Electronic Supplementary Information

Article title: "Probing supported bimetallic Pt-In sites in glycerol hydrogenolysis"

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1. Experimental

1.1. Catalyst preparation

Pt/Al$_2$O$_3$ and In/Al$_2$O$_3$ monometallic catalysts were prepared using the dry impregnation method with the respective aqueous solutions of the H$_2$PtCl$_6$, and In(NO$_3$)$_3$ precursors. The volume of each precursor solution was added in distilled water to complete the pore volume corresponding to the support mass used. For the Pt/Al$_2$O$_3$ catalyst, the solution volume was 1.25 mL added to 7.25 mL of distilled water on 9.90 g support, and for the In/Al$_2$O$_3$ catalyst the solution volume was 1.06 mL which was added to 7.5 mL of distilled water in 9.91 g of the support. The final solution was then slowly dripped into the support and macerated to evenly distribute the metal phase in the support. The impregnated solids were dried at 393 K for 12 h and then calcined at 723 K for 4h in a muffle furnace with a heating rate of 5 K/min.

As with the monometallic catalysts, the preparation of the Pt-In/Al$_2$O$_3$ catalyst was carried out by the successive dry impregnation method to obtain a 1% Pt and 1% In catalyst. 1.25 mL of the precursor solution In(NO$_3$)$_3$ was dissolved in 8 mL of distilled water to give a final volume corresponding the pore volume of 9.78 g support, and this solution was slowly dripped into Al$_2$O$_3$. After these steps the impregnated material was dried at 393 K for 12 h in an oven and calcined in the muffle at 723 K (5 K/min) for 4 h. Then 1.25 mL of the H$_2$PtCl$_6$ precursor solution was

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dissolved in an 8 mL volume of distilled water and then dripped onto the previously calcined material. After impregnation, the drying step was repeated at 393 K for 12 h and calcination at 723 K for 4 h.

Pt/SiO$_2$ and In/SiO$_2$ catalysts were prepared using the dry impregnation method based on reference [20] methodology. For the preparation of the In/SiO$_2$ catalyst, a volume of 1.06 mL of the precursor solution of In(NO$_3$)$_3$ was added to 8 mL of distilled water, followed by citric acid with a 1:3 molar ratio to the amount of In. Then 6 mL of a 25% NH$_4$OH solution was added to the above solution to obtain a final volume corresponding the pore volume of 9.91 g support, which precipitated and reached pH 11. This solution was stirred so that the precipitate formed was solubilized, and then dripped into SiO$_2$. The impregnated solids were dried at 393 K for 12 h and calcined at 723 K (5 K/min) for 4 h.

For the preparation of the Pt/SiO$_2$ catalyst, a 2.5 mL volume of the Pt(NH$_3$)$_4$(OH)$_2$ precursor solution was added to 11 mL of distilled water. This precursor was used due to the low pH of isoelectric point of the support (pH(I) = 2, as opposed to pH(I) = 9 for Al$_2$O$_3$), as a strategy for enhancing ion exchange. Then 1 mL of a 25% NH$_4$OH solution was added to the above solution, where a white precipitate formed upon reaching pH 11. This solution was stirred for homogenization and then dripped into 9.90 g of SiO$_2$. The impregnated solids were dried at 393 K for 12 h and then calcined at 723 K (5 K/min) for 4 h.

The preparation of the Pt-In/SiO$_2$ catalyst was carried out by the successive dry pH-controlled impregnation method to obtain a 1% Pt and 1% In catalyst based on the methodology of [16] [20]. A volume of 1.25 mL of the precursor solution In(NO$_3$)$_3$ was dissolved in 10 mL of distilled water, then added citric acid with a 1:3 molar ratio to the amount of In. Then 3 mL of a 25% NH$_4$OH solution was added to the above solution, which caused precipitation when it reached pH 11. This solution was stirred for homogenization and dripped into 9.78 g of SiO$_2$. After these steps the impregnated material was dried at 393 K and calcined in a muffle at 723 K with heating rate of 5 K/min for 4h. Finally, 1.25 mL of the Pt(NH$_3$)$_4$(OH)$_2$ precursor solution was diluted in a 14.5 mL volume of distilled water, and a 1.5 mL volume of 25% NH$_4$OH solution was added until pH

11. This solution was then dripped into 9.90 g of the previously calcined material. After impregnation, the drying step was repeated at 393 K for 12h and calcination at 723 K (5 K/min) for 4h.

