Supporting Information

Propylene from Renewable Resources: Catalytic Conversion of Glycerol into Propylene

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1. Materials and Methods

1.1 Catalytic materials

Glycerol, 1-propanol, 1,2-propanediol, 1,3-propanediol, methanol, ethanol, ethylene glycol, propylene, propane, methane, ethane, sodium chloride, *n*-propyl ether, $ZrOCl_2 \cdot 8H_2O$ and NH_4OH were supplied by Aladdin. Metal oxide SiO_2, Al_2O_3, TiO_2 and activated carbon were supplied from the Degussa. Palladium chloride ($PdCl_2$), rhodium chloride hydrate ($RhCl_3 \cdot xH_2O$), Ruthenium chloride hydrate ($RuCl_3 \cdot xH_2O$), chloroplatonic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$), Chloroiridic acid hexahydrate ($H_2IrCl_6 \cdot 6H_2O$), were supplied by Aldrich and used without further purification. HZSM-5, SAPO-34 and MCM-41 were supplied by Novel Chemical. The symbol HZSM-5-X denotes HZSM-5 zeolite with SiO_2/Al_2O_3 molar ratio of X. For example, HZSM-5-30 refers to HZSM-5 zeolite with SiO_2/Al_2O_3 molar ratio of 30.

1.2 Catalyst preparation

Preparation of zirconia (ZrO_2)

ZrO_2 powders were prepared by a conventional precipitation method following the reported procedure.[S1] Briefly, 12.9 g $ZrOCl_2 \cdot 8H_2O$ was dissolved in 200 mL deionized water at room temperature, the pH was adjusted to 9.0 by dropwise addition of NH_4OH (2.5 M). After 6 h stirring at room temperature, the resultant hydro gel was washed with deionized water until free of chloride ions. The precipitate was then dried at 110 °C overnight and calcined at 400 °C for 2 h in air. The BET surface area of the resultant material was 115 m^2 g^{-1} (Micromeritics TriStar 3000).

Preparation of Ir/ZrO_2, Pd/ZrO_2, Pt/ZrO_2, Ru/ZrO_2, Rh/ZrO_2 catalysts

1 wt% Ir/ZrO_2, 1 wt% Pd/ZrO_2, 1 wt% Pt/ZrO_2, 1 wt% Ru/ZrO_2 and 1 wt% Rh/ZrO_2 catalysts were prepared by incipient-wetness impregnation (IWI) of the support, with aqueous solution of $H_2IrCl_6 \cdot 6H_2O$, $PdCl_2$, $H_2PtCl_6 \cdot 6H_2O$, $RuCl_3$ or $RhCl_3$ precursors of appropriate concentrations (typically 1.0 mL g^{-1} support). After a perfect mixing of the corresponding slurries, the resulting mixture was vigorously stirred at 80 °C for 4 h. Then samples were dried under vacuum at room temperature for 12 h and then reduced in 5% H_2/Ar (80 mL min^{-1}) at 400 °C for 2 h.

Preparation of Ir/Al_2O_3, Ir/TiO_2, Ir/SiO_2, Ir/C catalysts

1 wt% Ir/Al_2O_3, 1 wt% Ir/TiO_2, 1 wt% Ir/SiO_2, 1 wt% Ir/C catalysts were prepared by incipient-wetness impregnation of the corresponding support, with aqueous solution of $H_2IrCl_6 \cdot 6H_2O$ precursors of appropriate concentrations (typically 1.0 mL g^{-1} support). After a perfect mixing of the corresponding slurries, the resulting mixture was vigorously stirred at 80 °C for 4 h. Then samples were dried under vacuum at room temperature for 12 h and then reduced in 5% H_2/Ar (80 mL min^{-1}) at 400 °C for 2 h.

1.3 Catalyst characterization

Elemental analysis: The metal loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

BET analysis: The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm.

X-ray diffraction (XRD): The crystal structures of various noble metal catalysts and HZSM-5 were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA.

X-ray absorption fine structure (XAFS): The X-ray absorption data at the Ir L_3-edge of the samples were recorded at room temperature in transmission mode using ion chambers or in the fluorescent mode with silicon drift fluorescence detector at beam line BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF), China. The station was operated with a Si (311) double crystal monochromator. During the measurement, the synchrotron was operated at energy of 3.5 GeV and a current between 150-210 mA. The photon energy was calibrated with standard Pt metal foil. Data processing was performed using the program ATHENA.[S2]

Transmission electron microscopy (TEM): TEM images for various noble metal catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

Thermogravimetry analysis (TGA): The used HZSM-5-30 after the reaction for 60 h was submitted to thermogravimetry analysis (TGA) in flowing air. Samples (10 mg) were heated from 30 to 800 °C in a Perkin-Elmer TGA-7 Thermogravimetric Analyzer under flow of air (10 mL min^{-1}) at a heating rate of 5 °C min^{-1}.

NH$_3$-temperatue-programmed desorption (NH$_3$-TPD): NH$_3$ was adsorbed at 60 °C for 0.5 h after pretreatment at 500 °C for 1 h in a He stream. The desorbed NH$_3$ in flowing He gas was quantified (NH$_2$ fragment of mass number 16) by mass spectroscopy (Balzers OmniStar) at 60–700 °C (ramp rate, 10 °C min^{-1}).

