

Catalysis Science & Technology

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Cite this: DOI: 10.1039/c0xx00000x

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

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s Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

In this work, bimetallic Ir-Re catalysts supported on KIT-6 are prepared by tuning the thermal treatment procedures, i.e., conventional calcination and reduction (Ir-Re/KIT-6-CR) and modified direct reduction (Ir-Re/KIT-6-R) after impregnation of two metal precursors. The structure of both catalysts is intensively to characterized by H₂-TPR, STEM-HAADF-EDX, XPS and CO-DRIFTS. Results indicate that an Ir-Re alloy forms on the KIT-6 support when direct reduction is employed, which exhibits excellent catalytic

performance in hydrogenolysis of glycerol. The formation rate of 1,3-propanediol over Ir-Re/KIT-6-R reaches 25.6 mol_{1,3-PD}mol_{Ir}- $^{1}h^{-1}$ at 63% glycerol conversion with the addition of amberlyst-15 under 8 MPa H₂, 393 K and 20 wt% glycerol aqueous solution, almost twice that over Ir-Re/KIT-6-CR. It is revealed that Re species without prior calcination treatment could be fully reduced and therefore couple with Ir to form Ir-Re alloy structure with enhanced resistance against particle aggregation, while the calcination and subsequent reduction leads to the formation of Ir-ReO_x structure since the rhenium oxide species generated during the calcination is difficult to be reduced.

1. Introduction

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- 20 Transformation of biomass and biomass-derivatives to fuels and valuable chemicals provides sustainable alternatives to the processes based on the fossil resources. Glycerol has been proposed as one of the most valuable biomass-derived platform feedstocks, since it is readily available in biodiesel process. 25 Tremendous efforts have been made to convert the biomassderived glycerol to valuable fine chemicals.¹ Hydrogenolysis of glycerol to 1,3-propanediol (1,3-PD) and 1,2-propanediol (1,2-PD) is an effective way of glycerol valorization.^{1,2} It has been shown that combination of Re or W species with a more 30 reducible transition metal (e.g., Ir, Pt, Rh or Ru) results in excellent catalytic performance in the selective hydrogenolysis of C-O bond, e.g., polyols.^{3,4,11} Specifically, the modification of Re species on an Ir/SiO₂ catalyst greatly improves the activity for glycerol hydrogenolysis as well as the selectivity to 1,3-PD, $_{35}$ which is the most valuable hydrogenolysis product.^{4a} The H₂SO₄promoted Ir-ReOx/SiO2 has shown the highest reported productivity of 1,3-PD so far (Table S1). However, the activity for the noble-metal based catalyst is still far too low for commercial application. Generally, high catalyst/glycerol loading 40 ratio and long reaction time are required for the batch-wise reaction to achieve high glycerol conversion, rendering the
- process inefficient. To date, several attempts have been made to optimize the catalytic performance of Ir-ReO_x/SiO₂ catalysts, such as adjusting the Ir/Re composition, screening additives and ⁴⁵ adding a third noble metal.^{4f,4i,4j} Yet, considerable improvements are needed to make such noble-metal based catalysts cost-

effective in commercial application.

For the typical structure-sensitive reaction of glycerol hydrogenolysis, the catalytic performance is closely related to the 50 structures of the bimetallic catalysts.^{2a,3c,4b} Density functional theory calculation revealed that surface-alloyed Rh-Re and atopbonded ReO_x-Rh clusters would have different properties, e.g., acidity, where the alloyed Rh-Re was expected to exhibit better performance in C-O bond hydrogenolysis reactions compared ⁵⁵ with the Rh-ReO_x.¹⁵ Inspired by the research above, for glycerol hydrogenolysis over the bimetallic Ir-Re based catalyst, where the catalyst with Ir-ReOx structure have been employed and extensively studied,^{4a,4f,5} it is reasonable to expect the appearance of improved performance when alloying Ir with Re metal. It was 60 demonstrated that the low-valent ReOx species forms after reduction, and is attached to the Ir metal surface, in forms of Ir-ReO_x structure.^{3a,5} The iridium species in the reduced Ir-ReO_x/SiO₂ catalyst was reduced to metallic state, while the oxidation state of rhenium species is ca. 2.5 The interface between 65 the low-valent ReO_x and the Ir metal was proposed to be active site for the core-shell like nanoparticles.^{3a} Similar situations were proposed for Ru-ReO_x and Rh-ReO_x based catalysts.^{3a,3b} The type of Ir-ReO_x/SiO₂ catalyst has also been employed in many other hydrogenation and hydrogenolysis reactions.³¹ Yet, to the best of 70 our knowledge, the synthesis of Ir-Re alloy, and its application in glycerol hydrogenolysis has not been reported in the literature. Therefore, it appears worthwhile to explore the preparation of Ir-Re alloy structures and to exploit the synergy between Ir and Re in glycerol hydrogenolysis. The relationship between the 75 bimetallic structure and the catalytic performance is also of great

interest.

