Supplementary Information

Mechanistic insights into acids affected hydrogenolysis of glycerol to 1,3propanediol over Ir-Re/SiO₂ catalyst

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Methods

Catalyst preparation. The silica (FuJi Silysia, G-6, <100 mesh) was used as a support for the catalyst, which was pre-calcined at 773 K for 3 hours. Bimetallic Ir-Re/SiO₂ catalyst was prepared by sequential impregnation of H₂IrCl₆ (Strem Chemical, 99.9%) and NH₄ReO₄ (Strem Chemical, 99.999%). Typically, G-6 was impregnated with a certain amount of H₂IrCl₆ solution firstly, and then the sample was aged at room temperature for 12 hours and dried at 383 K for 12 hours. After evaporating the solvent, a certain amount of NH₄ReO₄ solution was impregnated onto the sample, which was aged at room temperature for 12 hours and dried at 383 K for 12 hours. The nominal loadings of Ir and Re were both 4 wt.%. The dried sample was reduced under the atmosphere of H₂ (70 ml·min⁻¹) at 773 K for 4 h and then passivated at 298 K by O₂/Ar (V/V = 1:99) for 25 min in a fixed bed reactor.

Catalytic performance tests. An autoclave (Parr 4848, 100 ml) was used for catalytic performance tests. Typically, the reactor was packed with 20 g of glycerol aqueous solution (20 wt.%) and 0.15 g of catalyst pre-reduced by H_2 at 773 K for 4 h. Then, the autoclave was purged three times with 3MPa of H_2 and pressurized to 8 MPa. Afterward, the reaction system was heated to 393 K, and the stirrer was switched on with a rate of 500 rpm to eliminate the mass transfer effects. After 12 hours, the reaction system was cooled down to room temperature, and the reaction product were collected by centrifugation separation. The compositions of products were analyzed by a UPLC (Waters 2414) equipped with a C18 AQ column (Shiseido) and a refractive index detector. Conversion, selectivity and reaction rate are calculated as follows:

$$Conversion = \frac{(mol \ of \ glycerol \ converted)}{(mol \ of \ glycerol \ charged)} \times 100\%$$
(1)

$$Selectivity = \frac{(mol \ of \ product) \times (number \ of \ carbon \ atoms \ in \ the \ products)}{(Sum \ of \ carbon) - (based \ mol \ for \ all \ liquid \ products)} \times 100\%$$
(2)

$$(mol of 1,3 - PD converted)$$

$$1,3-PD formation rate = (reaction time) \times (the mounts of catalyst)$$

$$(mol of alveerol converted)$$
(3)

Glycerol reaction rate =
$$\overline{(reaction time)} \times (the mounts of catalyst)$$
 (4)

DFT Calculation details. All DFT calculations were performed with the Vienna ab initio simulation package (VASP),^{1, 2} the Perdew–Burke–Ernzerh of (PBE) exchange-correlation functional, the projector-augmented wave (PAW)³ method and a plane wave cutoff energy of 400 eV. A Monkhorst–Pack mesh of $3\times3\times1$ k-points was used for the Brillouin zone integration. A force convergence of 0.03 eV/Å was used in geometry optimization. The unit cell of IrRe alloy crystalline was obtained from Aflowlib.org.⁴ The optimum lattice parameters of the IrRe alloy unit cell was calculated to be a = 2.743 Å, b = 4.399 Å and c = 4.836 Å. The IrRe surface was modeled using a p (2×2) supercell four-layer slab, in which the bottom two layers were fixed at the bulk lattice position. A 20 Å-vacuum layer was employed to separate the surface from the periodic image in the direction along the surface of the slab. The dimer method ⁵⁻⁶ was applied to located the transition states, which were confirmed by the frequency analysis with only one imaginary frequency. The reliability of this method was first checked before the calculations for TS states. As an example, we performed the location for the TS state of the α O-H bond breaking of glycerol (TS_{aO-H} in Fig. 1) with the climbing