H$_2$ chemisorption experiments: H$_2$ chemisorption experiments were carried out in an Auto Chem II chemisorption Analyzer. 0.5 g catalyst sample (Ir/Al$_2$O$_3$, Ir/TiO$_2$, Ir/SiO$_2$, Ir/C, Ir/ZrO$_2$, Pd/ZrO$_2$, Pt/ZrO$_2$, Ru/ZrO$_2$, Rh/ZrO$_2$) was firstly treated in a flow of 10 vol % H$_2$/Ar at 400 °C for 1 h at a ramping rate of 5 °C /min. After purging with Ar for 10 min, the sample was cooled down to 50 °C in Ar before the chemisorption experiments were carried out. The adsorption of hydrogen was carried out by pulsing 10 vol % H$_2$/Ar until saturation. Hydrogen consumption was detected by a thermal conductivity detector (TCD).[S3]

2. Catalytic activity measurements

2.1 General procedure for the hydrogenolysis of glycerol to 1-PO

A mixture of glycerol (1.0 g), supported metal catalysts (metal 0.12 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (9 mL) were charged into a 100 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 5 MPa H$_2$ for given reaction time. The mixture of substrates and catalyst were heated to the desired temperature in less than 15 minutes. The liquid products were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and a flame ionization detector (FID). The hydrocarbon gas products were analyzed using a gas chromatograph (Type GC-122, Shanghai) equipped with a 6-m packed column of Porapak Q and FID. The gas products, including CO and CO$_2$, were analyzed on an Agilent 6820 gas chromatograph equipped with a TDX-01

column and TCD. The identification of the products was performed by using a GC-MS. The conversion and the selectivity were defined on the carbon basis.

2.2 Recovery and reuse of Ir/ZrO$_2$

The reused catalyst was recovered by filtering the solid Ir/ZrO$_2$ from liquid phase after the reaction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried under vacuum at room temperature for 12 h.

2.3 General procedure for the dehydration of 1-PO to propylene

The dehydration of 1-PO was carried out in a vertical fixed-bed reactor (i.d. 10 mm, length 500 mm) under atmospheric pressure at 250 $^{\circ}$C. The catalyst (2.0 g) was placed in the middle of a stainless reactor. The 1-PO feedstock was continuously introduced into the reactor by an HPLC pump with a WHSV of 1.0 h^{-1}. The products were obtained when the reaction reached the stead state. The liquid and gas products were cooled and collected in a gas-liquid separator immersed in an ice-water trap. The liquid products were analyzed on a Shimadzu GC-17A gas chromatograph equipped with a capillary column HP-FFAP (30 m × 0.25 mm) and FID. The hydrocarbon gas products were analyzed using a gas chromatograph (Type GC-122, Shanghai) equipped with a 6-m packed column of Porapak Q and FID. The gas products, including CO and CO$_2$, were analyzed on an Agilent 6820 gas chromatograph equipped with a TDX-01 column and TCD. The identification of the products was performed by using a GC-MS.

2.4 General procedure for integrated conversion of glycerol to propylene

The integrated conversion of glycerol to propylene was carried out in a vertical fixed-bed reactor (i.d. 10 mm, length 500 mm) under certain hydrogen pressure at 250 $^{\circ}$C using a double-bed reaction mode (see Scheme S2). The double-bed reaction mode comprised an upstream hydrogenolysis catalyst Ir/ZrO$_2$ (2.0 g catalyst, 20-40 mesh) and a downstream dehydration catalyst HZSM-5 (2.0 g catalyst, 20-40 mesh). Both catalysts were located in the temperature-homogeneous hot zone of the reactor, and they were separated with a thin layer of quartz wool. Glycerol was continuously introduced into the reactor with an HPLC pump with a WHSV of 1.0 h^{-1}. The products were obtained when the reaction reached the stead state. The liquid and gas products were cooled and collected in a gas-liquid separator immersed in an ice-water trap.

2.5 Procedure for kinetic experiments of the hydrogenolysis of 1,2-PDO (or 1,3-PDO) to 1-PO

A mixture of 1,2-PDO (0.83 g), Ir/ZrO$_2$ catalysts (Ir 0.03 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (9 mL) were charged into a 100 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 250 $^{\circ}$C under 5 MPa H$_2$ for 15 min to give 1-PO in 24% yield.

A mixture of 1,3-PDO (0.83 g), Ir/ZrO$_2$ catalysts (Ir 0.03 mol%), 2-methoxyethyl ether (2 mmol, internal standard), water (9 mL) were charged into a 100 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm at 250 $^{\circ}$C under 5 MPa H$_2$ for 15 min to give 1-PO in 15% yield.

3. Results

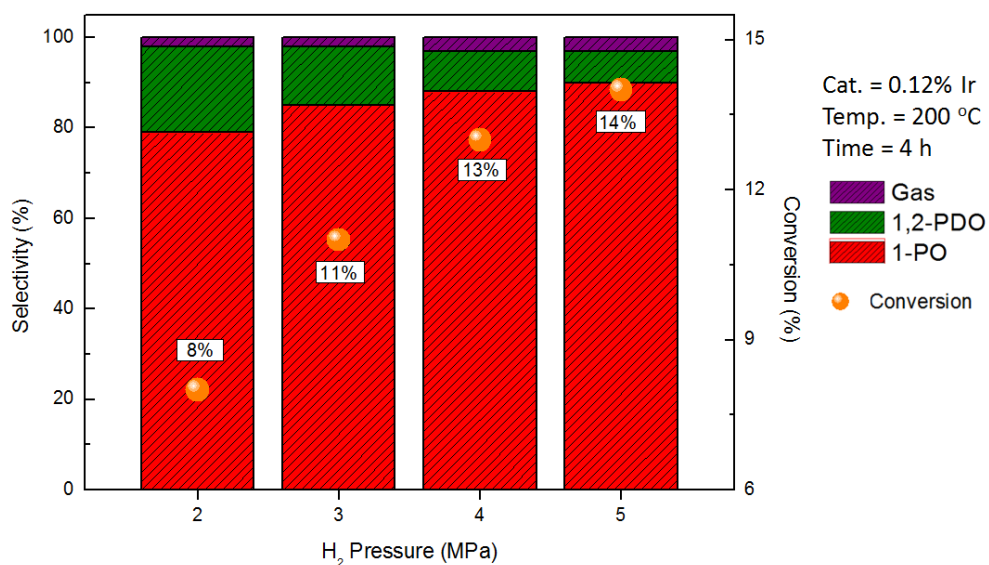## A. The effect of hydrogen pressure on glycerol hydrogenolysis over Ir/ZrO₂ catalyst

