

Supporting Information

Effects of Rare Earth Metal Doping on Au/ReZrO₂ catalysts for Efficient Hydrogen Generation from Formic Acid

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1. Experimental

1.1 Chemicals and materials

All reagents were used as received without further purification. (ZrOCl₂·8H₂O) (98.0%, AR grade), NH₃·H₂O (25-28%, AR grade), samarium nitrate (Sm(NO₃)₃), neodymium nitrate (Nd(NO₃)₃), cerium nitrate (Ce(NO₃)₃), triethylamine (NEt₃, 99.5wt%), formic acid (FA) were obtained from Aladdin (China). Tetrachloroauric (III) acid (HAuCl₄) was purchased from Shanghai Macklin Biochemical Co., Ltd. Nitric acid (HNO₃) and hydrochloric acid (HCl) were purchased from Tianjin Chemical Reagents, China. All the reagents were used as received without further purification.

1.2 Catalyst preparation

A series of ReZrO₂ (Re=Nd, Ce and Sm) catalysts (where the molar percentage of Re/(Re + Zr) and is maintained at 8%) were prepared by a modified coprecipitation method.[23] Typically, the adequate amounts of Zr (IV) chloride octahydrate and Nd (III) nitrate (The molar ratio of Zr to Nd is 1:8) were dissolved in 200 mL of deionized

water and stirred for 30 min to form a homogeneous solution. Then, the pH was adjusted to 9.0 by dropwise addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (2.5 M). After stirring for 8 h, the solid was washed with water and dried at 80 °C. Next, the precursor was calcined at 400 °C for 2 h and denoted as NdZrO_2 , CeZrO_2 , SmZrO_2 and pure ZrO_2 was synthesized by the same procedure.

A typical deposition-precipitation method was performed to prepare Au/ZrO_2 catalysts with Au loading of 1wt%.[23] In brief, the as-synthesized ZrO_2 were used as supports and HAuCl_4 and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solutions were used as the gold source and precipitant, respectively. In detail, 1.0 g ZrO_2 powders were dissolved with 200 mL 1 mM of aqueous solution of HAuCl_4 and the pH was adjusted to 9.0 by dropwise addition of 0.25 M $\text{NH}_3 \cdot \text{H}_2\text{O}$. The sample was washed and dried under vacuum at 25 °C for 12 h and followed by a careful reduction with a stream of 5 vol% H_2/Ar at 250 °C for 2 h. Similar to the denoted ZrO_2 supports, these catalysts were denoted as Au/ZrO_2 , Au/NdZrO_2 , Au/CeZrO_2 and Au/SmZrO_2 , respectively.

To confirm the contribution of doping effect, the mechanically mixed samples of ZrO_2 and Re_2O_3 (Re = Nd, Ce and Sm) were synthesized and corresponding hydrogen production rates were also calculated after supporting Au, which were denoted as Au/NZ-mix , Au/CZ-mix and Au/SZ-mix .

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Smart Lab 3000w powder diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermofisher ESCALAB 250Xi spectrometer. Nitrogen adsorption and desorption isotherms were

measured on a BELSORP-mini II sorption analyser at 77 K. The specific surface area was calculated by BET (Brunauer-Emmett-Teller) method, the pore-size distribution was calculated from the adsorption branch using BJH (Barett-Joyner-Halenda) method and the total pore volume was obtained at P/P_0 of 0.99. Transmission electron microscopy (TEM) was performed on a JEM-2800 microscope with energy dispersive X-ray spectroscopy (EDX) detector, working at 200 kV to analyse the surface morphology of the prepared samples. All the samples subjected to TEM measurements were ultrasonically dispersed in ethanol and dropped onto carbon films. The contents of Au were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) on Thermo Jarrell-Ash ICP-9000. H_2 -TPR (Temperature-programmed reduction) experiments were performed on Micromeritics Auto Chem II 2750 automated characterization system. The sample (0.1 g) was pretreated at 473 K for 1 h and cooled to 50 °C in flowing He. The temperature was then raised from 298 K to 973 K in a mixture flow of 5% H_2/Ar ($50 \text{ mL} \cdot \text{min}^{-1}$). CO chemisorption measurements: CO chemisorption measurements were performed at -116 °C. Before chemisorption the following standard pretreatment procedure was applied: the sample (0.2 g) was reduced in H_2 flow ($40 \text{ mL} \cdot \text{min}^{-1}$) at 250 °C for 30 min, cooled in H_2 to ambient temperature, purged in He flow to -116 °C (attained and maintained by an isopropanol-liquid nitrogen cryogenic mixture in a Dewar flask) for CO chemisorption. CO content in pulses (5 vol%), helium flow rate ($30 \text{ mL} \cdot \text{min}^{-1}$), pulse size (0.5 mL), time interval between pulses (4 min).