In this work, Ir and Re are designed to be supported on KIT-6 (an ordered mesoporous silica with a cubic arrangement of interconnected pores), because the silica support has weak 5 interaction with metal precursors and thus promotes the desired formation of active Ir-Re interfaces.^{4f,4i} The bimetallic Ir-Re structure is manipulated by thermal treatment, obtaining the target Ir-Re alloy catalyst and the conventional Ir-ReOx structured catalyst, respectively, which are analyzed by characterizations of 10 H2-TPR, STEM-HAADF-EDX, XPS and CO-DRIFTS. Comparison between Ir-Re alloy and Ir-ReOx structured catalyst was performed to investigate the bimetallic structure-performance relationship in glycerol hydrogenolysis.

2. Experimental

15 2.1 Catalyst preparation

KIT-6 was synthesized using P123 (Aldrich, MW=5800) as the structure-directing agent and TEOS (Shanghai Lingfeng Chemical Reagent co., Ltd., 99.0%) as the silica source, according to previously published reports.16, 17 In a typical 20 preparation procedure, 4.0 g P123 was dissolved in a mixture of 144 g distilled water and 7.9 g 35 wt% HCl solution by stirring at 35 °C for 3 h. After complete dissolution of P123, 4.0 g n-BuOH was added. Finally, 8.6 g TEOS was added to the mixture after stirring for 1 h. The mixture was then stirred at 35 °C for a further 25 24 h before hydrothermal treatment at 110 °C in a polypropylene bottle for another 24 h. The resulting precipitate was collected by filtration and then calcined at 550 °C in air for 5 h. The physical properties of the as-synthesized KIT-6 are shown in Fig. S1.

Bimetallic Ir-Re/KIT-6 catalysts were prepared by sequential 30 impregnation of KIT-6 with aqueous solutions of H₂IrCl₆ (Sigma-Aldrich, 99.9%) and NH₄ReO₄ (Sigma-Aldrich, 99.0%). In a typical procedure, Ir/KIT-6 was first prepared by incipient wetness impregnation of KIT-6 with an aqueous solution of H₂IrCl₆, then dried at 120 °C for 12 h. Dried Ir-Re/KIT-6 was 35 then synthesized by subsequent impregnation of the dried Ir/KIT-6 with an aqueous solution of NH₄ReO₄. After drying, Ir-Re/KIT-6 was reduced in flowing H₂ (70 mL/min) at 500 °C for 3 h. This uncalcined material after reduction is designated Ir-Re/KIT-6-R. As a reference, the bimetallic catalyst was also prepared 40 following a conventional route. The dried Ir-Re/KIT-6 was first

- calcined at 500 °C for 3 h in air (designated Ir-Re/KIT-6-C), followed by reduction in flowing H₂ (70 mL/min) at 500 °C for 3 h. The resulting material is designated Ir-Re/KIT-6-CR. All catalysts after reduction were passivated in 1% O₂/Ar for 20 min
- 45 (30 mL/min) at room temperature and then quickly transferred to the reactor. The metal loadings for Ir-Re/KIT-6, as determined by ICP-AES, are 4.0 wt% Ir and 3.8 wt% Re, which are exactly the same as the nominal loadings, as shown in Table 1. For comparison, monometallic Ir/KIT-6 and Re/KIT-6 catalysts were
- 50 also prepared by incipient wetness impregnation of KIT-6 with aqueous solutions of either H₂IrCl₆ or NH₄ReO₄. The nominal loading of Ir and Re for monometallic samples was 4.0 wt% and 3.8 wt%, respectively.

2.2 Glycerol hydrogenolysis

55 The catalyst evaluation was carried out in a 100-mL stainless steel autoclave (Parr Instruments) equipped with an electronic

temperature controller and a mechanical stirrer. In a standard procedure, 20 g aqueous glycerol (20 wt% unless stated otherwise) and 0.15 g pre-reduced catalyst were loaded into the 60 autoclave. In some cases, amberlyst-15 powder was used as externally added acid promoter. The usage amount was 50 mg. After sealing the reactor, it was purged three times with 2 MPa H₂, then heated to 120 °C, pressurized with 8 MPa H₂, and stirred at 500 rpm. After 12 h, the resulting reaction mixture was 65 analyzed by UPLC (Waters 2414) equipped with an RI detector and a C18 AQ column. The used catalyst was collected by centrifugation, washed extensively with de-ionized water and dried at 80 °C under vacuum. The carbon balance, representing the ratio of molar of carbon in all liquid products to molar of ⁷⁰ carbon in glycerol charged, was greater than 96% for each run.

Conversion and selectivity were calculated as follows:

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

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

2.3 Catalyst characterization

75 Before and after being used for glycerol hydrogenolysis, the metal loadings of the Ir-Re based catalysts were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Vanan 710). Powder X-ray diffraction (XRD) was performed on a Rigaku D/Max 2550VB/PC diffractometer, using 80 Cu Ka radiation. N2 physisorption measurements were performed at 77 K on an ASAP 2010C (Micromeritics, USA), after outgassing the samples at 573 K and 133.3 Pa for 6 h. The total pore volume was defined as the single-point pore volume at a relative pressure $p/p_0 = 0.95$. NH₃ temperature-programmed desorption 85 (NH₃-TPD) was carried out to analyze the acidity of the assynthesized samples. Samples were pre-reduced in hydrogen flow at 500 °C for 3 h before introduction of NH₃.