Figure S1. Catalytic performances for hydrogenolysis of diluted aqueous glycerol (10 wt%) over 1% Ir/ZrO₂ catalyst at different hydrogen pressure.
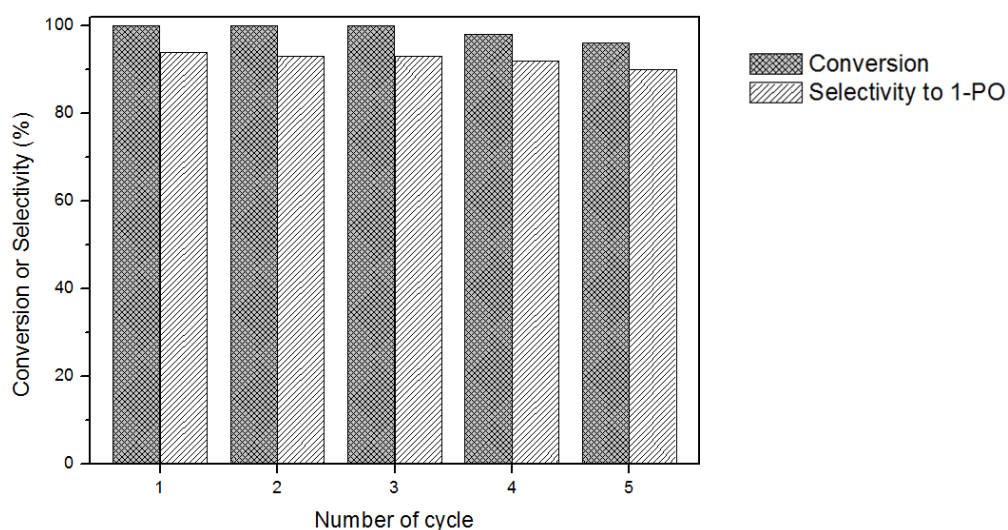
B. Reuse of Ir/ZrO₂ catalyst

Figure S2. Reuse of the Ir/ZrO₂ catalyst in the hydrogenolysis of glycerol to 1-PO. Reaction conditions: glycerol 1.0 g, catalyst Ir/ZrO₂ (Ir 0.12 mol%), water (9 mL), 250 °C, 4 h, 5 MPa H₂ (r.t.).

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C. Reaction profiles for the hydrogenolysis of glycerol with Ir/ZrO₂
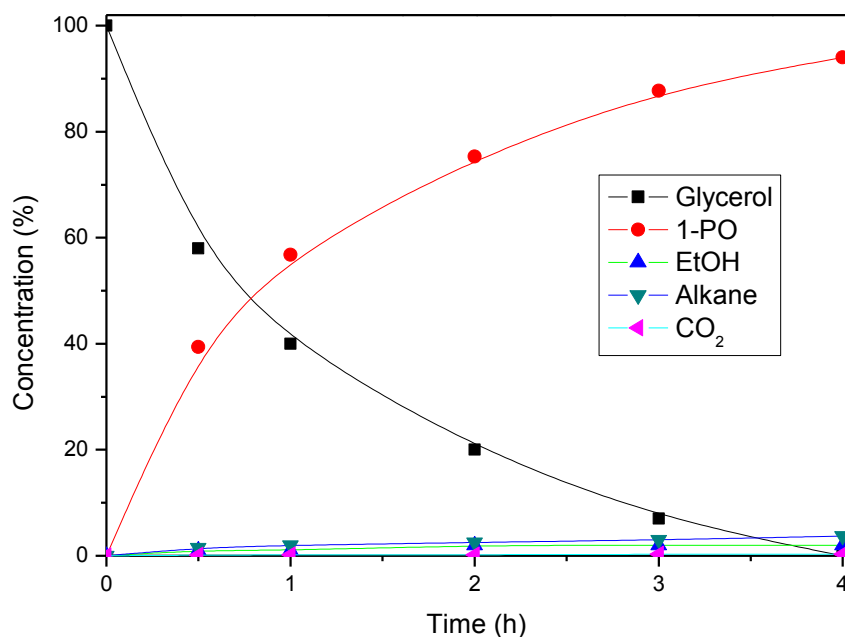
Figure S3. Time-course plot for the hydrogenolysis of glycerol with Ir/ZrO₂. Reaction conditions: glycerol 1.0 g, catalyst Ir/ZrO₂ (Ir 0.12 mol%), water (9 mL), 250 °C, 5 MPa H₂ (r.t.).

D. NH₃-TPD analysis of the different supports.
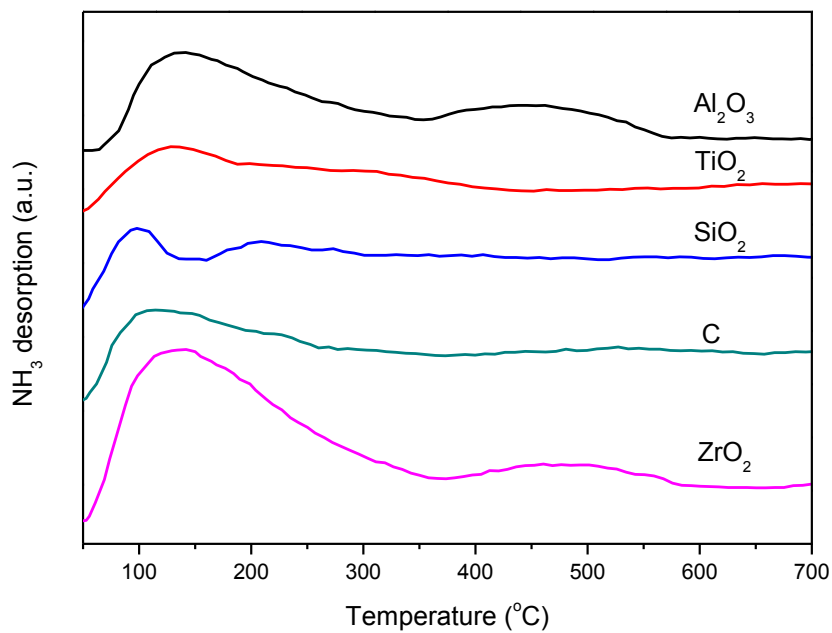
Figure S4. NH₃-TPD profiles of various supports.

