

CHEMISTRY 
A EUROPEAN JOURNAL

Supporting Information

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Aqueous Room Temperature Gold-Catalyzed Chemoselective Transfer Hydrogenation of Aldehydes

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Experimental Details

Catalytic materials

Gold catalysts including 1.5 wt% Au/TiO₂ (type A, lot no. Au/TiO₂ no. 02-1), 4.5 wt% Au/Fe₂O₃ (type C, lot no. Au/Fe₂O₃ no. 02-5) and 0.8 wt% Au/C (type D, lot no. Au/C no. 38D) were supplied by the World Gold Council (WGC). 0.9 wt% Au/Al₂O₃ was provided by Mintek. 5 wt% Pd/C, 5 wt% Pt/C were provided by Alfa Aesar.

Preparation of mesoporous (meso)-CeO₂: meso-CeO₂ was prepared by a template-assisted precipitation method. Typically, a solution of NaOH (2.0 g) in 300 ml distilled water was added dropwise over 1 h over a stirred solution to of CeNO₃·6H₂O (4.34 g) and CTAB (2.18 g) in 200 ml distilled water. The pH of the resulting mixture is 13. The mixture was then allowed to react in a sealed vessel under 90 °C for aging 7 days, and the pale yellow precipitate obtained was filtered and washed with hot water (80 °C) to remove the residual CTAB. The resultant yellow powder was dried at 110 °C for 12 h and then calcined in a tubular furnace at different temperatures (400-800 °C) for 2 h. With increasing calcination temperature of CeO₂ at 400, 600, and 800 °C, the BET surface area of these materials is 263, 189, and 123 m² g⁻¹, respectively. As a reference, CeO₂ (90 m² g⁻¹) provided by Degussa (Adnano 90) was used.

Preparation of Au/CeO₂ catalysts: 0.8 wt% Au/CeO₂ catalysts were prepared by deposition precipitation method by mixing CeO₂ powders (1.0 g) with appropriate amounts of aqueous solutions of chloroauric acid (HAuCl₄) at a fixed pH=9 adjusting with 0.2 M NaOH at 80 °C. The mixture was aged for 2 h, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried in flowing air at 80 °C for 12 h, and reduced in 5% H₂/Ar at 300 °C. Gold catalyst supported on meso-CeO₂ (263 m² g⁻¹) denoted as Au/meso-CeO₂.

Catalytic activity measurements

General procedure for the TH reaction of aldehydes: A mixture of aldehyde (1 mmol), metal catalysts (3 mol% metal), and formate salts (5 equiv), water (15 ml) was put into a flask (50 ml) fitted with a magnetic stirring bar and a reflux condenser. After the mixture was stirred at 25 °C (80 °C for α,β -unsaturated aldehydes) for a given reaction time, the product mixtures were extracted with Et₂O for 3 times and analyzed (the water phase was also analyzed) on a Shimadzu GC-17A gas chromatograph equipped with a HP-FFAP column (30 m×0.25 mm) and a flame ionization detector (FID). The identification of the products was performed in a GC-MS spectrometer comparing with commercially pure products. For isolation, the combined organic layer was dried over anhydrous Na₂SO₄, concentrated, and purified by silica gel column chromatography to give the product.

Recovery and reuse of Au/meso-CeO₂: The reused catalyst was recovered by separation of solid 0.8 wt% Au/meso-CeO₂ from liquid after filtering. Washing the recovered catalyst with acetone for three times and then wash with distilled water for several times. The catalyst was then dried at 100 °C for 12 h. In the five successive cycles, the conversion of benzaldehyde (1 mmol) was >99%, 96%, 95%, 94%, and 94%.

Large-scale transfer hydrogenation of benzaldehyde: A mixture of benzaldehyde (10 mmol), HCOOK (5 equiv), Au/meso-CeO₂ (1 mol% Au) and water (40 ml) were charged in a 100 ml round-bottomed flask with a magnetic stirring bar and a reflux condenser. The mixture was extensively stirred at 25 °C for 19 h. The mixture was extracted with Et₂O for 3 times and passed through a short silica gel column before GC analysis. For isolation, the combined organic layer was dried over anhydrous Na₂SO₄, concentrated, and purified by silica gel column chromatography. Benzyl alcohol (>96%) was obtained as a colorless liquid.

Competitive reaction of benzaldehyde and acetophenone: A mixture of benzaldehyde (1 mmol) and acetophenone (1 mmol), Au/meso-CeO₂ (3 mol% Au), HCOOK (5 equiv), water (15 ml) was put into a flask (50 ml) with a magnetic stirring bar. Benzyl alcohol was the only reduction product without formation of 1-phenylethanol from acetophenone.