image nudged elastic band (CI-NEB) method ^{7.9} to get the minimum energy paths (MEPs) first within the convergence criterion of force less than 0.05 eV/Å. The results of the TS states obtained by the dimer method is similar to that obtained by the combination of CI-NEB and dimer method (Fig. S10), which indicate that the TS states located by the dimer method without using the NEB one are reliable here. Thus, to improve the calculation efficiency for TS states, the dimer method was employed directly to search the TS states with confirmation of frequency analyses with only one imaginary frequency. The energy of adsorption (E_{ads}) were calculated using $E_{ads} = E_{complex} -$ ($E_{adsorbate} + E_{surface}$), where $E_{complex}$ represents the energy of adsorbate on the IrRe surface, $E_{adsorbate}$ and $E_{surface}$ are the energies of isolated adsorbate and IrRe surface, respectively. The surface energy γ was defined by $\gamma = (E_{slab}(n) - nE_{bulk})/2A$, ¹⁰ where n is the number of bulk units in the slab and A is the surface area of the slab. $E_{slab}(n)$ and E_{bulk} are the energies of slab model and bulk model, respectively.

Microkinetics modeling. Based on the DFT calculation results, the microkinetics modeling was carried with considering the elementary steps: i) glycerol molecular adsorption; ii) hydrogen molecular dissociative adsorption; iii) the β C-H bond scission; iv) the β C-O bond scission; v) hydrogenation; vii) H₂O formation; viii) 1,3-PD molecular desorption; ix) H₂O molecular desorption. For surface reaction steps, the rate constants for the forward and backward

elementary reactions were calculated according to the Eyring equation $k = Ae^{-\frac{E_a}{k_b T}}$, where k, A, k_b, T and E_a are the reaction rate constant (s⁻¹), pre-exponential factor (s⁻¹), Boltzmann constant, temperature (K), and the activation barrier (J/mol), respectively. Based on Hertz-Knudsen kinetics, the rate constants for adsorption (k_{ads}) and desorption (k_{des}) of gas molecules are given as $k_{ads} =$ $\frac{PA_i}{\sqrt{2\pi m k_b T}} S_{\text{and } k_{des}} = \frac{k_b T^3 A_i 2\pi k_b}{h^3 \alpha \theta_{rot}} e^{-\frac{E_{des}}{RT}}, \text{ where P, A_i, m, S, h, \alpha and } \theta_{rot} \text{ are partial pressure of the adsorbate (Pa), the surface area of the adsorption site (m²), mass of adsorbate (kg), sticking coefficient, Plank constants, the symmetry number, the characteristic temperature (K), respectively. The pre-exponential factors for all surface elementary reaction steps were approximately 10⁻¹³ s⁻¹.¹¹ The microkinetic simulations of glycerol hydrogenolysis were carried by the self-developed program code by Python. The degree of rate control (DRC) analysis proposed by Campbell et al.¹². ¹³ was applied to identify the rate-determining-step among the elementary steps. The DRC$

coefficient of elementary step i (i.e., X_{RC,i}) was calculated as:
$$X_{RC,i} = \frac{k_i}{r} (\frac{\partial r}{\partial k_i})_{k_j \neq i'^{K_i}} \approx \frac{k_i(r - r_0)}{r(k_i - k_i^0)}$$

with $k_i = (1 + x)k_i^0$, where k_i represents the reaction rate constants of step i. X_{RC,i} was calculated by changing the forward and reverse rate constants of step i simultaneously by 10% (x = 0.1).

