



Supporting Information

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# Gold Supported on Hydroxyapatite as Versatile Multifunctional Catalyst for the Direct Tandem Synthesis of Imines and Oximes

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## I. Preparation of hydroxyapatite

Hydroxyapatite (HAP) was prepared through a liquid-precipitation method according to ref 16. A solution of calcium nitrate tetrahydrate (6.3 g) in 60 ml mixed solvent (ethanol/water = 1/1 in volume) and a solution of diammonium hydrogenphosphate (2.112 g) in 60 ml water were prepared. Both of the two solutions were brought to pH = 10.5 by using aqueous ammonia before mixing. Then the phosphate solution was added dropwise into the calcium salt solution (drop rate < 5 ml/min) to produce a milky white precipitate and during the process the pH of the solution was also maintained at 10.5. The mixture was stirred for 2 h at 80 °C. After filtration, the precipitate was washed with distilled water for several times and dried overnight and finally calcined at 500 °C for 3 h.

## II. Catalysts preparation

Gold nanoparticles were deposited onto the support employing the homogeneous deposition-precipitation (HDP) method using urea as the precipitation agent originally developed by Zanella et al.<sup>[1]</sup> Typically, 1 g of HAP was added to an aqueous solution with the  $7.61 \times 10^{-2}$  mmol HAuCl<sub>4</sub> and 0.457 g urea (urea/Au = 100, molar ratio). The suspension was then heated to 90 °C and stirred for 4 h, followed by filtering and washing for several times with distilled water. The resulting solid product was dried overnight and finally the purple catalyst was obtained by calcination at 300 °C for 4 h.

Gold catalysts including 1.5 wt % Au/TiO<sub>2</sub> (type A, lot no. Au/TiO<sub>2</sub> no. 02-1), 4.5 wt % Au/Fe<sub>2</sub>O<sub>3</sub> (type C, lot no. Au/Fe<sub>2</sub>O<sub>3</sub> 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). 2.4 wt % Au/CeO<sub>2</sub> catalysts were prepared by deposition-precipitation method reported by Corma group.<sup>[2]</sup> 1.5 wt % Ru/HAP was prepared by partial replacement of Ca<sup>2+</sup> ions with Ru<sup>3+</sup>, 0.2 wt % Pd/HAP was prepared by interacting stoichiometric hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> with a solution of PdCl<sub>2</sub>(PhCN)<sub>2</sub> reported by Kaneda group in ref 17 in the text. K-OMS-2 was prepared by using a procedure reported in the literature by Suib and co-workers in ref 6c.

## III. Procedure for tandem reaction

**Synthesis of imines:** The tandem reaction was performed in a three-necked flask. Alcohol (1 mmol), amine (1 mmol), toluene (10 ml), sym-trimethylbenzene (1 mmol, internal standard) and 130 mg 1.5 wt % Au/HAP were added into the flask with O<sub>2</sub> bubbling (flow rate: 20 ml/min) under vigorous stirring. The reaction was carried out at 60 °C and the products were analyzed by gas chromatography (Trace GC Ultra) fitted with a HP-5 capillary column (25 m × 0.32 mm) and flame ionization detector. A gas chromatography-mass spectroscopy (GC-MS) method was applied for the identification product mixtures.

**Synthesis of oximes:** The tandem reaction was performed in a three-necked flask. Alcohol (0.5 mmol), hydroxylamine (0.5 mmol), toluene (10 ml), sym-trimethylbenzene (1 mmol, internal standard) and 130 mg 1.5 wt % Au/HAP were added into the flask with O<sub>2</sub> bubbling (flow rate: 20 ml/min) under vigorous stirring. The reaction was carried out at 90 °C and analysis process was the same as placed above.

**Synthesis of  $\alpha$ -aminophosphonates:** Au/HAP (0.3 g), benzyl alcohol (10 mmol), aniline (10 mmol) and

dimethyl phosphite (10 mmol) were successively placed in a stainless-steel autoclave reactor with sym-trimethylbenzene as an internal standard. The reaction mixture was vigorously stirred (approx. 1100 rpm) at 100 °C under 1 atm of oxygen with non-solvent. The conversion and product selectivity were determined by GC analysis. The final product was isolated by column chromatography and identified by <sup>1</sup>H NMR spectroscopy. After the reaction was completed, the spent catalyst was separated by filtration, washed with aqueous NaOH solution and acetone in ultrasonic, and finally dried in *vacuo* prior to being recycled.