Competitive reaction of benzaldehyde and styrene: A mixture of benzaldehyde (1 mmol) and styrene (1 mmol), Au/meso-CeO₂ (3 mol% Au), HCOOK (5 equiv), water (15 ml) was put into a flask (50 ml) with a magnetic stirring bar. When the yield of benzyl alcohol was >99%, the conversion of styrene did not exceed 7%.

Characterization

Elemental analysis: The Au loading of the catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after an aliquot of the sample was dissolved in a mixture of HCl and HNO₃.

Nitrogen adsorption-desorption: The surface areas of the meso-CeO₂ were determined by nitrogen porosimetry (Micromeritics Tristar 3000). Prior to analysis, the samples were outgassed at 423 K for 2 h.

X-ray photoelectron spectroscopy: XPS analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg K α ($h\nu = 1253.6$ eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C1s peak at 284.6 eV.

In situ diffuse reflectance Fourier-transformed infrared spectroscopy (DRIFTS) for CO adsorption: The CO adsorption DRIFTS experiments were carried out on a Bruker Vector 22 FT-IR spectrometer equipped with a MCT detector and Harrick diffuse reflectance accessory. *In situ* pretreatment was performed with 30 ml min⁻¹ of H₂ at 300 °C for 0.5 h, as in the case of activity measurements. Background signals from gas-phase CO were subtracted before the spectra were reported.

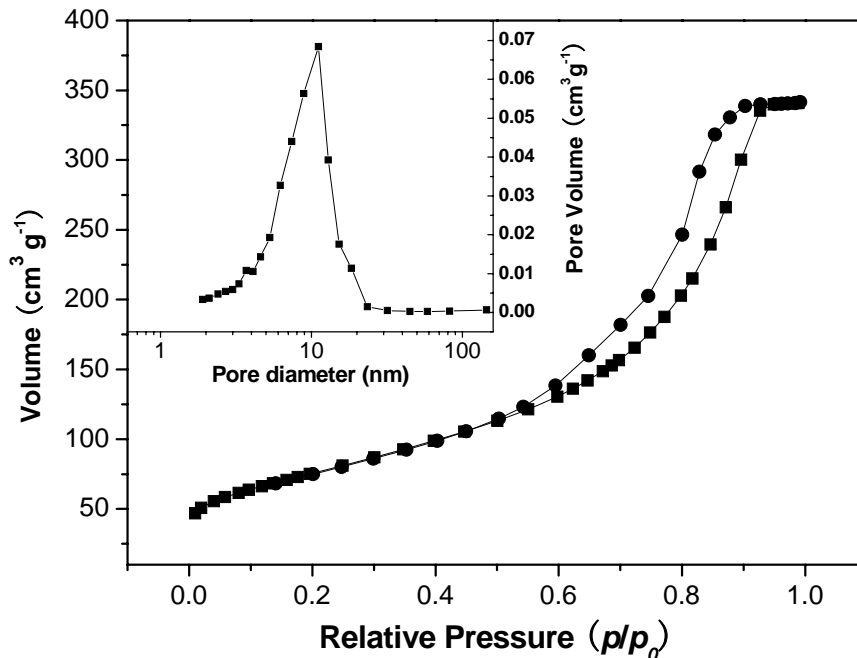


Figure S1. N₂ adsorption/desorption isotherm and pore size distribution for meso-CeO₂ (BET surface area: 263 m² g⁻¹)