1.3 Catalytic activity test

The hydrogen production from FA solution was carried out in a 25-ml flask. Typically, 5.0 mL scale of adducts with 53.0 mmol FA and 21.2 mmol NEt_3 was kept in the flask and mixed well, then 0.1 g of catalyst was injected quickly. The catalytic reaction began after the catalyst was added into the flask under continuous magnetic stirring (600 r/min) at 50 °C. The evolution of gas was monitored by using a gas burette. Concentrations of H_2 , CO_2 and CO were measured on a GC (SP-2100A) with thermal conductivity detector (TCD) and flame ionization detector (FID)-Methanator and the detection limit for CO was 10 ppm. Apparent activation energies and turnover frequencies (TOFs) were based on the total number of Au atoms in catalyst, which is calculated from initial TOF value when the reaction of FA dehydrogenation proceeds after 20 min. The equation is calculated as follows:

$$TOF = \frac{\text{generated } H_2 \text{ (mol)}}{\text{total Au atoms (mol)} * \text{time (h)}}$$

For the durability performance, the catalyst from parallel activity tests were collected by filtration, washing, drying at 25 °C for under vacuum for 12 h and reduction at 250 °C for 2 h under 5 vol% H_2/Ar atmosphere (ramping rate of 10/min) after catalytic reaction. All catalytic activity tests were carried out following the same procedure as described above.