#### IV. Characterization of the catalysts

The X-ray powder diffraction (XRD) of the catalysts was carried out on a German Bruker D8 Avance X-ray diffractometer using nickel filtered Cu K $\alpha$  radiation at 40 kV and 20 mA. X-ray photoelectron spectroscopy (XPS) data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K $\alpha$ ,  $h\nu = 1253.6$  eV) was used. The C 1s line (284.6 eV) was used as the reference to calculate the binding energies (BE). A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids.

The surface basicity and acidity were measured by CO<sub>2</sub>- and NH<sub>3</sub>-TPD in a flow-type fixed-bed reactor at ambient pressure. The sample (100 mg) was pretreated at 500 °C for 2 h and cooled to 120 °C in flowing He. At this temperature, sufficient pulses of CO<sub>2</sub> and NH<sub>3</sub> were injected until adsorption saturation, followed by purging with He (30 ml/min) for about 2 h. The temperature was then raised from 120 °C to 500 °C at a ramp rate of 10 °C/min to desorb CO<sub>2</sub> and NH<sub>3</sub>. The CO<sub>2</sub> and NH<sub>3</sub> desorbed were collected in a liquid N<sub>2</sub> trap and detected by on-line gas chromatography.

The surface acidity was also monitored from the FT-IR spectra recorded after the adsorption of pyridine, using a Bruker Vector 22 spectrometer coupled to a conventional high-vacuum system. The sample was compacted to a self-supporting wafer and calcined at 400 °C for 1h in an *in situ* IR gas cell under vacuum before pyridine adsorption. Pyridine was adsorbed at room temperature from an argon flow (30 ml/min) containing 2 vol % pyridine. Then the samples were heated to 100 °C and evacuated to remove physisorbed and weakly chemisorbed pyridine. Temperature-programmed desorption of the adsorbed pyridine starting at 100 °C was studied by stepwise heating of the sample under vacuum to characterize the types and strengths of the acid sites. Each spectrum was obtained by subtracting the background (base spectrum) of the unloaded sample.

#### Reference:

- [1] R. Zanella, S. Giorgio, C. R. Henry, C. Louis, *J. Phys. Chem. B.* **2002**, *106*, 7634.
- [2] S. Carrettin, J. Guzman, A. Corma, *Angew. Chem.* **2005**, *117*, 2282; *Angew. Chem. Int. Ed.* **2005**, *44*, 2242.

Table S1. Surface basicity and acidity properties of various catalysts.

Catalysts	CO <sub>2</sub> desorbed (mmol/g <sub>cat</sub> )	NH <sub>3</sub> desorbed (mmol/g <sub>cat</sub> )
HAP	0.49	0.20
Au/HAP	0.68	0.44
Au/ $\beta$ -Ga <sub>2</sub> O <sub>3</sub>	0.22	0.60
Au/TiO <sub>2</sub>	0.27	0.30
Au/Fe <sub>2</sub> O <sub>3</sub>	0.21	0.28
Au/CeO <sub>2</sub>	0.32	0.23
K-OMS-2	0.25	0.70