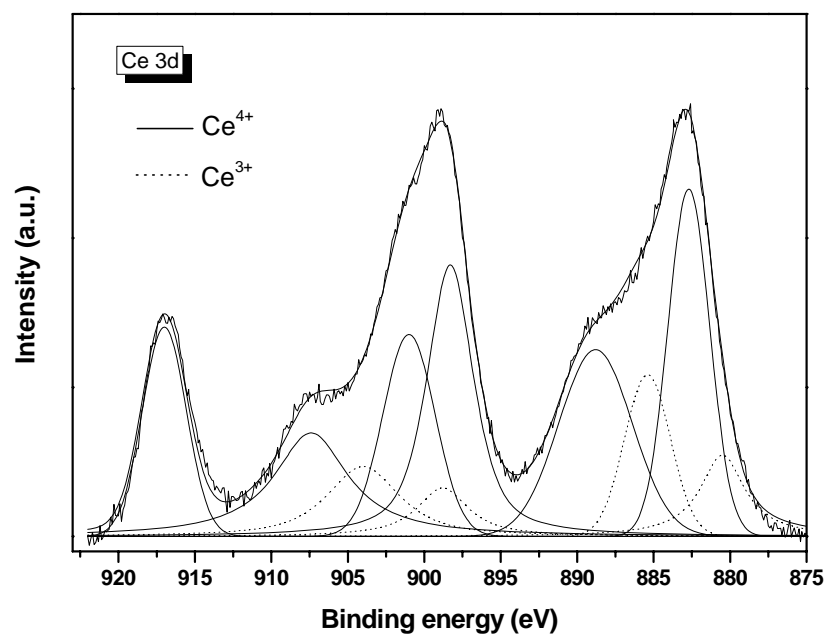
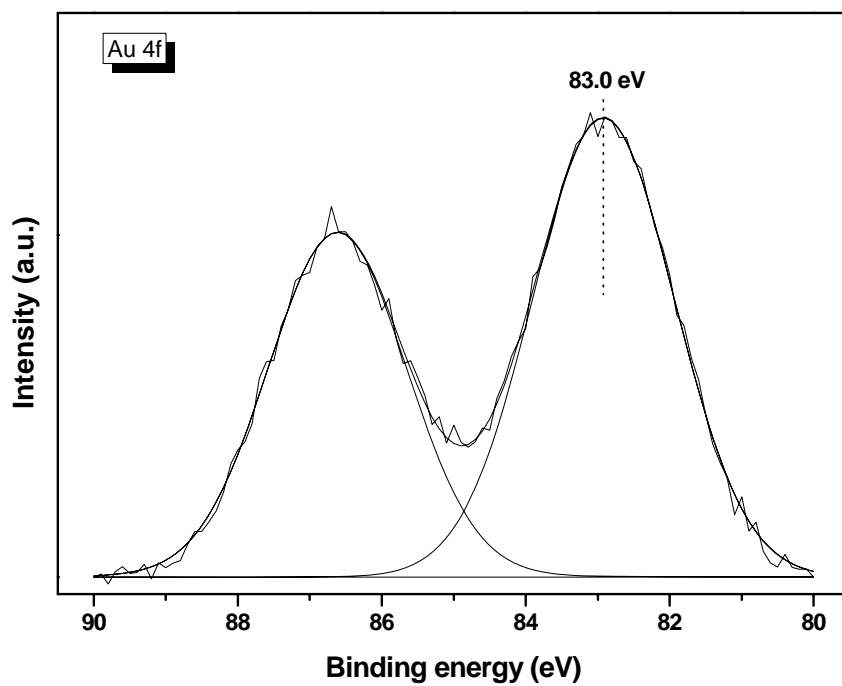