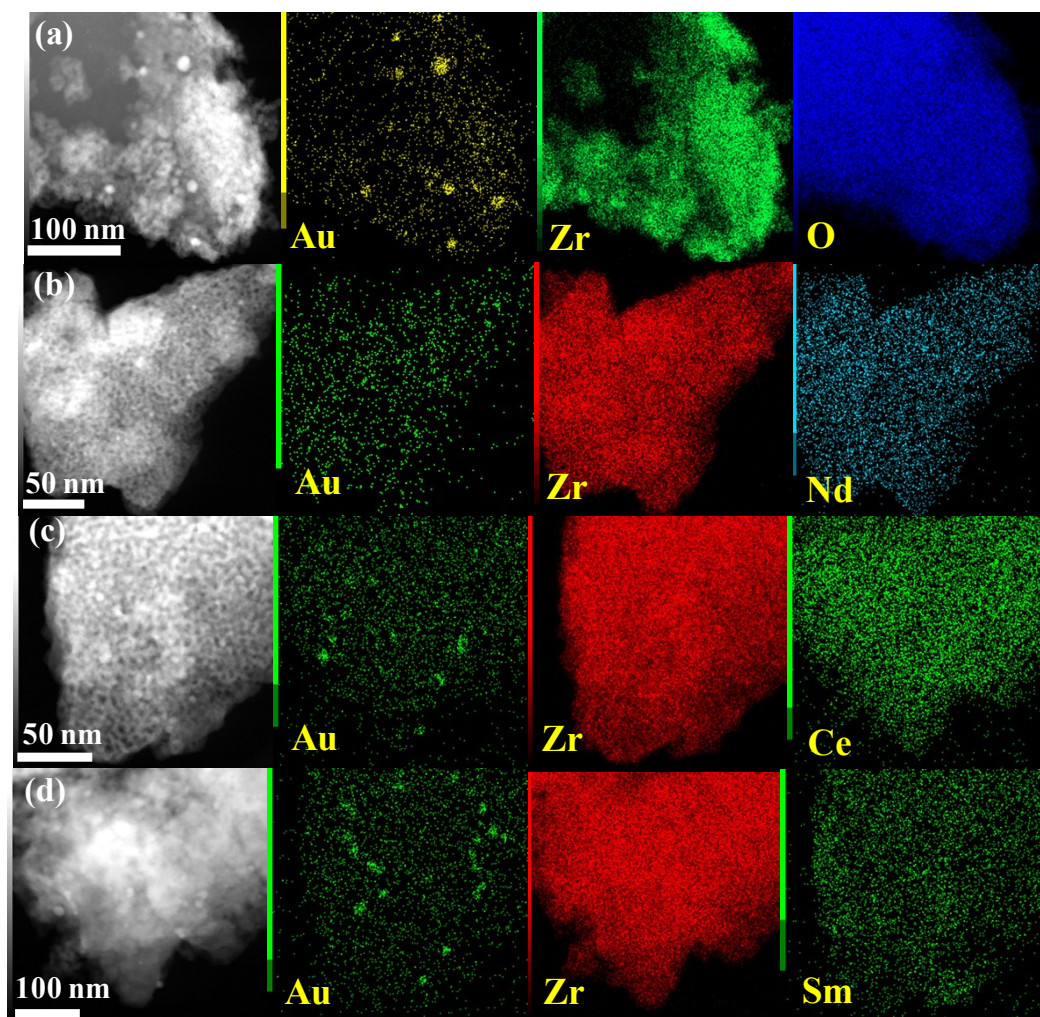


Figure S1. TEM images of (a) Au/ZrO₂, (b) Au/NdZrO₂, (c) Au/CeZrO₂, (d) Au/SmZrO₂, and corresponding EDX mappings.

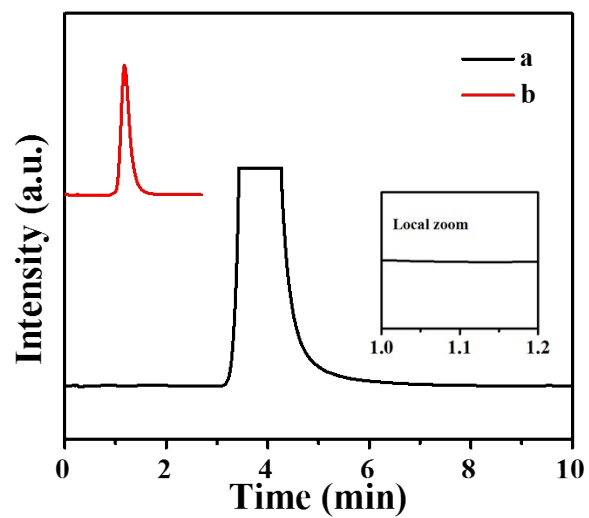


Figure S2. GC spectrum using FID-Methanator for (a) the evolved gas from FA/NET₃ solution (53.0 mmol FA, 21.2 mmol NET₃) over Au/NdZrO₂ catalyst at 323 K, (b) commercial pure CO. The detection limit for CO is 10 ppm.

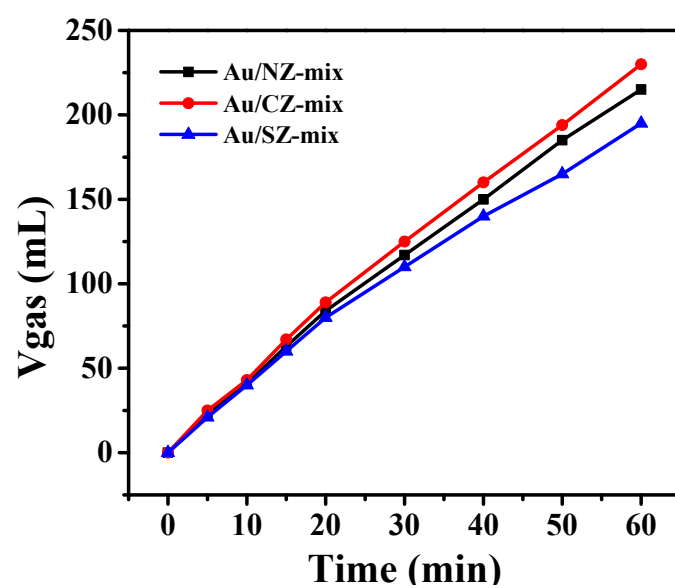


Figure S3. Volume of the gas evolution ($H_2 + CO_2$) versus time over the as-prepared Au/NZ-MIX, Au/CZ-MIX and Au/SZ-MIX catalysts at 50 °C in FA/ NEt_3 solution (53.0 mmol FA, 21.2 mmol NEt_3).