1.2. Catalyst Characterizations

1.2.1. Nitrogen physysorption

To determine the specific area, volume and average pore diameter distribution of all catalysts and supports, the nitrogen physysorption technique was used. The analyses were performed on a Micromeritics ASAP 2020 device. Performing this technique involved a vacuum degassing step (4 mbar) at a temperature of 523 K for 4 hours. The analysis was then performed using liquid nitrogen which has a boiling temperature of 77 K at atmospheric pressure. The Brunauer-Emmet-Teller (BET) equation was applied to calculate the specific area. Total pore volume and pore diameter distribution were estimated by the BJH (Barrett-Joyner-Halenda) method using the adsorption curve.

1.2.2. X-Ray Diffraction

All prepared supports and catalysts were characterized by XRD by the powder method on a Rigaku Miniflex II equipment using a CuKα radiation (1.540 Å). Analyzes were performed at 2θ between 5º and 100º, using a 0.05º step and a counting time of 1 second per step.

1.2.3. Temperature Programmed Reduction

Temperature programmed reduction technique was performed in a multipurpose unit coupled to a mass spectrometer (HPR20-Hiden). Quantities of 1 g of calcined samples were dried in 30 mL/min helium flow at 423 K (10 K/min) and allowed to cool to room temperature in He flow. After drying, a 5% H_2/Ar mixture (30 mL/min) was passed through the sample and the temperature was maintained until the H_2 baseline signal stabilized on the mass spectrometer. TPR analysis was performed by heating the sample to 1273 K with a heating rate of 10 K/min.

1.2.4. Pyridine DRIFTS

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of adsorbed pyridine was performed using a Nicolet iS50 equipment with a Harrick Praying Mantis in situ reflectance cell. The catalysts were dried at 423 K in He (30 mL/min) for 30 min. After that, the samples were cooled to room temperature and then reduced to 723 K for 2h with H_2 (30 mL / min), purged with He (30 mL / min) at this temperature for 30 min and cooled in He. Then, a reference interferogram (background) was collected at 298 K. Pyridine was adsorbed by bubbling through a saturator at a flow rate of 20 mL/min for 1h at room temperature (298 K). After adsorption, physically adsorbed pyridine was removed with He (30 mL/min for 30 min). Thus, a new interferogram was obtained and related to the reference one, in order to obtain the spectrum of acid sites in solids. The resolution of the spectra was 2 cm^{-1} and 250 scans were performed.

1.2.5. H_2 and CO Chemisorption and Temperature-Programmed Desorption

H_2 and CO chemisorption measurements were performed in a multipurpose unit coupled to a mass spectrometer (HPR20-Hiden). Approximately 1.5 g of the sample was dried in a 30 mL/min He flow at 423 K (10 K/min) until the H_2O signal stabilized in the mass spectrometer, and then cooled to room temperature in He flow. Sample reduction was performed at 723 K for 1h in H_2 flow rate of 30 mL/min. After reduction time, the sample surface was cleaned with 30 mL/min He flow for 1h at reduction temperature, and then cooled to 298 K. Once this temperature was reached, H_2 pulses were injected through a 100 µL loop until the H_2 peak areas were constant on the mass spectrometer, indicating that the catalyst surface was saturated. At this point, desorption analysis at the programmed temperature was performed by increasing the sample temperature to 723 K with heating rate of 10 K/min.