TEM characterization was carried out using a Tecnai G2 F20 S-Twin (FEI) with an accelerating voltage of 200 kV and a point 90 resolution of 0.24 nm. The metal particle sizes and their corresponding size distributions were estimated by measuring more than 250 randomly selected particles. Images were also captured in STEM mode with the annular dark-field detector. The EDX signals of the particles were obtained in STEM mode by 95 focusing the electron beam on the selected areas or individual particles and accumulating the spectra. Both reduced and passivated catalysts were used as samples for TEM observation.

H₂-Temperature-programmed reduction (H₂-TPR) was carried out using a Micromeritics AutoChem 2920, in a U-shaped quartz ¹⁰⁰ reactor using 5% H₂ diluted with Ar (30 mL/min). The Autochem is equipped with a thermal conductivity detector. The amount of sample used was 30-70 mg, and the temperature was increased from room temperature to 800 °C at the heating rate of 10 °C/min.

IR spectra were recorded on a Nicolet 6700 FTIR 105 spectrophotometer in diffuse reflectance mode, using an in-situ cell equipped with a sample cup, heater and ZnSe windows. Prereduced or passivated samples were placed into the sample cup and reduced in situ at 350 °C in flowing H₂ for 1 h. The sample 110 was cooled to room temperature, then 2% CO/Ar was introduced.

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After the CO coverage reached its saturation level, IR spectra were collected at room temperature.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Multilab 2000 spectrometer (Thermo VH $_5$ Scientific) using Al K_a radiation (1486.6 eV). The aluminum anode was operated at an accelerating voltage of 15 kV, 15 mA, 20 V. The pressure in the analysis chamber was maintained in the range of 5×10^{-9} mbar. Binding energies were calibrated using the binding energy of the C 1s peak (284.6 eV) as a reference.

10 Table 1 Physical properties of the materials

Sample	Ir/Re loading (wt %) ^a	${S_{BET} \over (m^2/g)^{b}}$	$\frac{V_p}{(cm^3/g)^c}$	d _p (nm) ^c	$d_{av.}$ (nm) ^d
KIT-6	-	812	1.34	7.0	-
Ir/KIT-6-R	4.1	721	1.18	6.6	2.3 ± 0.29
Ir-Re/KIT-6-R	4.0/3.8	580	0.94	6.9	2.5 ± 0.17
Ir-Re/KIT-6-CR	4.0/3.8	617	1.08	7.2	3.2 ± 0.33

^{*a*} Determined by ICP-AES.^b Pore volume was calculated using the BET method.^c Pore diameter was calculated using the BJH method.^d Mean metal particle size was estimated from TEM observations.

3. Results and discussion

15 3.1 Catalyst characterization



Fig. 1 Typical HAADF-STEM images for Ir-Re/KIT-6-R (A) and Ir-Re/KIT-6-CR (B); Spot EDX elemental analysis on randomly selected individual metal particles (marked by red arrows) for Ir-Re/KIT-6-R (C)
 20 and Ir-Re/KIT-6-CR (D). Insets are the corresponding metal particle size distribution obtained from STEM images.

Fig. 1 shows typical HAADF-STEM images and corresponding particle size distributions of the reduced Ir-Re/KIT-6 catalysts without and with calcination treatment, i.e., Ir-Re/KIT-6-R and ²⁵ Ir-Re/KIT-6-CR, respectively. For both bimetallic materials, the metal nanoparticles are highly dispersed on the KIT-6 support

metal nanoparticles are highly dispersed on the KIT-6 support. Some metal particles are observed locating inside the mesoporous channels, accounting for the decrease in pore volumes and

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surface areas measured by N₂-sorption (Table 1). The mean ³⁰ particle size for Ir-Re/KIT-6-R is slightly smaller than that for Ir-Re/KIT-6-CR, i.e., 2.5 vs. 3.2 nm. Furthermore, the spectra of STEM-EDX elemental analysis on randomly selected individual metal particles reveal the co-existence of both Ir and Re in a single metal particle, indicating the close contact of Ir and Re in ³⁵ both materials (Figure 1, C-D).



Fig. 2 TPR profiles of uncalcined materials (A), and calcined materials (B). Conditions: sample mass 30-70 mg; H_2/Ar 10 % v/v, 30 mL/min; heating rate 10 °C/min.

 H_2 -temperature-programmed reduction (H_2 -TPR) was performed to evaluate the influence of thermal treatment on the reducibility of the metal species (Fig. 2). As shown in Fig. 2A, the TPR profile of Ir/KIT-6 shows three main hydrogen consumption peaks. The one appears at temperature lower than 45 200 °C corresponds to the iridium species interacts weakly with the KIT-6 support, while the peaks at higher temperature range (200-430 °C) can be ascribed to iridium species interacts strongly with the support.²⁶ Re/KIT-6 displays two hydrogen consumption peaks at around 300 °C and 430 °C, ascribing to the the rhenium 50 species interacts weakly and strongly with the support, respectively. The reduction peaks of Ir-Re/KIT-6 shift to lower temperature compared with that of the Re/KIT-6, indicating that the reduction of rhenium species is promoted by Ir due to the hydrogen spillover effects. On the other hand, as shown in Fig. 55 2B, calcined Ir/KIT-6-C and Re/KIT-6-C show respective hydrogen consumption peak centered at 190 °C and 320 °C, which can be ascribed to the reduction of IrO2 and rhenium oxide, respectively.4a,4f For the calcined Ir-Re/KIT-6-C material, a shift of the reduction peak to lower temperature range is observed 60 compared with the TPR profiles of the monometallic materials. This phenomenon suggests that the close contact of Ir and Re species promotes the reduction of both metal species.^{4a,5}