	Additive	Conv. (%)	Selectivity (%)				Formation Rate
Entry			1,3-PD	1,2-PD	1-PO	2-PO	(mmol _{1,3-}
							$_{PD} \cdot g_{cat} \cdot h \cdot h \cdot 1)$
1	None	31.1	35.3	27.7	28.6	8.4	2.7
2	Amberlyst-15 (50 mg)	55.3	39.3	12.3	38.7	9.7	5.2
3	Amberlyst-15 (100 mg)	58.4	38.8	11.9	39.1	10.1	5.5
4	H-ZSM-5 (50 mg)	49.8	39.4	12.8	37.4	10.4	4.7
5	H-ZSM-5 (100 mg)	52.8	39.5	13.2	36.9	10.4	5.0
6	$H_2SO_4 (H^+/Ir = 1)$	< 1	N.D.	N.D.	N.D.	N.D.	
7	$H_2SO_4 (H^+/Ir = 2)$	< 1	N.D.	N.D.	N.D.	N.D.	
8	$HNO_3 (H^+/Ir = 1)$	14.5	28.0	53.9	9.1	9.0	1.0
9	$HNO_3 (H^+/Ir = 2)$	11.2	22.3	56.2	13.4	8.1	0.6
10	$\mathrm{HCl}(\mathrm{H}^{+}/\mathrm{Ir}=1)$	38.8	38.2	24.6	28.7	8.5	3.6
11	$HCl (H^{+}/Ir = 2)$	36.6	36.9	26.0	28.6	8.5	3.3
12	Amberlyst-15 ^a (100 mg)	< 1	N.D.	N.D.	N.D.	N.D.	
13	H-ZSM-5 ^a (100 mg)	<1	N.D.	N.D.	N.D	N.D	

Table S1. Effects of acids on glycerol hydrogenolysis over Ir-Re/SiO₂ catalyst

Reaction condition: glycerol 0.043 mol, aqueous solution 20 g, catalyst 0.15 g, 493 K, 8 MPa H_2 , $H^+/Ir =$

1(molar ratio), 12 h.

N.D.: Not detected.

a: Only solid acids addition.

surface	010	111	011	001	100	110
γ (J/m ²)	1.84	2.74	2.60	2.45	2.42	2.51

Table S2. Summary of the surface energy for investigated surfaces of IrRe alloy.

For IrRe alloy, the surface energy of six low Miller index (010), (111), (011), (001), (100) and (110) planes were calculated in order to determine the most thermodynamically stable surface of the alloy, and summarized in **Table S2** and **Fig. S1**. As listed in **Table S2**, the (010) plane exhibits the lowest surface energy, suggesting the (010) surface is the most thermodynamically stable. Furthermore, the distance between Ir and Re is determined to 0.25 nm, which agrees well with the results seen with TEM image of IrRe/SiO₂ catalyst (**Fig. S2**). Thus, the IrRe (010) surface was chosen as the model surface for studying glycerol hydrogenolysis to 1,3-PD.



Fig. S1. The side view and top view on the surface structures of (010), (111), (011), (001), (100) and (110) surfaces.



Fig. S2. Typical HR-TEM image of the IrRe/SiO₂ alloy catalyst, which was acquired using a JEOL

JEM 2100F with accelerating voltage of 200 kV.



Fig. S3. Optimized configuration of isolated glycerol molecule.



Fig. S4. Glycerol adsorption models on the IrRe (010) surface of (a) configuration 1, (b) configuration 2 and (c) configuration 3.



Fig. S5. The configurations of the transition states and the intermediates involved in the four pathways for the scission of β C-OH.



Fig. S6. The configurations of the transition states and intermediates involved in pathway of glycerol hydrogenolysis to 1,3-PD initialized with the scission of β C-H bond followed by that of β C-OH bond on the IrRe surface.