1.2.6. Cyclohexane dehydrogenation

The rate, activation energy and TOF of the cyclohexane dehydrogenation reaction were estimated based on experiments performed in a reaction unit coupled to a Hewlett-Packard 5890 Series II gas chromatograph with a Carbowax column equipped with a flame ionization detector

(FID). The reaction charge was obtained through a cyclohexane containing saturator maintained at 285 K and using hydrogen as a carrier gas (total flow 100 mL/min). The reaction was carried out at atmospheric pressure in a U-shaped quartz tubular reactor containing 10 mg of catalyst. Prior to the model reaction, the catalyst was dried in a 30 mL/min He flow at 423 K for 30 min and reduced at 723 K for 1h, and then cooled to room temperature. Then the system was gradually heated and samples were taken at temperatures set of 523, 533, 543, 553, 563, 573 and 583 K, two samples per temperature, varying by 10 K, and then reducing the temperature to the initial condition of 523 K.

1.2.7. Transmission electronic microscopy

Supported metal particle were examined by transmission electron microscopy (TEM) using a JEOL JEM-2100F equipment operating at 200 kV. The reduced samples were prepared by suspending the catalyst in ethanol and shaken in an ultrasound bath, and then the sample was dripped onto copper grids. Particle sizes were estimated using ImageJ 1.48v software, where approximately 200 particles were counted for each catalyst in different images. The average superficial particle sizes (đ) were calculated by equation 1:

$$\bar{d} = \frac{\sum d^3}{\sum d^2}$$

(1)

where d is the particle size measured by TEM.

The dispersion obtained from the H_2 chemisorption (D) was used to calculate the particle size of the platinum catalysts (d_p) by the equation 2:

$$d_p = \frac{1}{D}$$

(2)

1.3. Catalytic Tests

APH of glycerol was performed in a 300 mL capacity stainless steel high pressure batch reactor equipped with a mechanical stirrer, electronic temperature controller and a steel collecting tube for removal of reaction aliquots (Parr Instruments 4848).

Before each test, catalysts were previously reduced by 5% H_2/Ar at 723 K for 2 h and passivated with 5% O_2/He for 1 h using a catalyst mass of approximately 0.5 g. All reactions were carried out with 150 g of 20%wt. aqueous glycerol solution under the conditions of 2.5 MPa (356 psi) of absolute initial hydrogen pressure at 298 K, 513 K reaction temperature, 500 rpm rotational speed and 12 hours of reaction time.

In a typical reaction run, the reactor was charged with the stipulated amounts of catalyst, water and glycerol and properly sealed. Then, the system was purged with nitrogen to remove air, and then purged with hydrogen to remove N_2, with the flow rates of 30 mL/min for both gases. H_2 was passed at an approximate flow rate of 30 mL/min for 1h to activate the catalyst. Thereafter, the assembly was pressurized with H_2 to the desired pressure and heating was turned on to reach the reaction temperature while stirring at 500 rpm. The experiments were conducted for 12 hours and after this time the heating was automatically stopped. Aliquots for kinetic study were collected during the first two hours after stabilization of the reaction temperature at 30 minute intervals. The reaction endpoint was also collected for the study. All samples were centrifuged and filtered with 0.2 μm pore size membrane. The liquid phases were analyzed with a gas chromatograph coupled to a Shimadzu GCMS-QP2010S mass spectrometer (GC-MS) equipped with a SUPELCOWAX 10 polyethylene glycol capillary column.

From carbon balances, all gas-phase products could be neglected. Conversion, X, and yield, Y_i, are defined based on carbon balance, for the purpose of instrument sensitivity, as:

$$X = \frac{j_i x_i}{3 x_{G,t} + \sum j_i x_i}$$

(3)

$$Y_i = \frac{j_i x_i}{\sum j_i x_i}$$

(4)

Where j_i is the number of carbon atoms on product i; x_i is the molar fraction of product i in the liquid phase at a certain time, and $x_{G,t}$ is the molar faction of glycerol at a certain time $t \neq 0$. The reaction frequency (TOF), on the other hand, was estimated by the initial reaction rate,

considering a first order reaction, and taking H_2 dissociative chemisorption as a measurement parameter of the active sites (M) of the materials ($1H_2$:2M);

$$TOF = \frac{k_{ap}c_G}{2n_{H_2,ch}}$$

(5)

The parameter k_{ap} was obtained by linear regression from the kinetic points, $L.g^{-1}.s^{-1}$, c_G is the (initial) concentration of glycerol, $mol.L^{-1}$, and $n_{H2,ch}$ is the chemisorbed amount of H_2, mol/g.

