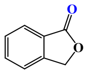
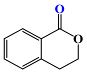
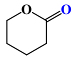


Fig. S3 Isotope abundance of THF in H-D exchange experiment. Reaction conditions: D_2O (10 mmol), T (100°C), t (6 h) and stirring speed (600 rpm). (A) THF (2 mL), (B) THF (2 mL), PO_2(1 MPa), (C) THF (2 mL), CeO_2(20 mg), (D) THF (2 mL), Au/CeO_2(20 mg).

The isotope abundance of m/z 73 can be calculated using the following formula:

$$Isotope\ abundance\ of\ 73\ = \frac{m/z\ of\ 73}{m/z\ of\ 73 + m/z\ of\ 72 + m/z\ of\ 71}$$

Table S1 Au/CeO$_2$-catalyzed aerobic C-H oxidation of different ether substrates [a]

Product					
Yield[b](%)	13.7%	9.0%	26.2%	49.3%	2.2%
Selectivity[c](%)	90.5%	27.3%	94.7%	91.8%	70.0%

[a] Reaction conditions: substrate (2 mL), catalyst (20 mg), T (100℃), t (6 h), PO_2(1MPa) and stirring speed (600 rpm). [b] Yield of product was determined by GC with n-decane as internal standard. [c] Selectivity based on the peak area of all the products detected.

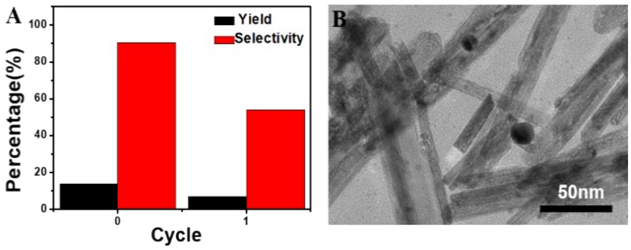


Fig. S4 (A) Reusability of Au/CeO_2 under the optimized conditions. (B) TEM images of the catalyst after the first cycling.

References:

1 X. G. Liu, K. B. Zhou, L. Wang, B. Y. Wang and Y. D. Li, *J. Am. Chem. Soc.*, 2009, 131, 3140-3141.