Figure S2. XPS spectra of Au/meso-CeO₂

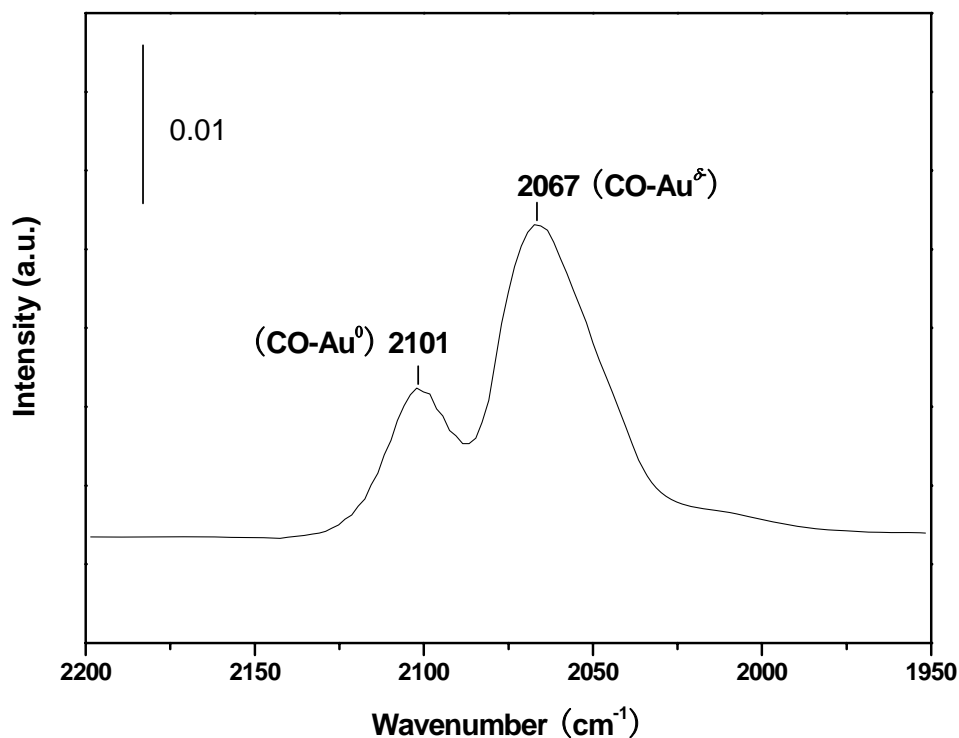


Figure S3. DRIFT spectrum of CO adsorption on the Au/meso-CeO₂ catalyst after CO adsorption for 5 min at 25 °C. The band at 2101 cm⁻¹ is generally attributed to CO adsorption on the step/kink defect sites of the oxide-supported gold nanoparticles (CO-Au⁰),¹ while the band at 2067 cm⁻¹ could be ascribed to CO adsorption on negatively charged gold species (CO-Au^{δ-}).²

Results of mechanistic studies

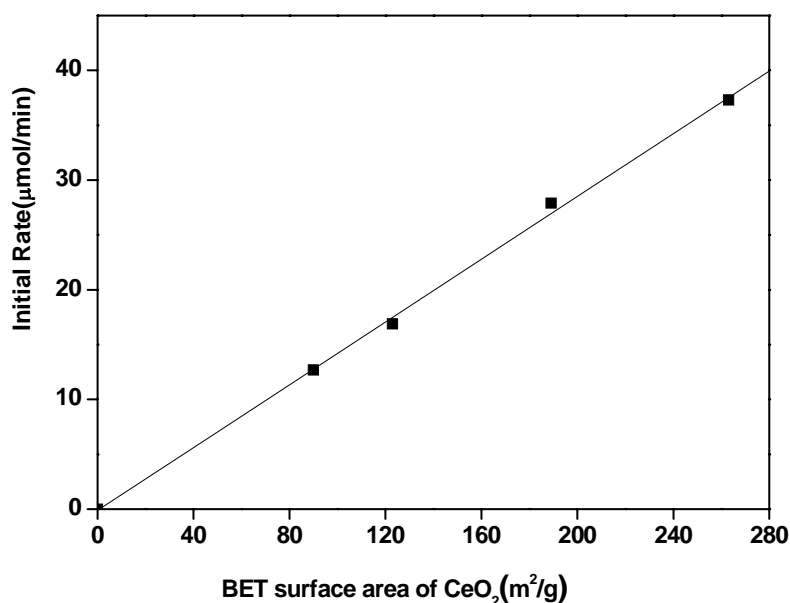


Figure S4. Dependence of the initial reaction rates on the BET surface area of CeO₂ for the TH of benzaldehyde. Reaction conditions: benzaldehyde (1 mmol), Au/CeO₂ (1 mol% Au), HCOOK (5 equiv), water (15 ml), 80 °C, in air.

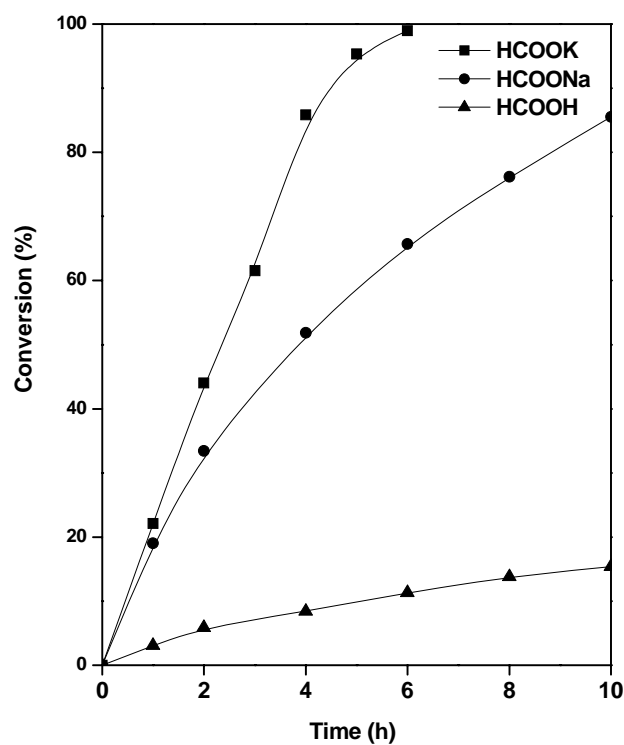


Figure S5. Effect of the donor on the TH of benzaldehyde. Reaction conditions: benzaldehyde (1 mmol), Au/meso-CeO₂ (3 mol% Au), formate salts or formic acid (5 equiv), water (15 ml), 25 °C, in air.