The mean valence of each metal after reduction is estimated from the amount of H₂ consumed in H₂-TPR, which is ⁶⁵ summarized in Table 2. Ir precursors are readily reduced to the metallic state, regardless of whether the material has been calcined or not. However, the reducibility of Re species varies considerably, depending on which thermal treatment procedure was employed. For the uncalcined materials (i.e., Re/KIT-6 and Ir-Re/KIT-6), Re species can be fully reduced to metallic state. ⁵ This is further supported by the XRD results. The XRD pattern of Re/KIT-6-R exhibits diffraction peaks assignable to the metallic phase of Re (Fig. S2), suggesting the formation of Re crystal even without the promotion of Ir by hydrogen spillover.

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Furthermore, as shown in Fig. S3, the XRD pattern of the Ir-¹⁰ Re/KIT-6 without calcination treatment suggests that the Re species exists as ReO₄⁻ species after drying, which is highly reducible.

Table 2 Average metal valence, obtained by quantitative analysis of H_2 consumption in TPR profiles.

Sample	Valence of metal			
	Ir	Re ^a		
Ir/KIT-6-C	0	-		
Re/KIT-6-C	-	4.7		
Ir-Re/KIT-6-C	0	2.4		
Ir/KIT-6	0	-		
Re/KIT-6	-	0		
Ir-Re/KIT-6	0	0		

15 ^a Re valence = 7-2×[(amount of H₂ consumed, mol)-2×(Ir loading, mol)]/(Re loading, mol).

In contrast, for the materials pre-calcined in air (i.e., Re/KIT-6-C and Ir-Re/KIT-6-C), the extent of Re reduction is limited. For the Ir-Re/KIT-6-C, the amount of H₂ consumed cannot cover the ²⁰ complete reduction of both metals. Since IrO₂ is easily reduced to metallic state in low temperature range, the mean valence of Re is estimated by eliminating the amount of H₂ consumed by complete reduction of IrO2 to Ir.4a,4f,24 The valence of Re is estimated to be 2.4 for the Ir-Re/KIT-6-CR, which is lower than 25 that of the Re/KIT-6-CR (i.e., 4.7) because of the promotion of Ir by hydrogen spillover. Such a valence of Re suggests the formation of low-valent ReO_x species upon reduction, analogous to previous reports for bimetallic Ir-ReOx,^{4a,4f} Ru-ReOx,^{3a} Ir- VO_x^{24} , Rh-ReO_x²⁹ and Pt-ReO_x.³⁰ It has been proposed that, for 30 supported Re₂O₇ catalyst, the Re reducibility was significantly decreased by calcination treatment due to the formation of Re⁷⁺-O-support bond.⁶⁻⁷ As a result of the formation of the Re⁷⁺-Osupport bond, the mobility of Re species also decreased. Tomishige et al. showed that the low-valent ReO_x species for the 35 pre-calcined Ir-ReOx/SiO2 material was rather stable, and the ReOx species with the valence of ca. 2 remained almost unchanged even when the reduction temperature was as high as 895 K.⁵ This indicates that the interaction between the trioxo Re species (-O-Re⁷⁺) and support surface or IrO₂ surface can be ⁴⁰ rather strong. Based on these results, it can be concluded that the

- highly reducible ReO₄ species exists in the Ir-Re/KIT-6 prior to calcination, favoring the formation of Ir-Re alloy during reduction. On the other hand, the calcination treatment on Ir-Re/KIT-6 immobilized the trioxo Re species on the support ⁴⁵ and/or IrO₂ metal surface, resulting in decreased reducibility of Re species and the formation of Ir-ReO_x structure during
- reduction. The surface properties of the bimetallic Ir-Re materials were investigated by DRIFT spectra of CO adsorbed on the reduced ⁵⁰ materials (Fig. 3). Two CO adsorption bands at 2068 cm⁻¹ and 1800 cm⁻¹ are observed for the Ir/KIT-6-R, which are assignable

to linearly adsorbed CO and bridged CO on the surface Ir, respectively. For the Re/KIT-6-R, a weak adsorption band at 2040 cm⁻¹ due to the linearly adsorbed CO is observed. Because ⁵⁵ Re oxides cannot adsorb CO,¹⁸ the result indicates the presence of surface metallic Re in Re/KIT-6-R. Yet, Re/KIT-6-CR shows no CO adsorption bands, indicating that the surface Re species is in oxidation state (not shown here).



60 Fig. 3 DRIFT spectra of CO adsorbed onto Ir/KIT-6-R, Ir-Re/KIT-6-CR, Ir-Re/KIT-6-R and Re/KIT-6-R. The inset displays enlarged spectra for Ir-Re/KIT-6-R and Re/KIT-6-R.