Step	Elementary step	Reaction rate equation	$^{a}a_{ m for}$ (k _{ads})	^b a _{rev} (k _{des})	$^{c}E_{a}^{for}$	${}^{d}E_{a}{}^{rev}$	X _{RC}
R1	$C_3H_8O_3(g) + * \Leftrightarrow C_3H_8O_3*$	$r_1 = k_{ads} P_{C_3 H_8 O_3} - k_{des} \theta_{C_3 H_8 O_3 *}$	139	1.03×10 ⁶		8.93×10 ⁴	
R2	$H_2(g) + 2 * \Leftrightarrow 2H^*$	$r_2 = k_{ads} P_{H_2} \theta_*^2 - k_{des} \theta_{H_*}^2$	940	6.81×10 ³		8.64×10 ⁴	
R3	$C_3H_8O_3* + * \Leftrightarrow C_3H_7O_3* + H*$	$r_{3} = k_{for} \theta_{C_{3}H_{8}O_{3}*} \theta_{*} - k_{rev} \theta_{C_{3}H_{7}O_{3}*} \theta_{H}$	- 10 ¹³	10 ¹³	6.04×10 ⁴	1.06×10 ⁴	0.178
R4	$C_3H_7O_3* + * \Leftrightarrow C_3H_6O_2* + OH*$	$r_{4} = k_{for} \theta_{C_{3}H_{7}O_{3}*} \theta_{*} - k_{rev} \theta_{C_{3}H_{6}O_{2}*} \theta_{OH}$	10 ¹³	1013	4.22×10 ⁴	9.12×10 ⁴	0
R5	$C_3H_6O_2^* + H^* \Leftrightarrow C_3H_7O_2^*$	$r_{5} = k_{for} \theta_{C_{3}H_{6}O_{2}*} \theta_{H*} - k_{rev} \theta_{C_{3}H_{7}O_{2}*}$	10 ¹³	10 ¹³	4.99×10 ⁴	5.32×10 ⁴	0
R6	$C_3H_7O_2^* + H^* \Leftrightarrow C_3H_8O_2^*$	$r_6 = k_{for} \theta_{C_3 H_7 O_2 *} \theta_{H*} - k_{rev} \theta_{C_3 H_8 O_2 *}$	1013	1013	6.14×10 ⁴	6.30×10 ⁴	0
R7	$\mathrm{H}^{*} + \mathrm{OH}^{*} \Leftrightarrow \mathrm{H}_{2}\mathrm{O}^{*}$	$r_7 = k_{for} \theta_{H*} \theta_{OH*} - k_{rev} \theta_{H_2O*}$	1013	1013	9.12×10 ⁴	5.28×10 ⁴	0.775
R8	$C_3H_8O_2^* \Leftrightarrow C_3H_8O_2(g)^+ *$	$r_8 = k_{des} \theta_{C_3 H_8 O_2 *} - k_{ads} P_{C_3 H_8 O_2} \theta_*$	152	2.07×10 ⁶	8.64×10 ⁴		
R9	$H_2O^* \Leftrightarrow H_2O(g) + *$	$r_9 = k_{des}\theta_{H_2O*} - k_{ads}P_{H_2O}\theta_*$	313	9.5×10 ⁷	6.24×10 ⁴		

Table S3. Elementary steps and corresponding information for microkinetics modeling.

a. The pre-exponential factor for forward reaction step or rate constants for adsorption, in s⁻¹.

b. The pre-exponential factor for reverse reaction step or rate constants for desorption, in s⁻¹.

c. The energy barrier for forward reaction step, in J/mol.

d. The energy barrier for reverse reaction step, in J/mol.



Fig. S7. Adsorption configurations of glycerol and 1,3-PD on the clean IrRe and hydroxyl covered IrRe surfaces: (a) glycerol on clean IrRe surface, (b) glycerol on hydroxyl covered IrRe surface, (c) 1,3-PD on clean IrRe surface, and (d) 1,3-PD on hydroxyl covered IrRe surface.

Table S4. Comparison for the 1,3-PD hydrogenolysis over Ir-Re/SiO₂ catalyst with and without amberlyst-15.

Substrate/Additive	Conversion (%)	1-PO Selectivity (%)	Rate $(mmol_{1,3-PD} \cdot g_{cat}^{-1} \cdot h^{-1})$
1,3-PD/None	10.7	100	2.4
1,3-PD/Amberlyst-15	37.7	100	9.1

Reaction condition: 0.043 mol of 1,3-PD, 20 g of aqueous solution, 0.15 g of catalyst (50 mg of

Amberlyst-15), 493 K of temperature, 8 MPa of H₂, 12 h of reaction time.



Fig. S8. The adsorption configurations of glycerol on IrRe-OH (ML = 0.06) surface with (a) $H_7O_3^+$ and (b) without $H_7O_3^+$.



Fig. S9. The configurations of the transition state structure of H_2O formation with the assistance of $H_7O_3^+$.



Fig. S10. (a) MEPs for the αO-H scission of glycerol with the configurations for (b) initial state, (c-f) the configurations of four inserted images and (g) the configurations of final state. (h) The configurations of transition state obtained by the combination of NEB and dimer methods and (i) that obtained by with dimer method directly.

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