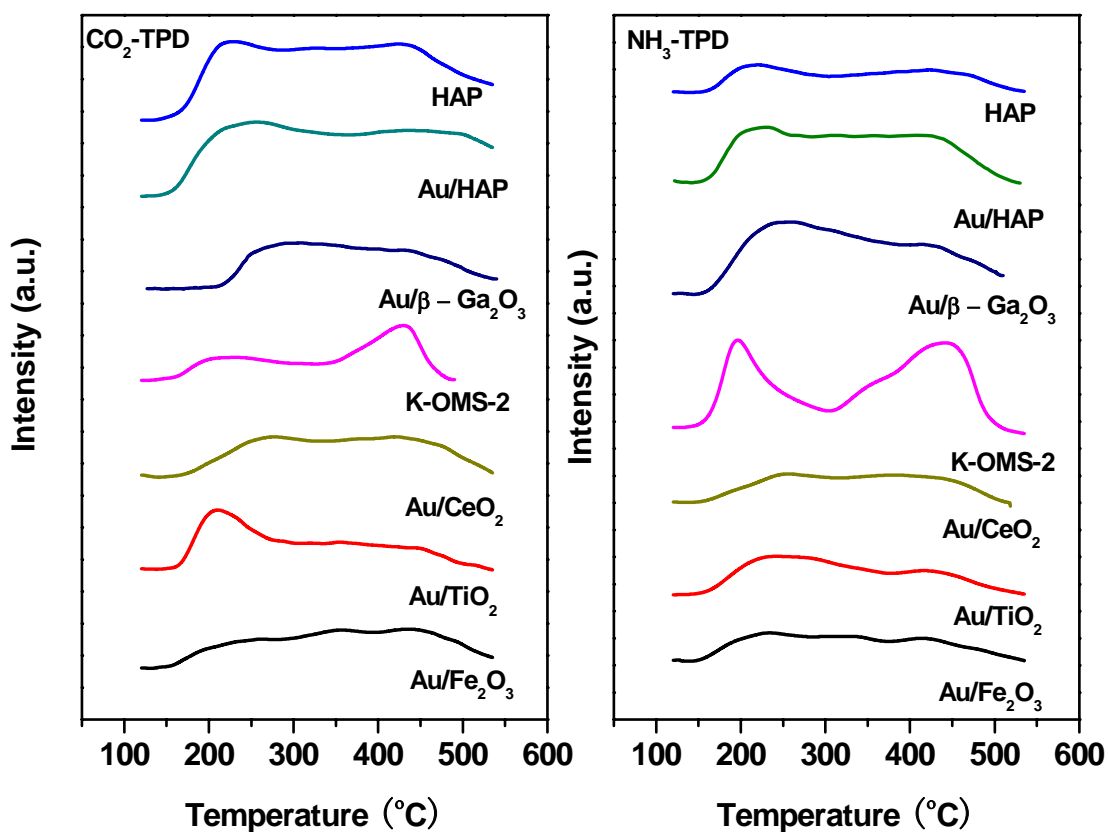


Figure S1. NH<sub>3</sub>- and CO<sub>2</sub>-TPD profiles of various catalysts.

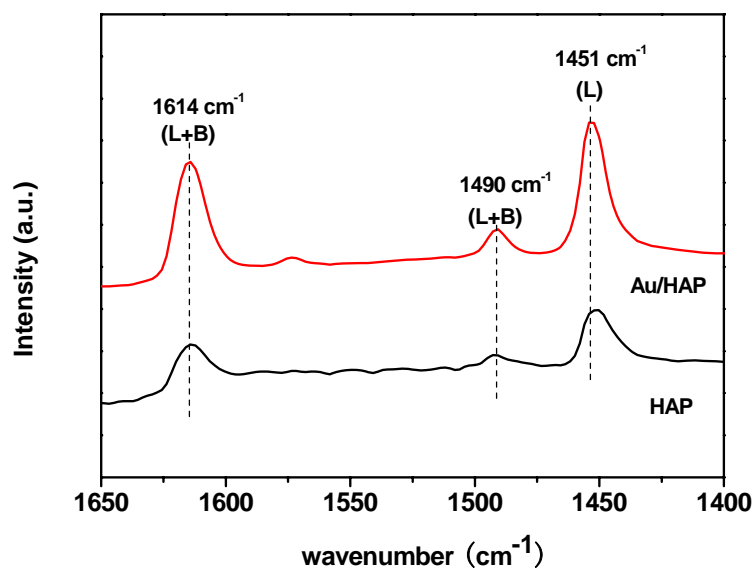


Figure S2. FTIR spectra of pyridine adsorbed on HAP and Au/HAP.  
L: Lewis acid site; B: Brønsted acid site.

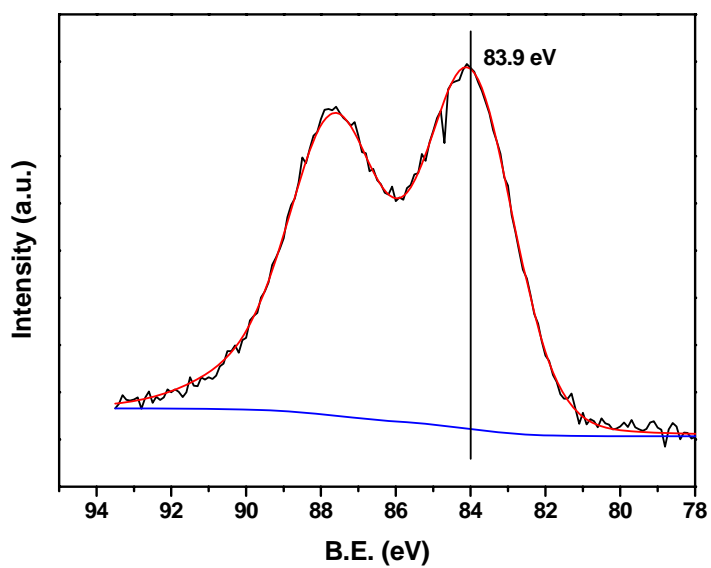


Figure S3. XPS Au 4f spectrum of Au/HAP.

