Supporting Information

Ir-Re Alloy as a highly active catalyst for the hydrogenolysis of glycerol to 1,3-propanediol

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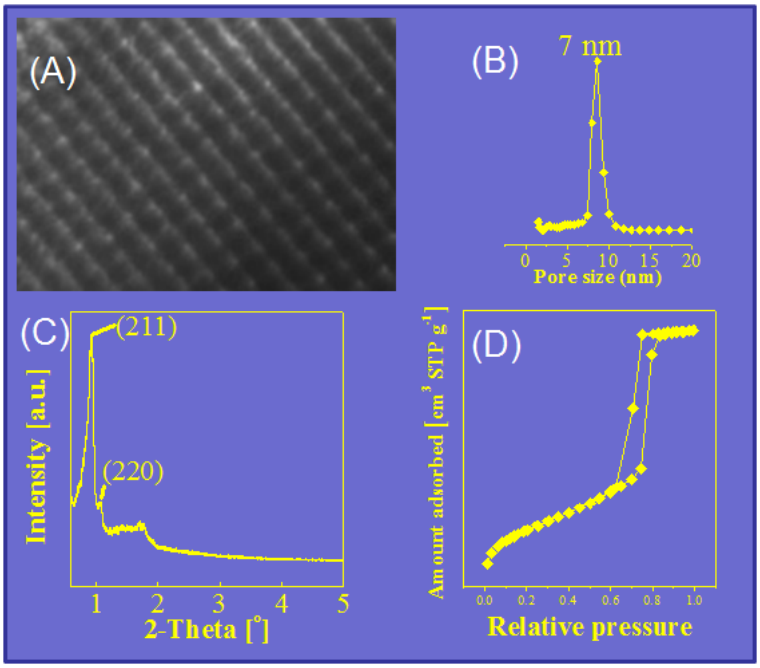

Figure S1. Properties of as-synthesized KIT-6 support: (A) TEM, (B) pore size distribution, (C) small-angle XRD, and (D) N_2-adsorption isotherm.

Table S1. Comparison of performance of heterogeneous catalysts in batch glycerol hydrogenolysis

Catalyst	Solvent /additive	P_{H2} [a]/T [b]/t [c]/GLY [d]	1,3-PD formation rate [e]	Ref.
Ir-Re/KIT6-R	H_2O/Amberlyst-15	8.0/393/12/43	25.6	This work
Ir-Re/KIT6-R	H_2O	8.0/393/12/43	17.2	This work
Ir-ReO_x/SiO_2	H_2O/H_2SO_4	8.0/393/24/43	15.4	[4i]
Ir-ReO_x/SiO_2	H_2O	8.0/393/24/43	9.1	[4i]
Pt/sulfated ZrO_2	DMI [c]	7.3/443/24/43	6.8	[4e]
Pt/WOx/AlOOH	H_2O	5.0/453/12/1.0	6.0	[4h]
Pt-Re/C	H_2O	4.0/443/8.0/2.2	5.7	[4b]
Pt/WO_3/ZrO_2	DMI [f]	8.0/443/24/3.0	4.0	[12]
Pt/WO_3/TiO_2/SiO	H_2O	5.5/453/12/43	2.8	[13]
2				

[a] Hydrogen pressure (MPa); [b] Reaction temperature (K); [c] Reaction time (h); [d] Glycerol (mmol); [e] $mol_{1,3PD}\ mol_{metal}^{-1}\ h^{-1}$; [f] Dimethyl imidazolinone (DMI).

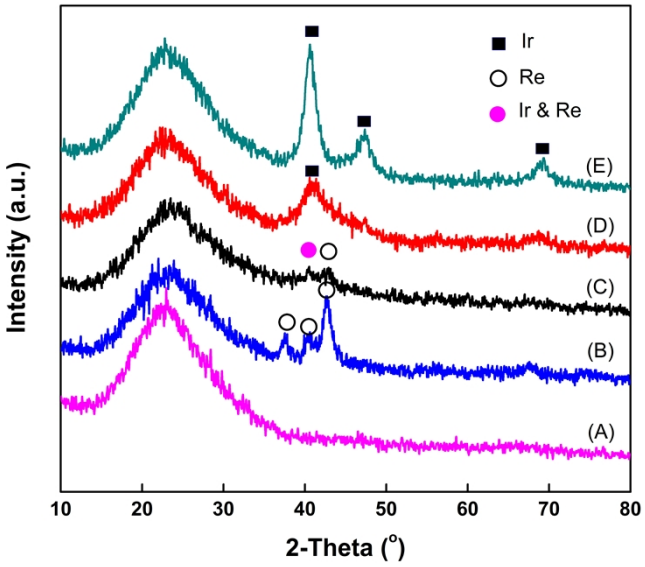

Figure S2. Powder XRD patterns for KIT-6 (A), Re/KIT-6-R (B), Ir-Re/KIT-6-R (C), Ir-Re/KIT-6-CR (D) and Ir/KIT-6-CR (E).