For the bimetallic Ir-Re materials, the band due to the bridged CO on the surface Ir is absent. This indicates that the continuous ⁶⁵ surface Ir ensembles are separated by Re species. For the Ir-Re/KIT-6-CR, CO adsorption band is observed at 2070 cm⁻¹, ascribing to the linearly adsorbed CO on Ir.^{4f} The band shape and position are similar to that of the Ir/KIT-6-R, but the intensity is much lower. The decreased band intensity for the Ir-Re/KIT-6-⁷⁰ CR can be rationalized to the partial coverage of low-valent ReO_x on the particle surface.^{3a,4f,24} After all, if metallic Re was present on the surface of Ir-Re/KIT-6-CR, the band should be at least broadened. Accordingly, we conclude that the surface of the Ir-Re/KIT-6-CR is probably Ir-ReO_x.

⁷⁵ For the Ir-Re/KIT-6-R, the CO adsorption band appears at 2055 cm⁻¹, an intermediate position between the band positions for Ir/KIT-6-R and Re/KIT-6-R, suggesting the formation of Ir-Re alloy. The observed red-shift of about 13 cm⁻¹ of the linearly adsorbed CO on Ir could be due to the increased electron back-⁸⁰⁰ donation from Ir to the adsorbed CO.^{23,24} This is because alloying Ir with Re results in electron transfer from Re to Ir, leading to the electron enrichment of Ir. Moreover, the intensity of the CO adsorption band for the Ir-Re/KIT-6-R is also lower than that for the Ir/KIT-6-R. This may be a consequence of changed electronic ⁸⁵ properties by alloying Ir with Re,²⁵ and/or dilution of surface Ir atoms by Re atoms on the Ir-Re alloy surface because CO adsorption ability for Re/KIT-6-R is very weak.

The bulk Ir-Re structure for the Ir-Re/KIT-6-R without calcination treatment was further investigated using STEM-EDX ⁹⁰ line scans on individual metal particles (Fig. 4). In order to increase the EDX signal intensity, the metal loadings of the studied catalyst were doubled, i.e., 8.0 and 7.6 wt% for Ir and Re, respectively. The spectra shown in Fig. 4 confirm that both Ir and

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Re are present in the same metal nanoparticle. Moreover, the STEM-EDX spectrum (Fig. 4E) demonstrates the formation of bulk Ir-Re alloy for the Ir-Re/KIT-6-R.



5 Fig. 4 STEM-EDX line scans on a randomly selected individual metal particle in the Ir-Re/KIT-6-R catalyst: images before (A) and after EDX line scanning (B); STEM-EDX spectra for Ir (C), Re (D); and combined results for Ir (green) and Re (orange) (E).

The metal oxidation states in the reduced bimetallic Ir-Re 10 materials were investigated by ex-situ XPS (Fig. 5). In both materials, the presence of Ir 4f doublets at binding energies of 60.4 and 63.3 eV is the characteristic of $Ir^0 (4f_{7/2} = 60.3 \pm 0.2 \text{ eV})$, $4f_{5/2} = 63.4 \pm 0.2$ eV).^{5,19a} A small contribution from an Ir 4f doublet assigned to Ir⁴⁺ is also present, likely due to the oxidation 15 of metallic Ir by contact with air during XPS sample preparation. The Re 4f region indicates the presence of several Re oxidation states in both materials. Because of the greater oxophilicity of Re compared with Ir,^{3e,4b,8-10} Re metal is more easily oxidized during XPS sample preparation, leading to the formation of Re⁴⁺, Re⁶⁺ 20 and even Re7+. Nevertheless, metallic Re is observed for Ir-Re/KIT-6-R (4 $f_{7/2}$ = 39.7 ± 0.2 eV, 4 $f_{5/2}$ = 42.1 ± 0.2 eV), suggesting the presence of Re⁰ species on the bimetallic surface.^{19b} In contrast, the lowest energy Re $4f_{7/2}$ signal for Ir-Re/KIT-6-CR is located between the expected binding energies 25 for Re⁰ and Re⁴⁺, suggesting the Re oxides with low positive

oxidation states.



Fig. 5 High resolution XPS scans for Ir-Re/KIT-6-R and Ir-Re/KIT-6-CR, in the Ir 4*f* region (left panel), and the Re 4*f* region (right panel).

Based on these results, the influence of thermal treatment on bimetallic Ir-Re structure is unravelled. Alloyed Ir-Re/KIT-6-R can be synthesized by direct reduction of the dried Ir-Re/KIT-6 without calcination treatment. In contrast, Ir-Re/KIT-6-CR with Ir-ReO_x structure is synthesized when calcination treatment is ³⁵ retained, which is analogous to the previous reports.^{4a,4f,5} The evolution of the two types of Ir-Re structure is illustrated in Scheme 1. After drying the impregnated sample, Ir and Re species are in close contact. The metal precursors existing as Ir⁴⁺ and ReO₄ species are highly reducible and mobile in the hydrated 40 layer on the support surface. Eliminating further calcination treatment on the impregnated sample renders their reducibility and mobility. As a result, the formation of Ir-Re alloy is preferred. In contrast, further calcination treatment on the impregnated sample will strengthen the Re^{7+} -support and Re^{7+} -IrO₂ 45 interactions via the formation of chemical bonds, and decrease the reducibility and mobility of the Re species. The Re species can be then partially reduced to ReO_x species in the valence of ca. 2.4, which is probably attached on the particle surface in forms of Ir-ReO_x.