E. XANES analysis of Ir/ZrO₂ catalyst
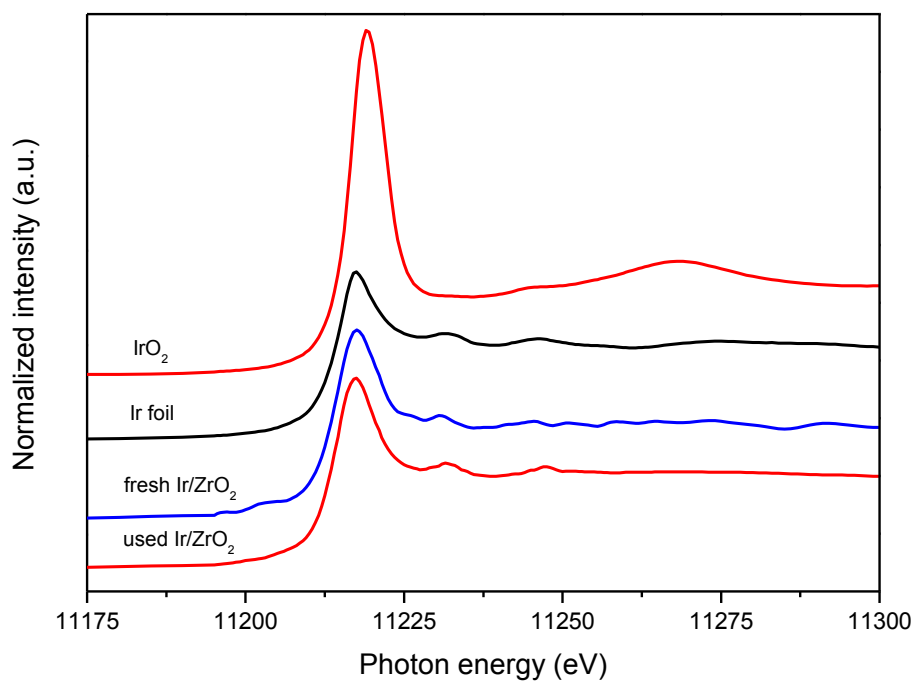
Figure S5. XANES for fresh Ir/ZrO₂ catalyst before reaction and used Ir/ZrO₂ catalyst after five runs. Note that Ir L_3-edge XANES data of the fresh and used Ir/ZrO₂ catalyst were clearly different from that of IrO₂ (as a reference compound for ionic Ir^{4+} species) but rather similar to that of Ir foil, which indicated that Ir species in the fresh and used Ir/ZrO₂ catalyst exist in metallic state.