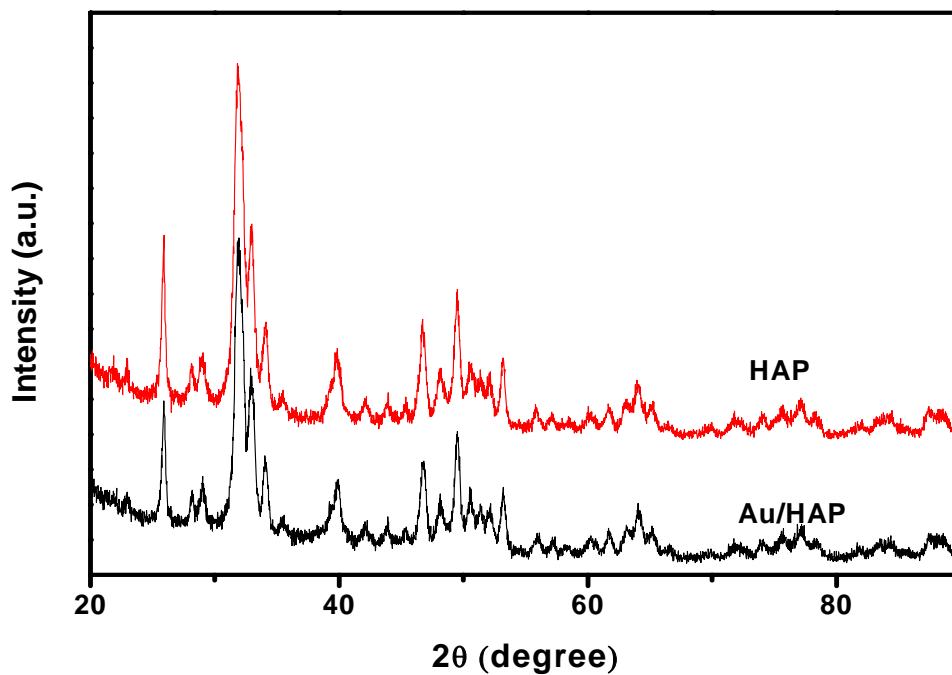


Figure S4. XRD patterns of HAP and Au/HAP.

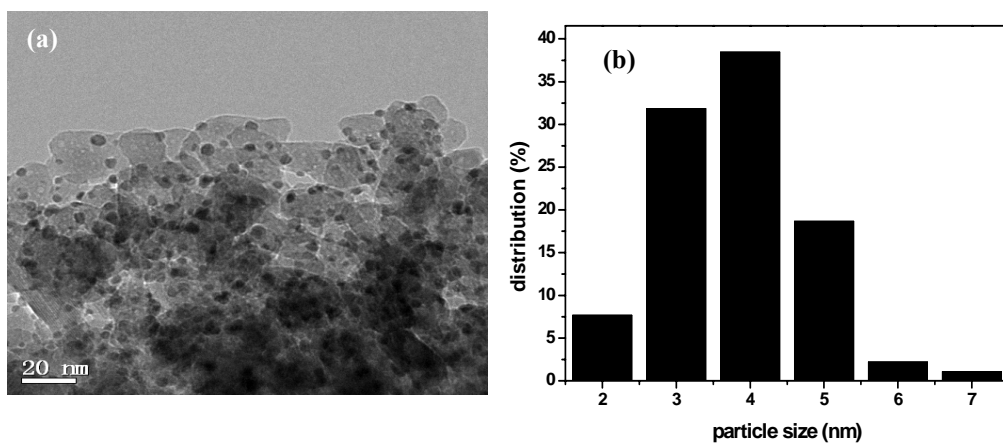


Figure S5. Representative TEM image (a) and size distribution of the gold particles (b) for Au/HAP.