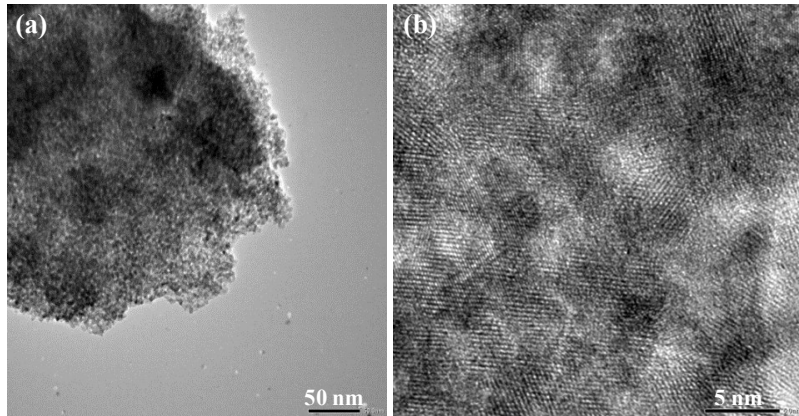


Figure S4. TEM images of Au/NdZrO₂ after recycling.

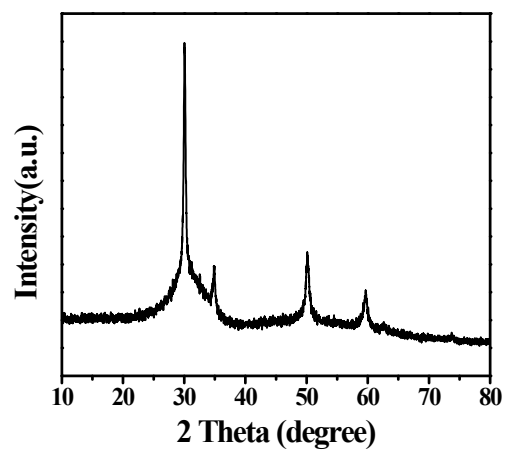


Figure S5. XRD pattern of Au/NdZrO₂ after recycling.

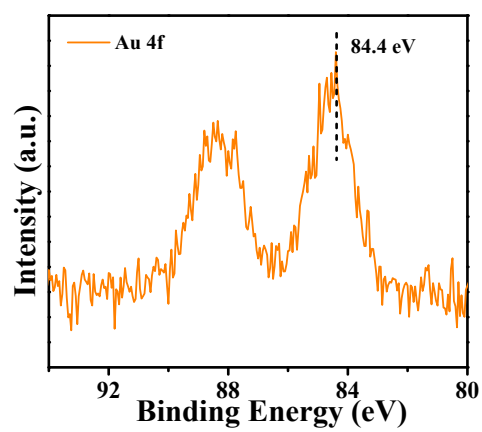


Figure S6. XPS spectrum of Au/NdZrO₂ after recycling.

Table S1. The content of Au obtained from EDX and ICP results.

Catalyst	wt% by EDX	wt% by ICP ^a	wt% by ICP ^b
Au/ZrO ₂	0.76	0.81	0.79
Au/NdZrO ₂	0.74	0.74	0.71 ^c
Au/CeZrO ₂	0.83	0.69	0.67
Au/SmZrO ₂	0.81	0.83	0.77

^a fresh catalyst.

^b after reaction.

^c after 5th run.

Table S2. Au dispersion and the Au particle diameter determined by CO chemisorption.

Sample	mL _{co(STP)} /g _{Au}	mol _{co} /mol _{Au}	Dispersion (%)	Size (nm)
Au/ZrO ₂	37.8	0.332	94.6	< 1.0
Au/NdZrO ₂	38.5	0.338	96.3	< 1.0
Au/CeZrO ₂	38.7	0.343	97.0	< 1.0
Au/SmZrO ₂	38.2	0.336	95.8	< 1.0

According to the relationship between particle size and dispersion reported in the literature, [1] when Au nanoparticle size is 1 nm, the dispersion (D) is ~89%. Au dispersion measured by CO pulse is greater than 94%, which means Au particle size is less than 1 nm. It is consistent with the literature, which reported that very small Au metallic particles (<1 nm) are barely detectable by TEM. [2]

References

- [1] G. C. Bond and D. T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, **41**, 319.
- [2] F. Menegazzo, M. Manzoli, A. Chiorinob, F. Boccuzzi, T. Tabakova, M. Signoretto, F. Pinna and N. Pernicone, *J. Catal.*, 2006, **237**, 431-434.