Scheme 1 Possible evolution pathway of the bimetallic Ir-Re structures catalysts upon different thermal treatment procedures.

3.2 Catalytic performance

Glycerol hydrogenolysis was conducted in order to compare the ss catalytic performance of different structured Ir-Re/KIT-6 catalysts. As can be seen in Table 3, the activities for the two catalysts are quite different. The glycerol conversion of the Ir-Re/KIT-6-R is higher than that of the Ir-Re/KIT-6-CR, i.e., 39.7% Published on 24 November 2014. Downloaded by University of California - Santa Cruz on 03/12/2014 04:09:17.

vs. 24.4% in 12 h under 8 MPa, 393 K and 20 wt% glycerol aqueous solution. The evaluation results at similar level of glycerol conversion, i.e., 23±1% (Entry 1 and 3) are also provided in order to compare the selectivity to 1,3-PD over the 5 two catalysts. The selectivity to 1,3-PD of the Ir-Re/KIT-6-R is ca. 10% higher than that of the Ir-Re/KIT-6-CR, i.e., 43.9% vs. 33.5%. This fact suggests that the bimetallic Ir-Re catalyst with different structures shows different catalytic performance, probably due to their different catalytic active sites. The different 10 active sites are further verified by measuring the reaction order with respect to glycerol (Fig. S4). Zero and first order with respect to glycerol are obtained for Ir-Re/KIT-6-R and Ir-Re/KIT-6-CR, respectively. As a result, the rate of 1.3-PD formation over the Ir-Re/KIT-6-R is almost twice that of the Ir-Re/KIT-6-CR. 15 Notably, the rate of 1,3-PD formation over the Ir-Re/KIT-6-R is comparable to that reported for H₂SO₄-promoted Ir-ReO_x/SiO₂,⁴ⁱ i.e., 17.2 vs. 15.4 mol_{1,3-PD} mol_{Ir}⁻¹ h⁻¹, which can be further

i.e., 17.2 vs. 15.4 $\text{mol}_{1,3\text{-PD}} \text{mol}_{\text{Ir}}^{-1} \text{h}^{-1}$, which can be further enhanced to 25.6 $\text{mol}_{1,3\text{-PD}} \text{mol}_{\text{Ir}}^{-1} \text{h}^{-1}$ by adding amberlyst-15 as promoter. In 12 h, the glycerol conversion achieved by ²⁰ amberlyst-15 promoted Ir-Re/KIT-6-R is similar to that reported for H₂SO₄-promoted Ir-ReO_x/SiO₂ in 24 h, indicating the greatly improved activity of the alloyed Ir-Re catalyst compared with Ir-ReO_x. To the best of our knowledge, the Ir-Re/KIT-6-R with alloyed Ir-Re structure is so far the most active catalyst for ²⁵ glycerol hydrogenolysis (Table S1).

Table 3 Glycerol hydrogenolysis tests for Ir-Re/KIT-6-R and Ir-Re/KIT-6-CR. $^{\rm a}$

Entry	Catalyst	Conv.	1,3-PD	Carbon	Selectivity (%)	
		(%)	formation	balance	1,3-	1,2- 1- 2-
			rate ^b	(%)	PD	PD PO PO
1	Ir-Re/KIT-6-CR	24.4	9.5	98.2	33.5	28.7 28.1 9.7
2	Ir-Re/KIT-6-R	39.7	17.2	96.8	37.1	25.8 28.0 9.1
3	Ir-Re/KIT-6-R °	22.4	-	97.5	43.9	26.8 20.0 9.3
4	Ir-Re/KIT-6-R	63.3	25.6	96.0	34.7	12.6 43.2 9.5
5	+Amberlyst-15 Ir-ReO _x /SiO ₂ +H ₂ SO ₄ ^d	61.1	15.4	-	43.2	9.2 36.6 9.7

^a Reaction conditions: 120 °C, 20 wt% aqueous glycerol, 8 MPa H₂, 12 h, catalyst (150 mg), additive (50 mg). ^b In mol_{1,3-PD} mol_{1r}⁻¹ h⁻¹; ^c 2 h reaction
 ³⁰ time; ^d 120 °C, 20 wt% aqueous glycerol, 8 MPa H₂, catalyst (150 mg), H⁺/Ir=1 mol, 24 h reaction time from ref [4i]. PD: propanediol; PO: propanol.