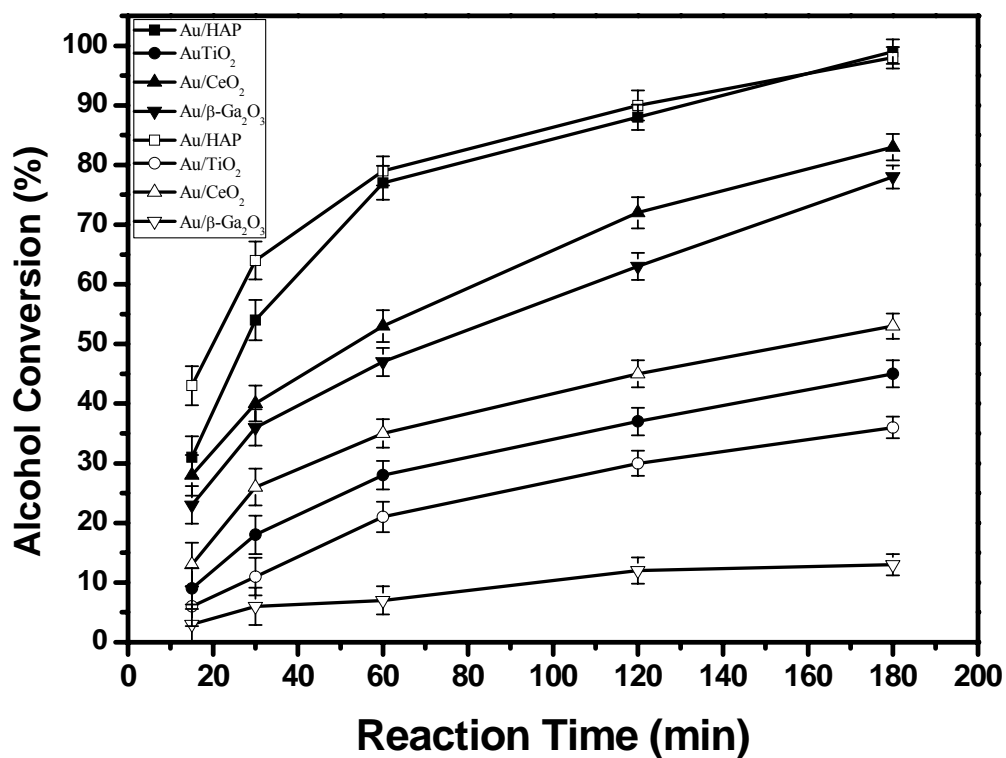
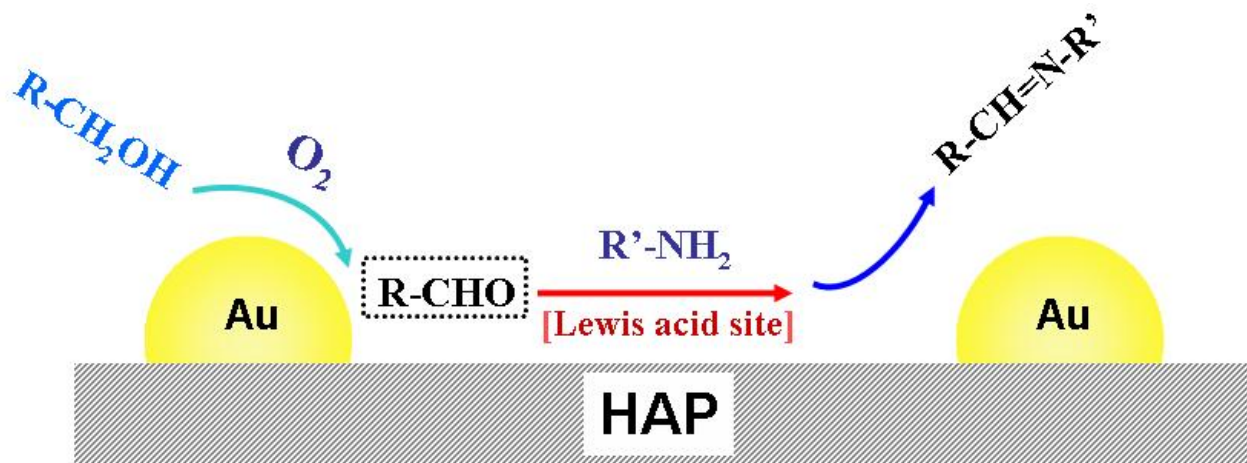
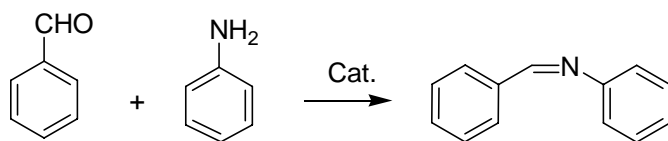


Figure S6. Time course for alcohol oxidation over various catalysts at 60 °C. (filled points: alcohol conversion in the absence of aniline; open points: alcohol conversion in tandem reaction)



Scheme S1. Proposed mechanism for the tandem process on Au/HAP.