2. Results and Discussion

2.1. Nitrogen physisorption

Table E1. Specific Area and Pore Volume obtained by the BET method

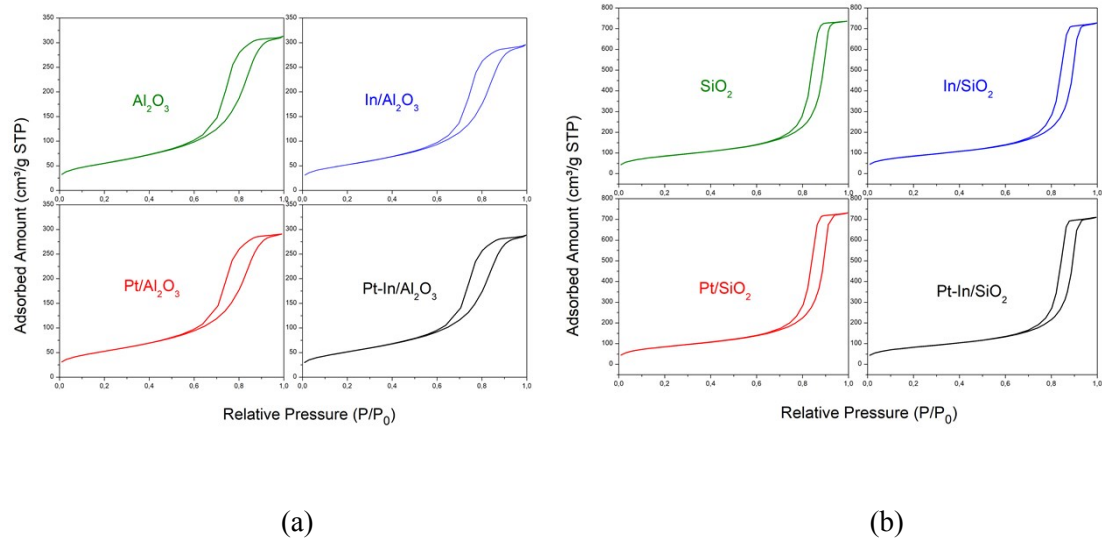| Material	Surface Area (m²/g)	Pore Volume (cm³/g)	Average pore diameter (Å)
Al_2O_3	199	0.49	96
In/Al_2O_3	188	0.46	96
Pt/Al_2O_3	190	0.45	94
$Pt-In/Al_2O_3$	186	0.45	94
SiO_2	310	1.14	146
In/SiO_2	309	1.13	144
Pt/SiO_2	309	1.13	145
$Pt-In/SiO_2$	299	1.10	146

(a)   (b)