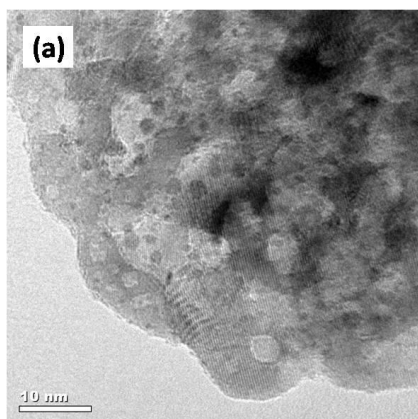# F. XRD analysis of various noble metal catalysts
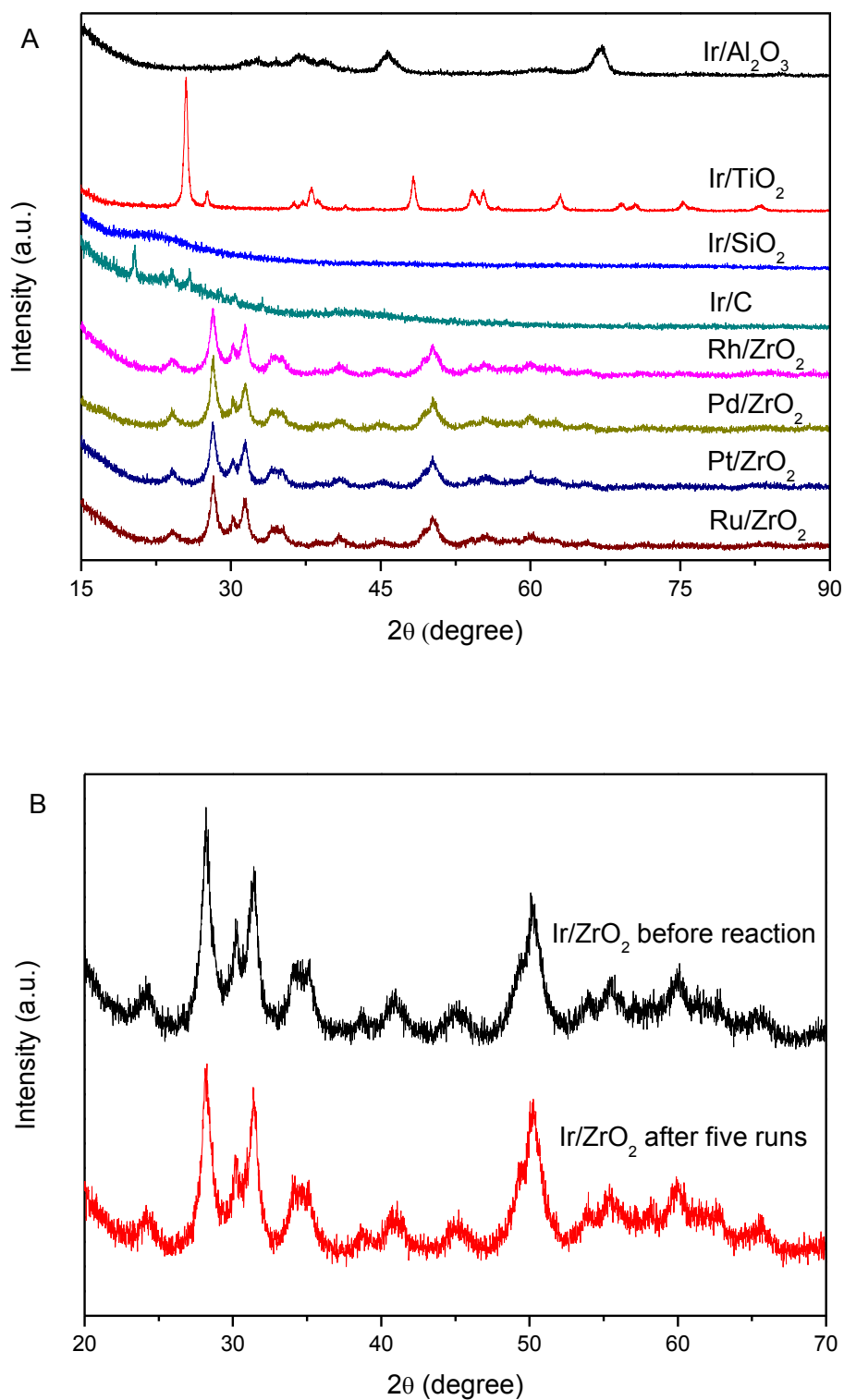
Figure S6. X-ray diffraction (XRD) patterns for various fresh noble metal catalysts (A) and Ir/ZrO$_2$ catalysts before reaction and after five runs (B).
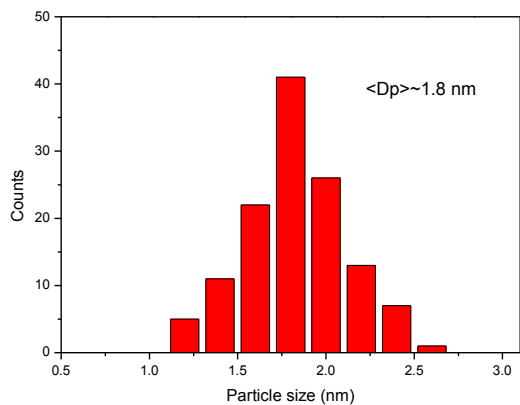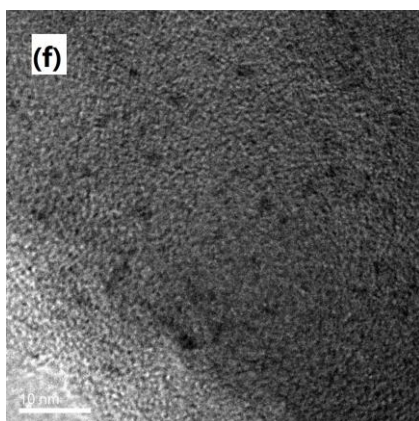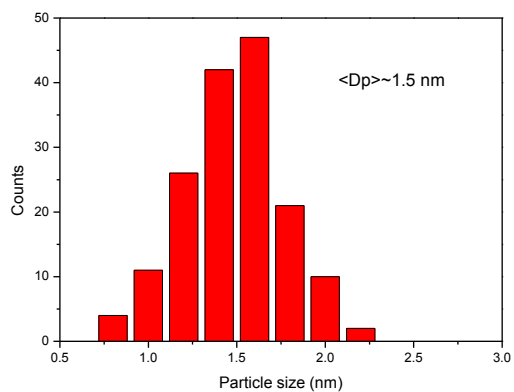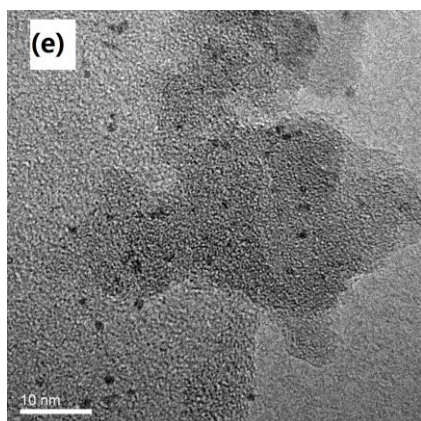
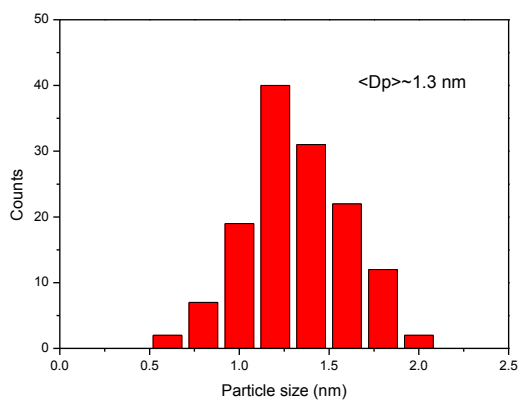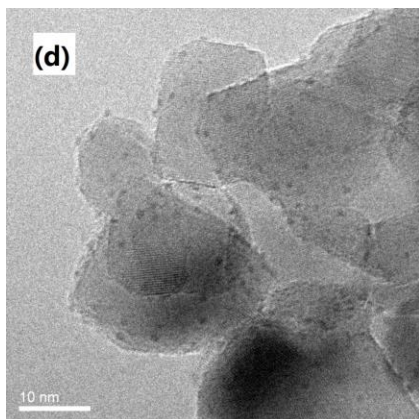# G. TEM analysis of various metal catalyst
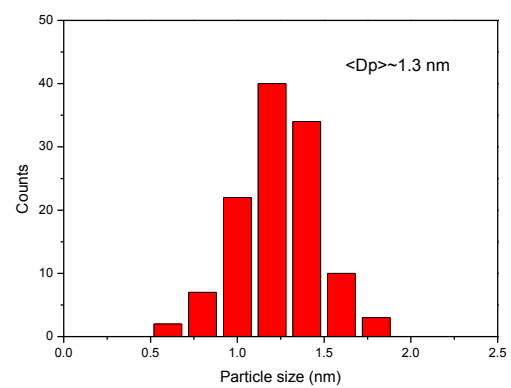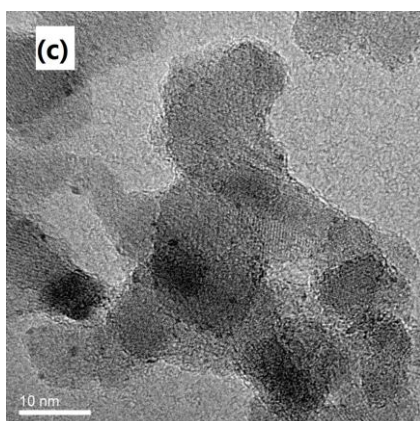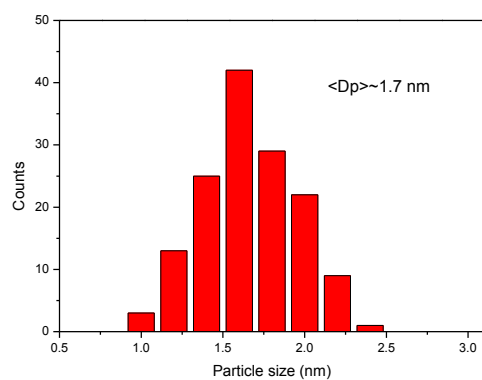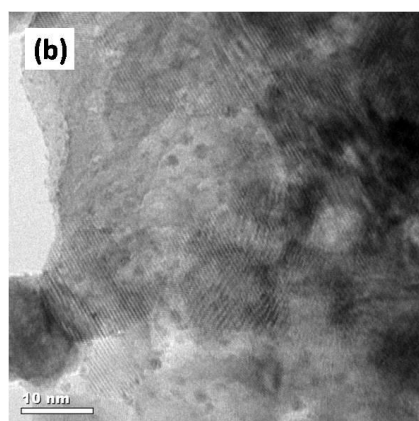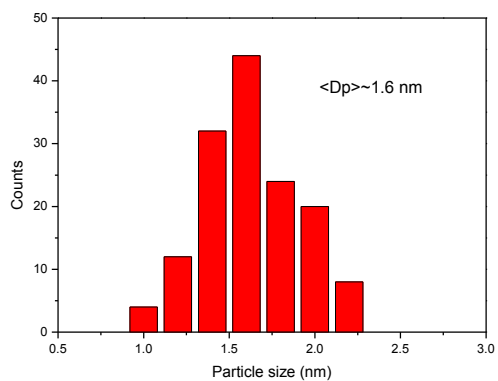
Figure S7. TEM images and metal particle size distribution of various catalysts a) Ir/ZrO$_2$ before reaction; b) Ir/ZrO$_2$ after five runs; c) Ir/Al$_2$O$_3$ before reaction; d) Ir/TiO$_2$ before reaction; e) Ir/SiO$_2$ before reaction; f) Ir/C before reaction.