**Table S2. Imine synthesis via the direct dehydrative condensation of benzaldehyde with aniline over various gold-based catalysts.**

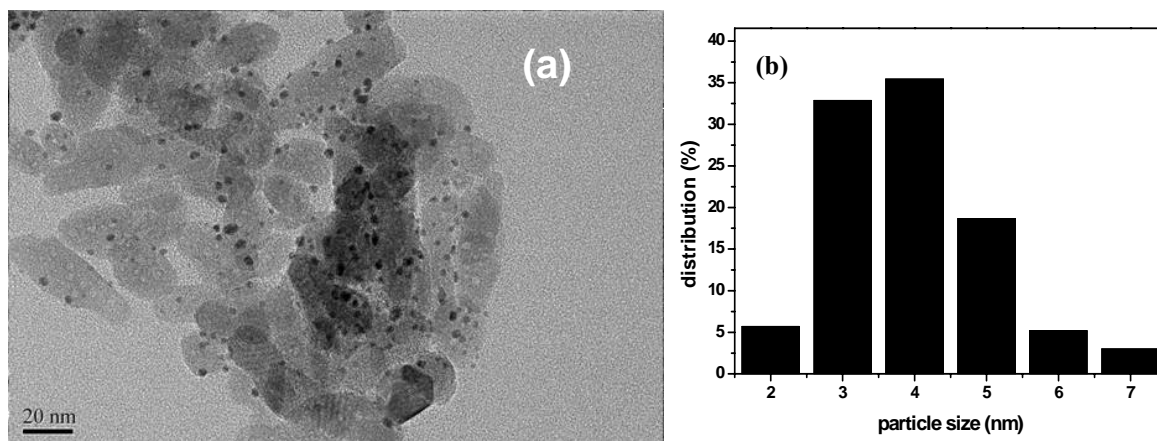


Cat. <sup>[a]</sup>	Yield (%)
Au/HAP	94
Au/HAP-MgO	65
HAP	72
Non Cat.	63
Au/TiO <sub>2</sub>	86
Au/CeO <sub>2</sub>	77
Au/Fe <sub>2</sub> O <sub>3</sub>	79
Au/ $\beta$ -Ga <sub>2</sub> O <sub>3</sub>	59
K-OMS-2	46

[a] Reaction condition: 5 mmol substrates, respectively. 60 °C, toluene (5 ml), time = 1 h.

**Table S3. Au/Ca ratios of surface and bulk Au/HAP, as determined by XPS and inductively coupled plasma emission spectroscopy (ICP-AES), respectively.**

Catalysts	Surface ratio (Au/Ca)	Bulk ratio (Au/Ca)
Au/HAP (fresh)	0.016	0.0075
Au/HAP (3rd times recycled)	0.015	0.0076



**Figure S7. Representative TEM image (a) and size distribution of the gold particles (b) for 3rd times recycled Au/HAP.**

### <sup>1</sup>H NMR spectroscopy of $\alpha$ -aminophosphonate

Purification: silica gel column chromatography (EtOAc/hexane, 20:80), isolated yield 86%, white solid, mp 90-91 °C, <sup>1</sup>H NMR  $\delta$ H (500 MHz, CDCl<sub>3</sub>): 7.48-7.46 (d, 2H, J = 10 Hz), 7.35-7.32 (t, 2H, J = 7 Hz), 7.28-7.27 (m, 1H, J = 9 Hz), 7.11-7.08 (t, 2H, J = 7.4 Hz), 6.71-6.68 (t, 1H, J = 7.4 Hz), 6.60-6.59 (d, 2H, J = 7.6 Hz), 4.82-4.77 (d, 1H, J = 24 Hz), 3.76-3.74 (d, 3H, J = 10.5 Hz), 3.48-3.45 (d, 3H, J = 10.5 Hz).