The powder X-ray diffraction (XRD) patterns are shown in Figure S2. For Ir-Re/KIT-6-CR, only a broadened diffraction peak at 40.6° assignable to Ir metal is detected; no diffraction peaks due to a Re-containing phase is observed, consistent with previous observations.[4a,4f,5] This result suggests high dispersion of the Re species on the catalysts.[4f] Furthermore, no shift of the diffraction peak was observed for Ir-Re/KIT-6-CR, indicating that no Ir-Re alloy is formed. The XRD pattern for Ir-Re/KIT-6-R exhibits diffraction peaks assignable to the metallic phase of Re, while peaks assignable to the metallic Ir phase cannot be clearly distinguished due to the overlap of Ir(111) at 40.6° (PDF#87-0599) with Re(002) at 40.4° (PDF#87-0715), as shown in Figure S2-C. In addition, the intensity of the diffraction peaks for Ir-Re/KIT-6-R is very weak. This phenomenon is similar to the case observed by H. Karan et al., where they studied the Pt deposition on Ir and Re alloy nanoparticles for oxygen reduction reaction.[S1] They

attributed the phenomenon, for the very small particles, to the surface-segregation of Ir in the Ir-Re alloy.[S1,S3] As a result, sufficient XRD signal could not be produced for such a layer. For this reason, the existence of an Ir-Re alloy phase could not be assessed in the freshly reduced catalyst by XRD. This phenomenon is possibly due to the presence of amorphous Ir-Re alloy for the bimetallic nanoparticles as well as its high dispersion on the support surface.[S1,S2]

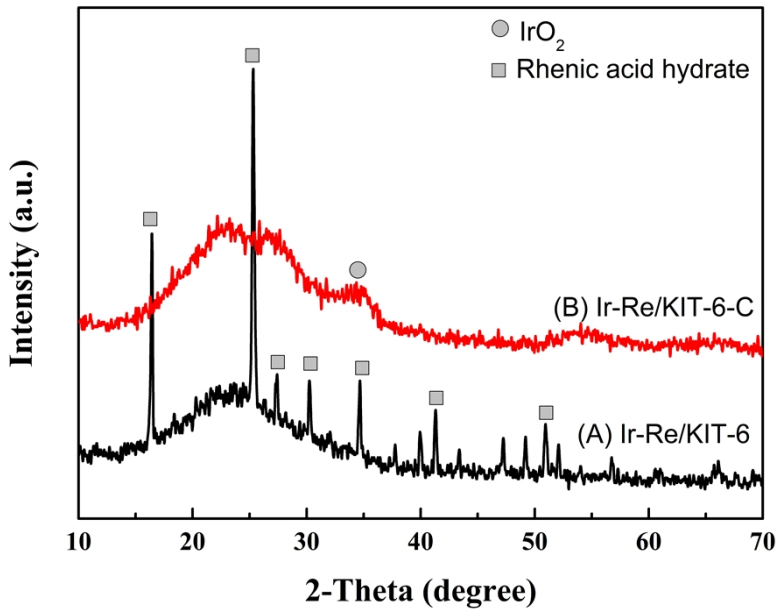

Figure S3. XRD patterns of dried Ir-Re/KIT-6 (A) and Ir-Re/KIT-6-C (B).