H. Physicochemical properties for various noble metal catalysts

Table S1. Physicochemical properties for various noble metal catalysts

Catalyst	Metal loading[a] [wt%]	S_{BET} [$m^2\,g^{-1}$]	Particle size[b] [nm]	Metal dispersion[c] [%]
Ir/Al$_2$O$_3$	1.0	173	1.3	84
Ir/TiO$_2$	1.0	72	1.3	85
Ir/SiO$_2$	1.0	475	1.5	79
Ir/C	1.0	1361	1.8	69
Ir/ZrO$_2$	1.0	126	1.6	76
Rh/ZrO$_2$	1.0	129	-	75
Pd/ZrO$_2$	1.0	127	-	74
Pt/ZrO$_2$	1.0	125	-	78
Ru/ZrO$_2$	1.0	129	-	76

[a] Determined by ICP-AES analysts. [b] Average metal particle size estimated by statistic analysis from TEM results. [c] Metal dispersions determined by H$_2$ chemisorption experiments.

I. The hydrogenolysis of 1,2-PDO (or 1,3-PDO) to 1-PO with Ir/ZrO$_2$

Table S2. Catalytic performances for the hydrogenolysis of 1,2-PDO and 1,3-PDO to 1-PO with Ir/ZrO$_2$.[a]

Feed composition	t [h]	Conv. [%]	Selectivity [%]	
			1-PO	others[b]
1,2-PDO	0.25	24	99	1
1,3-PDO	0.25	15	98	2

[a] Reaction conditions: 1,2-PDO (0.83 g), 1,3-PDO (0.83 g), catalyst Ir/ZrO$_2$ (Ir 0.03 mol%), water (9 mL), 250 °C, 5 MPa H$_2$ (r.t.). [b] Others including ethanol, propane and methane.

J. The possible reaction route involved in glycerol hydrogenolysis to 1-PO
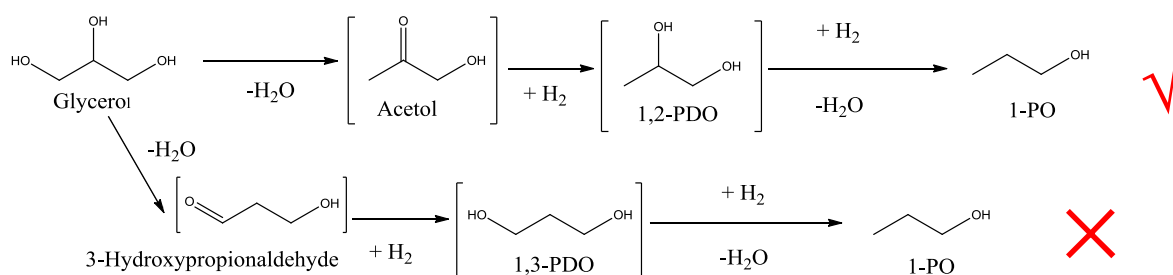
Scheme S1. Proposed reaction routes involved in glycerol hydrogenolysis over Ir/ZrO$_2$ catalyst.