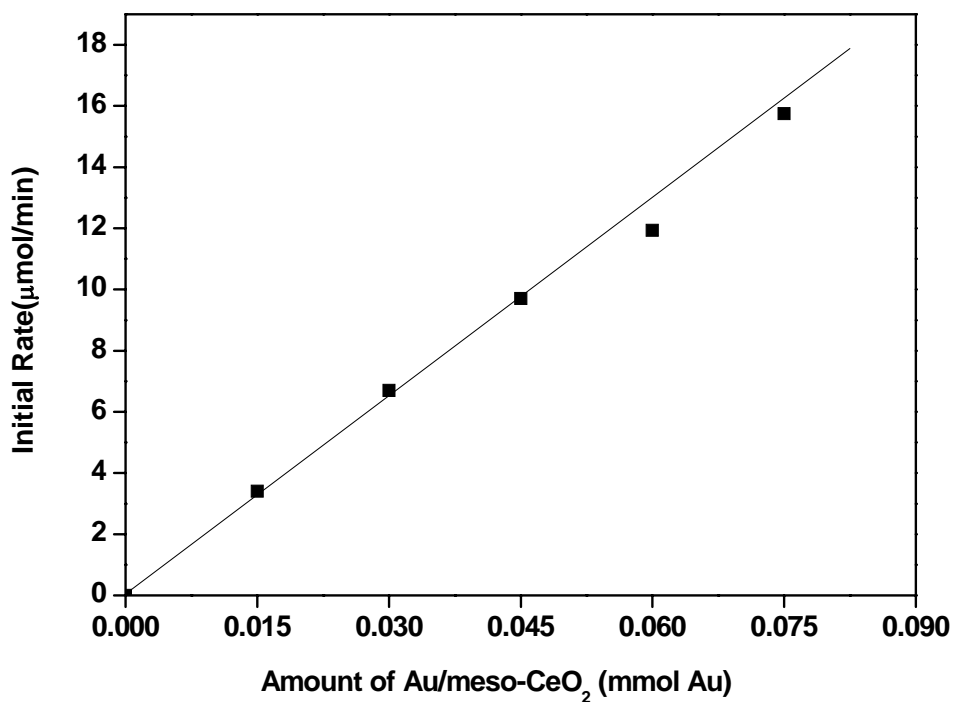


Figure S6. Dependence of the rates on the amounts of catalyst for the TH of benzaldehyde. Reaction conditions: benzaldehyde (1 mmol), HCOOK (5 equiv), water (15 ml), 25 °C, in air.

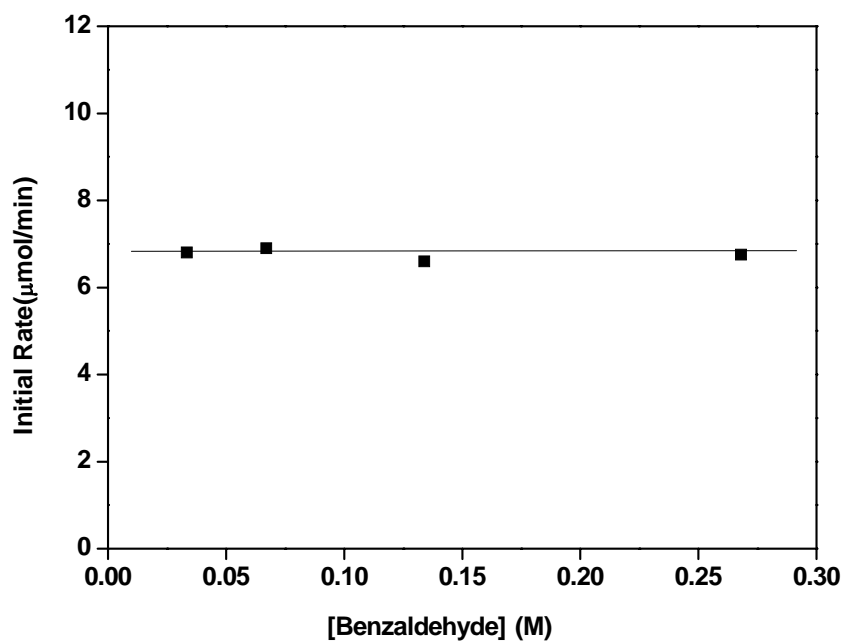


Figure S7. Dependence of the rates on concentration of benzaldehyde. Reaction conditions: Au/meso-CeO₂ (0.030 mmol Au), HCOOK (0.33 M), water/ethanol (7.5 ml /7.5 ml), 25 °C, in air.