Figure E1: Adsorption-desorption isotherms of (a) Al$_2$O$_3$ supported catalysts and (b) SiO$_2$ supported catalysts.
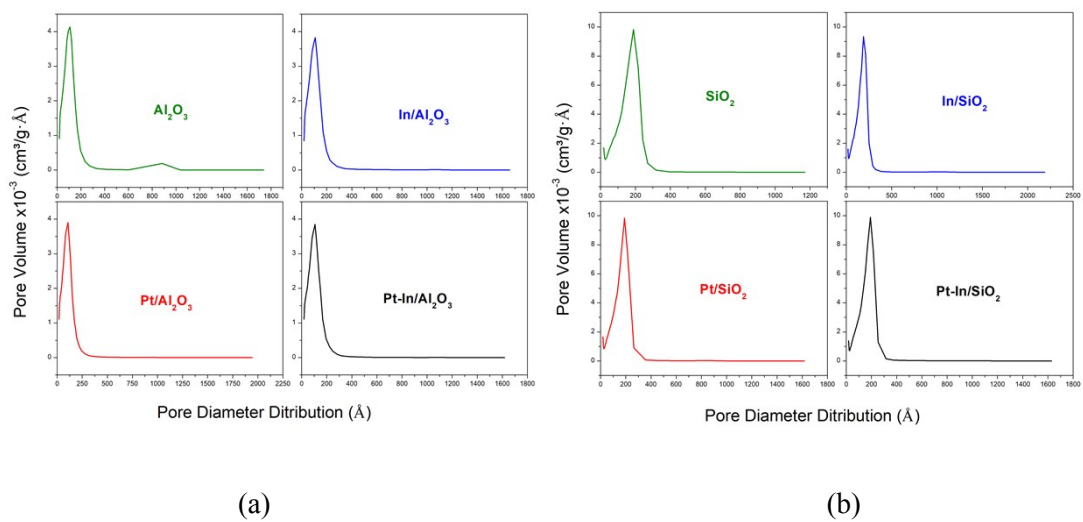

(a)   (b)

Figure E2: Pore diameter distribution of (a) Al$_2$O$_3$ supported catalysts and (b) SiO$_2$ supported catalysts.

2.2. X-ray Diffraction

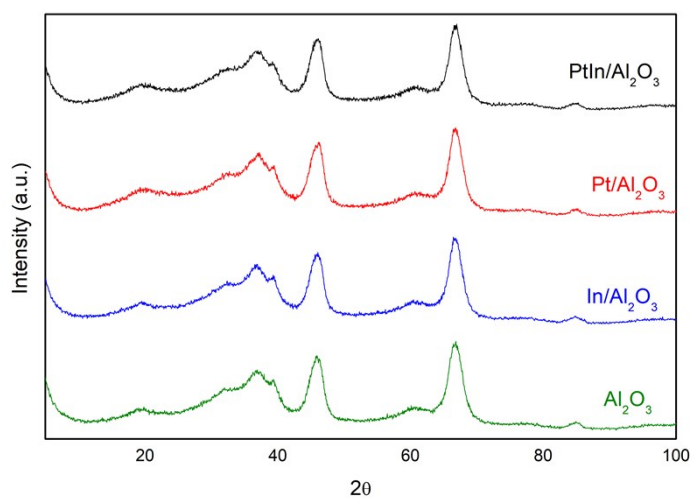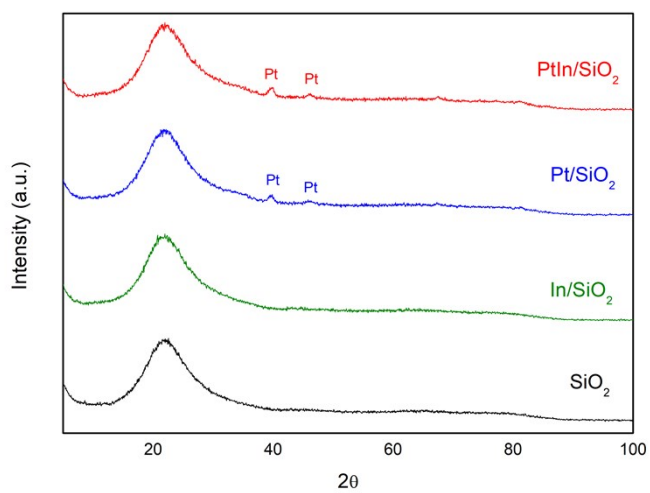Figure E3: X-ray diffractograms of Al$_2$O$_3$ supported catalysts.