K. The effect of reaction temperature on dehydration of 1-PO to propylene

Table S3. Dehydration of 1-PO to propylene under HZSM-5-30 catalyst at different temperatures.[a]

Temperatrue [$^{\circ}$C]	Conv. [%]	Selectivity [%]			Propylene yield [%]
		Propylene	n-propyl ether	Higher hydrocarbons	
220	81	98	2	trace	79
250	>99	>99	trace	trace	>99
280	>99	74	trace	26	74
300	>99	37	trace	63	37

[a] Reaction conditions: catalyst HZSM-5-30 2.0 g, neat 1-PO feedstock, WHSV = 1.0 h^{-1}, at atmosphere pressure, N$_2$ flow rate 20 mL min^{-1}, time on stream 2 h.

L. Physical properties of different solid acid catalysts.

Table S4. Texture characteristics of different solid acid catalysts.

Catalyst	S$_{BET}$ [m^2 g^{-1}]	V$_p$ [cm^3 g^{-1}]	Pore diameter [nm]
HZSM-5-30	350	0.200	0.55
HZSM-5-60	347	0.207	0.56
HZSM-5-100	351	0.209	0.58
HZSM-5-200	352	0.209	0.58
SAPO-34	393	0.265	0.52
MCM-41	710	0.456	3.02
Al$_2$O$_3$	190	0.428	4.35

M. XRD analysis of various HZSM-5 with different SiO_2/Al_2O_3 molar ratio.
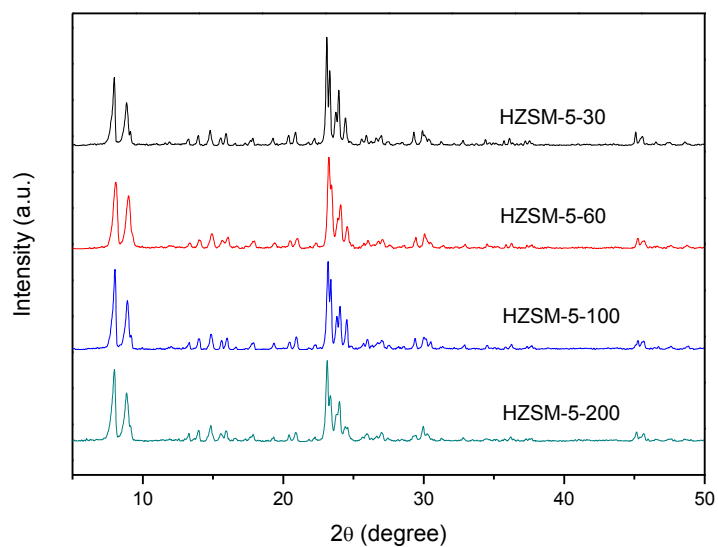

Figure S8. X-ray diffraction (XRD) patterns for different HZSM-5 with different SiO_2/Al_2O_3 molar ratio.

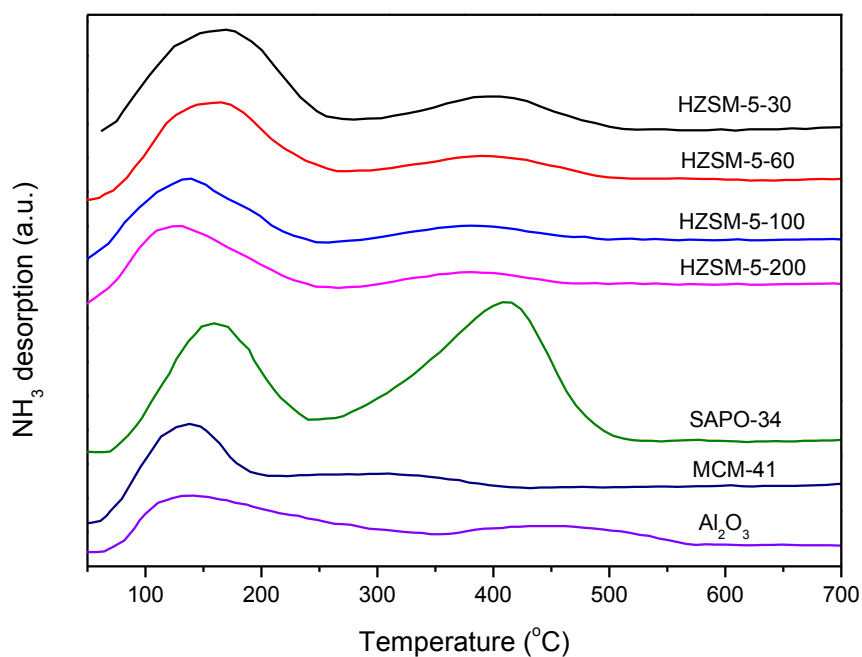## N. NH_3-TPD analysis of the different solid acid catalysts.

Figure S9. NH_3-TPD profiles of various solid acid catalysts.