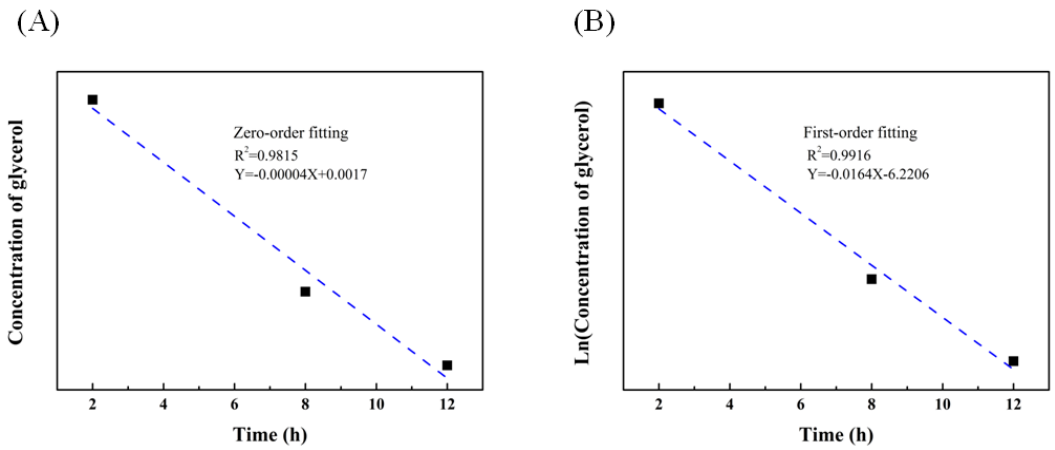

Figure S4. Plots of Concentration of glycerol vs. time for Ir-Re/KIT-6-R (A), and ln(Concentration of glycerol) vs. time for Ir-Re/KIT-6-CR.

It is known that, in a batch reactor, zero-order and first-order reaction of reactant "A" follows the equations: $C_A=C_{A0}-kt$ and $kt=\ln(C_{A0}/C_A)$, respectively, where the C_A represents the concentration of reactant A at reaction time "t", the C_{A0} represents the initial concentration of reactant A.[S4] We fitted the relationship between concentration of glycerol and time for the two catalysts based on the equations (Fig. S4). It is found that the concentration of glycerol changes with time in a line for Ir-Re/KIT-6-R, demonstrating the reaction order with respect to glycerol is nearly zero. In contrast, ln(Concentration of glycerol) changes with time in a line for Ir-Re/KIT-6-CR, showing that the reaction order of glycerol is ca. one rather than zero.

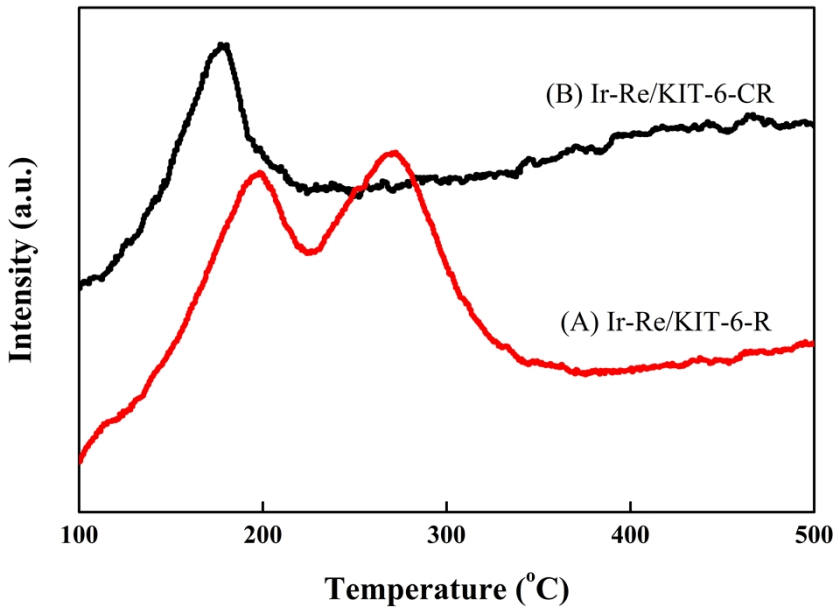

Figure S5. NH_3-TPD profiles of Ir-Re/KIT-6-R (A) and Ir-Re/KIT-6-CR (B).

Table S2. Hydrogenolysis of various substrates (glycerol, 1,3-PD and 1,2-PD over Ir-Re/KIT-6-R.

Substrate	Conv. (%)	Selectivity (%)			
		1,3-PD	1,2-PD	1-PO	2-PO
1,2-PD	80.0	-	-	81.9	18.1
1,3-PD	13.6	-	-	100.0	-
Glycerol	39.7	37.1	25.8	28.0	9.1

Reaction conditions: 120 °C, 43 mmol substrate, 8 MPa H_2, 12 h, catalyst (150 mg).

References

S1 H. I. Karan, K. Sasaki, K. Kuttiyiel, C. A. Farberow, M. Mavrikakis and R. R. Adzic, *ACS Catal.,* 2012, **2**, 817.

S2 S. Hirasawa, H. Watanabe, T. Kizuka, Y. Nakagawa and K. Tomishige, *J. Catal.,* 2013, **300**, 205.

S3 B. Hammer, L. B. Hansen and J. K. Nørskov, *Phys. Rev. B,* 1999, **59**, 7413.

S4 O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed., New York: John Wiley, 1972.