There are still large amount of by-products (1,2-PD, 1-PO and ³⁵ 2-PO), accompanying with the production of 1,3-PD. The 1,3-PD and 1,2-PD are the primary products of glycerol hydrogenolysis, which can be further converted to products of 1-PO and/or 2-PO. Moreover, as shown in Table 3, with the addition of amberlyst-15 to Ir-Re/KIT-6-R as an acidic promoter, the selectivity to 1,2-PD ⁴⁰ remarkably decreases, while the selectivity to 1,3-PD remains almost unchanged (Entry 2 and 4). As a result, the ratio of 1,3-PD to 1,2-PD increases from ca. 1.4 to 3.0 with the addition of amberlyst-15. As shown in Table S2, the activity for Ir-Re/KIT-6-R catalyzed hydrogenolysis of 1,2-PD is higher than that of ⁴⁵ glycerol and 1,3-PD, which is ca. 2 times that of glycerol and ca. 6 times that of 1,3-PD. Since the solid acid promoter could enhance the activities for the hydrogenolysis of both glycerol and propanediols, the much higher activity for 1,2-PD compared with

glycerol and 1,3-PD remarkably promotes the conversion of 1,2-

⁵⁰ PD to 1-PO. Consequently, a higher ratio of 1,3-PD to 1,2-PD is obtained by adding acid promoter.

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Interestingly, as shown in Fig. 6, TEM images recorded for the used Ir-Re/KIT-6-R indicate that the Ir-Re alloy nanoparticles of Ir-Re/KIT-6-R are still highly dispersed and stable during ⁵⁵ reaction, suggesting the high resistance against metal aggregation. In contrast, large aggregates (>10 nm) are observed for the used Ir-Re/KIT-6-CR. Meanwhile, as studied by ICP-AES analysis, no detectable leaching of active metals occurred during the reaction.



⁶⁰ Fig. 6 TEM images of Ir-Re/KIT-6-R (A and C) and Ir-Re/KIT-6-CR (B and D), after catalytic use. Reaction conditions: 120 °C, 20 wt% aqueous glycerol, 8 MPa H₂, 12 h.

It has been shown that the monometallic Ir and Re was inactive in glycerol hydrogenolysis.^{4a} The remarkably enhanced activity 65 for Re-modified Ir catalyst is ascribed to the synergy between the Ir and Re. Chia et al. suggested that the combination of oxophilic promoters such as Re species with an easily reducible metal, e.g., Pt, Rh, leads to the formation of bifunctional catalysts, exhibiting both metallic and acid sites.^{3b,11,25} The acid sites, likely M(Pt, Rh, 70 Ir)-Re-OH groups at the metal-solution interface form by interaction between oxophilic Re and water molecule, 3b,11,25,28 and can be assessed by NH₃-TPD technique.^{3b,11,25} Thus, the NH₃-TPD technique was employed to assess the acidity generated from (Ir)-Re-OH bond for bimetallic Ir-Re catalyst. Furthermore, 75 the (Ir)-Re-OH is probably the adsorption site for glycerol, analogous to the case of glycerol hydrogenolysis over Pt-Re based catalyst.^{3c} As indicated from NH₃-TPD profiles (Fig. S5), the Ir-Re/KIT-6-R shows much higher acidity than Ir-Re/KIT-6-CR, suggesting the higher number of (Ir)-Re-OH sites. Therefore, 80 the higher activity for Ir-Re/KIT-6-R could be ascribed to the higher number of glycerol adsorption site, (Ir)-Re-OH, which will facilitate the reaction.

A possible reaction mechanism for the alloyed Ir-Re/KIT-6-R catalyzed glycerol hydrogenolysis is proposed in Scheme 2. On ⁸⁵ the surface of an Ir-Re alloy particle, metallic Re activates the water molecule to form an (Ir)-Re-OH absorption site.^{11,15} The (Ir)-Re-OH acts as an absorption site for glycerol molecule. Meanwhile, the hydride species formed from H₂ activated on

Cite this: DOI: 10.1039/c0xx00000x

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metallic Ir attacks the C-O bond of the adsorbed glycerol to generate unsaturated intermediates.^{4f,27} Subsequent hydrogenation of these unsaturated intermediates leads to the formation of the observed hydrogenolysis products, while further deoxygenation ⁵ of these unsaturated intermediates results in the formation of over-hydrogenolysis products (1-PO/2-PO).



Scheme 2 Possible reaction pathway for glycerol hydrogenolysis over alloyed Ir-Re/KIT-6-R.

10 4. Conclusions

In summary, the correlation between bimetallic Ir-Re structure and thermal treatment is investigated, and the resulting different structured bimetallic Ir-Re catalysts are applied in glycerol hydrogenolysis to examine the relationship between bimetallic Ir-

- ¹⁵ Re structure and catalytic performance. It is revealed that, direct reduction of the impregnated sample without prior calcination renders Re species fully reducible, favoring the formation of Ir-Re alloy. In contrast, when calcination treatment is employed, reduction of Re species is inhibited, resulting in the formation of
- $_{20}$ Ir-ReO_x after the subsequent reduction of the bimetallic catalyst. Compared with the catalyst with Ir-ReO_x structure, the Ir-Re alloy catalyst shows remarkably improved activity in glycerol hydrogenolysis and doubled 1,3-propanediol formation rate, which results from the higher density of active center. Besides,
- ²⁵ the Ir-Re alloy catalyst also exhibits enhanced resistance against particle sintering. This readily-prepared alloyed Ir-Re catalyst may be useful in other C-O bond hydrogenolysis reactions, such as the disassembly of lignin.

Acknowledgements

³⁰ This work was supported by the National Natural Science Foundation of China (21106047). S.L.S. thanks the Center for Enabling New Technologies through Catalysis (CENTC) for financial support.