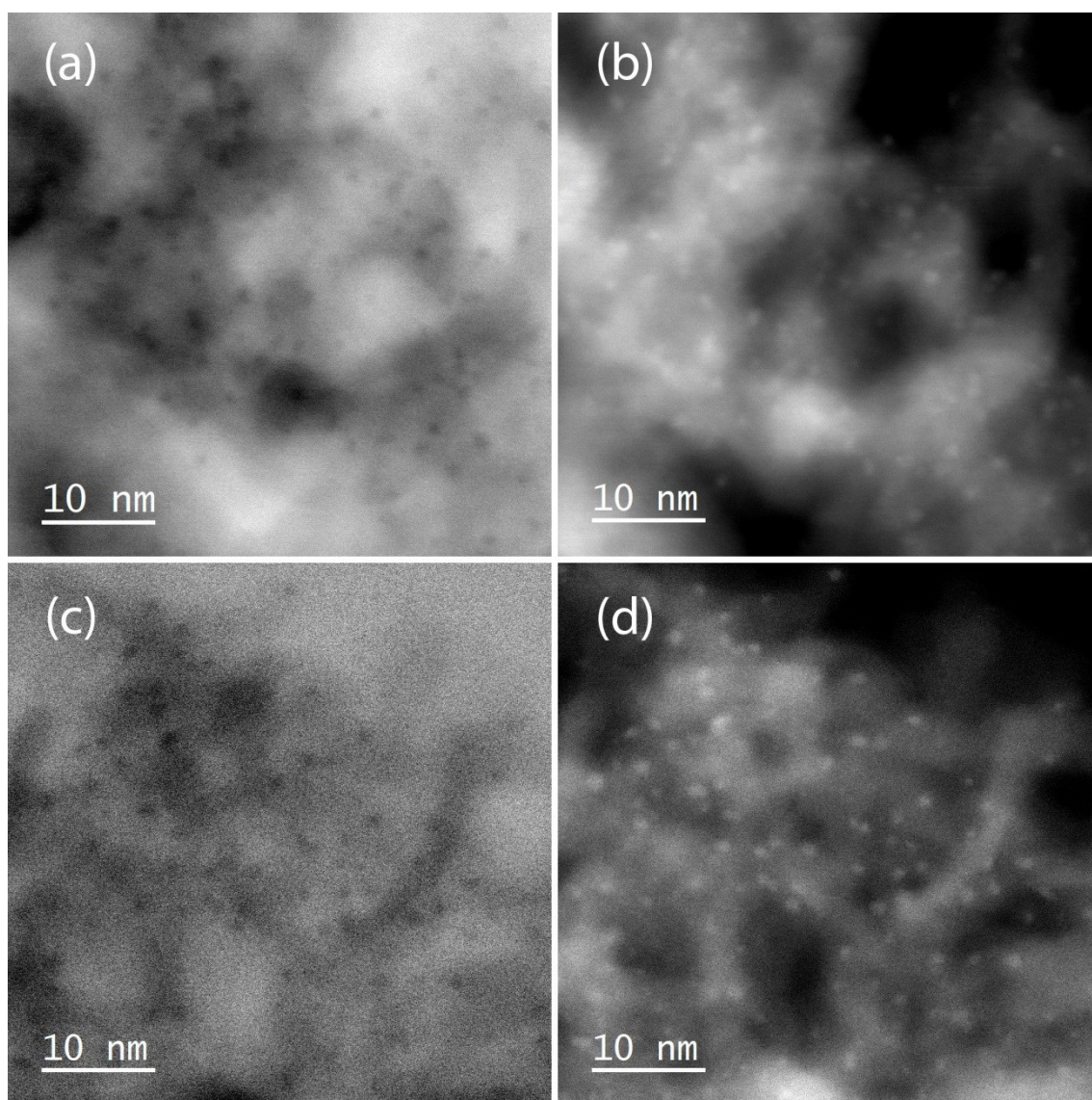Figure E4: X-ray diffractograms of SiO$_2$ supported catalysts.

Figure E5: (a) Bright field and (b) high-angle annular dark field STEM images for Pt/Al_2O_3. (c) Bright field and (d) high-angle annular dark field STEM images for $Pt-In/Al_2O_3$.