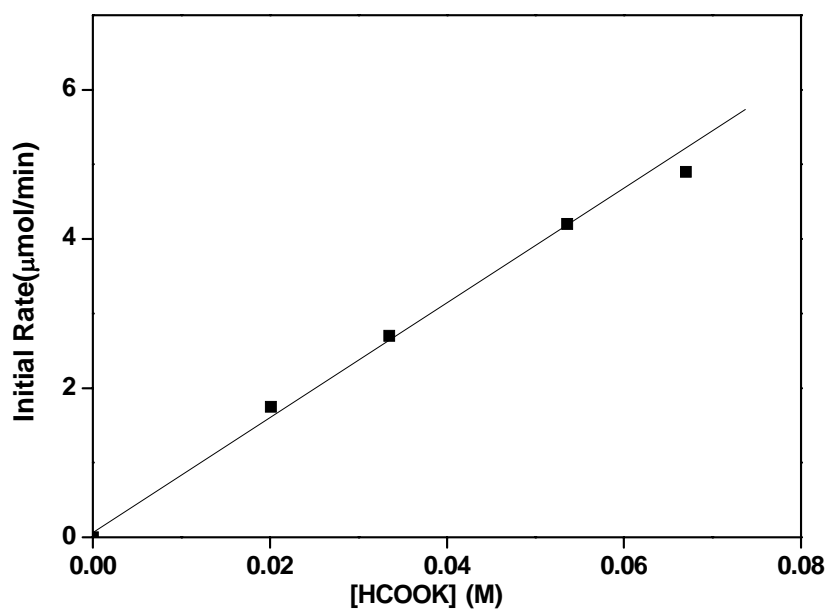


Figure S8. Dependence of the rates on concentration of benzaldehyde HCOOK. Reaction conditions: benzaldehyde (1 mmol), Au/meso-CeO₂ (0.030 mmol Au), water (15 ml), 25 °C, in air.

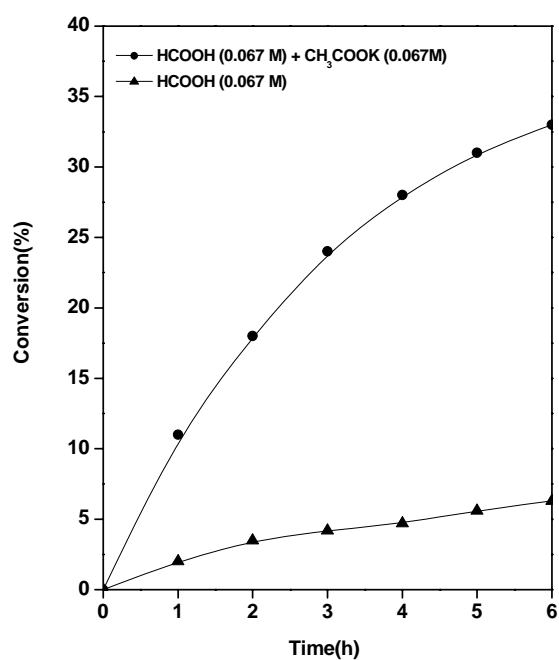


Figure S9. Effect of K ion on the hydrogen-donating efficiency of HCOOH. Reaction conditions: benzaldehyde (1 mmol), Au/meso-CeO₂ (3 mol% Au), water (15 ml), 25 °C, in air.

Table S1 Ionic size of elements (H, Na, and K) and their cations³

Element	Size (Å)	
	element	cation
H	0.37	negligibly small
Na	1.54	0.95
K	1.96	1.33

References

1. M. A. Bollinger, M. A. Vannice, *Appl. Catal. B.* **1996**, 8, 417-443.
2. A. Chiorino, M. Manzoli, F. Menegazzo, M. Signoretto, F. Vindigni, F. Pinna, F. Boccuzzi, *J. Catal.* **2009**, 262, 169-176.
3. S. Rajagopal, A. F. Spatola *J. Org. Chem.* **1995**, 60, 1347-1355.