O. TG analysis of the used HZSM-5-30 that reacted 60 h on steam
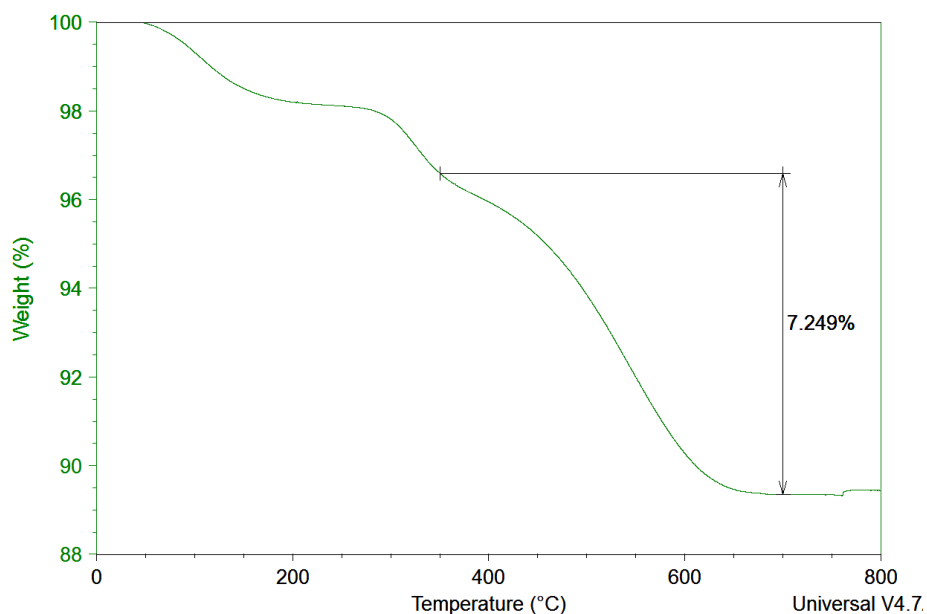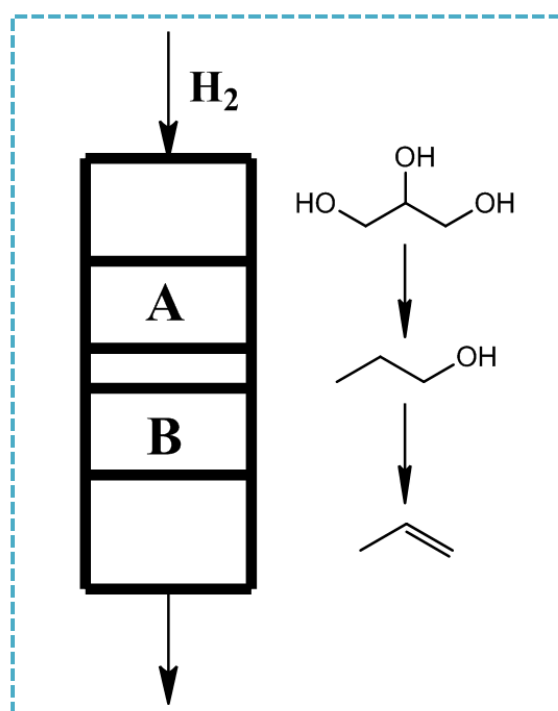

Figure S10. TG curve of the used HZSM-5-30 after the reaction for 60 h. The weight loss between 350 and 700 °C was ascribed to coke deposit burning.

P. Direct conversion of glycerol to propylene in a fixed-dual-bed reactor.

Scheme S2. Direct conversion of glycerol to propylene in a fixed-dual-bed reactor over catalyst A (Ir/ZrO$_2$) and catalyst B (HZSM-5).

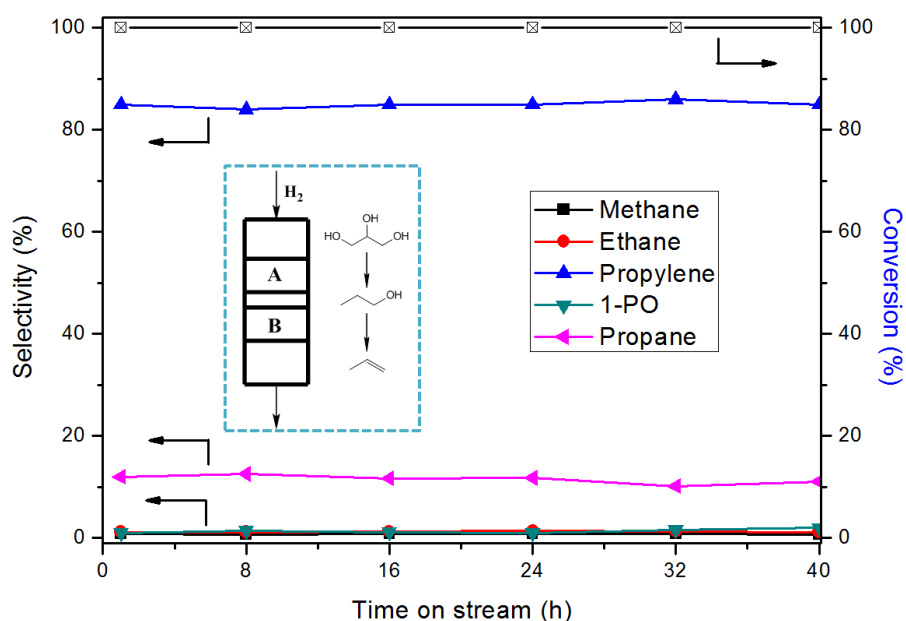## Q. Direct conversion of glycerol to propylene over Ir/ZrO$_2$ and HZSM-5-30.

Figure S11. Integrated conversion of glycerol to propylene over Ir/ZrO$_2$ and HZSM-5. Reaction conditions: 2.0 g Ir/ZrO$_2$, 2.0 g HZSM-5-30, 250 °C, 30 wt% glycerol aqueous feedstock, WHSV = 1.0 h^{-1}, H$_2$/glycerol = 100 (molar ratio), 1.0 MPa H$_2$.

References

[S1]   X. L. Du, L. He, S. Zhao, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2011**, *123*, 7961–7965; *Angew. Chem. Int. Ed.* **2011**, *50*, 7815–7819.

[S2]   B. Ravel, M. Newville, *J. Synchrotron Rad.* **2005**, *12*, 537-541.

[S3]   L. He, J. Q. Wang, Y. Gong, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem.* **2011**, *123*, 10398–10402; *Angew. Chem. Int. Ed.* **2011**, *50,* 10216–10220.