Notes and references

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- ⁴⁰ † Electronic Supplementary Information (ESI) available: [N₂-adsorption of KIT-6, Table of currently developed catalytic system for glycerol hydrogenolysis, XRD and NH₃-TPD is available in supporting information]. See DOI: 10.1039/b000000x/
- 1 a) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411; b)
- Y. Nakagawa and K. Tomishige, *Catal. Sci. Technol.*, 2011, 1, 179;
 c) M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. Della Pina, *Angew. Chem. Int. Ed.*, 2007, 46, 4434.
- a) E. S. Vasiliadou, T. M. Eggnenhuisen, P. Munnik, P. E. de Jongh, K. P. de Jong and A. A. Lemonidou, *Appl. Catal. B*, 2013, 145, 108;
- ⁵⁰ b) S. Zhu, X. Gao, Y. Zhu, Y. Zhu, H. Zheng and Y. Li, *J. Catal.*, 2013, **303**, 70; c) Y. Nakagawa, M. Tamura and K. Tomishige, *J. Mater. Chem. A*, 2014, **2**, 6688.
- 3 a) L. Ma and D. He, *Catal. Today*, 2010, **149**, 148; b) M. Chia, Y. J. Pagan-Torres, D. Hibbitts, Q. Tan, H. N. Pham, A. K. Datye, M. Neurock, R. J. Davis and J. A. Dumesic, *J. Am. Chem. Soc.*, 2011, **133**, 12675; (c) C. H. Deng, X. Z. Duan, J. H. Zhou, D. Chen, X. G. Zhou and W. K.Yuan, *Catal. Today*, 2014, **234**, 208.
- Representative reports on glycerol hydrogenolysis to 1,3-propanediol: 4 a) Y. Nakagawa, Y. Shinmi, S. Koso and K. Tomishige, J. Catal., 2010, 272, 191; b) O. M. Daniel, A. Delariva, E. L. Kunkes, A. K. Datve, J. A. Dumesic and R. J. Davis, ChemCatChem, 2010, 2, 1107: c) Y. Zhang, X. C. Zhao, Y. Wang, L. K. Zhou, J. Y. Zhang, J. Wang, A. Q. Wang and T. Zhang, J. Mater. Chem. A, 2013, 1, 3724; d) L. Z. Qin, M. J. Song and C. L. Chen, Green Chem., 2010, 12, 1466; e) J. Oh, S. Dash and H. Lee, Green Chem., 2011, 13, 2004; f) Y. Amada, Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa and K. Tomishige, Appl. Catal. B, 2011, 105, 117; g) J. Ten Dam, K. Djanashvili, F. Kapteijn and U. Hanefeld, ChemCatChem, 2013, 5, 497; h) R. Arundhathi, T. Mizugaki, T. Mitsudome, K. Jitsukawa and K. Kaneda, ChemSusChem, 2013, 6, 1345; i) Y. Nakagawa, X. 70 Ning, Y. Amada and K. Tomishige, Appl. Catal. A., 2012, 433, 128; j) M. Tamura, Y. Amada, S. Liu, Z. Yuan, Y. Nakagawa and K. Tomishige, J. Mol. Catal. A: Chem., 2014, 388-389, 177.

Catalysis Science & Technology Accepted Manusci

- 5 Y. Amada, H. Watanabe, M. Tamura, Y. Nakagawa, K. Okumura and 5 K. Tomishige, *J. Phy. Chem. C*, 2012, **116**, 23503.
- a) D. S. Kim and I. E. Wachs, J. Catal., 1993, 141, 419; b) M. A.
 Vuurma, D. J. Stufkens and A. Oskam, J. Mol. Catal., 1992, 76, 263.
- 7 X. She, J. Hun Kwak, J. Sun, M. Y. Hu, C. Wang, C. H. F. Peden and Y. Wang, *ACS Catal.*, 2012, 2, 1020.
- 80 8 Z. Wang, S. Skiles, F. Yang and D. W. Goodman, *Catal. Today*, 2012, **181**, 75.
- 9 M. J. P. Botman, K.D. Vreugd, H. W. Zandbergen, R. D. Block and V. Ponec, *J. Catal.*, 1989, **116**, 467.
- E. L. Kunkes, D. A. Simonetti, J. A. Dumesic, W. D. Pyrz, L. E.
 Murillo, J. G. G. Chen and D. J. Buttrey, *J. Catal.*, 2008, 260, 164.

- 11 M. Chia, B. J. O'Neill, R. Alamillo, P. J. Dietrich, F. H. Ribeiro, J. T. Miller and J. A. Dumesic, *J. Catal.*, 2013, 308, 226.
- 12 T. Kurosaka, H. Maruyama, I. Naribayashi and Y. Sasaki, *Catal. Commun.*, 2008, **9**, 1360.
- 5 13 L. F. Gong, Y. A. Lu, Y. J. Ding, R. H. Lin, J. W. Li, W. D. Dong, T. Wang and W, M. Chen, *Appl. Catal. A*, 2010, **390**, 119.
 - 14 A. Ciftci, S. Eren, D. A. J. Ligthart and E. J. M. Hensen, *ChemCatChem*, 2014, **6**, 1260.
- 15 D. Hibbitts, Q. Tan and M. Neurock, J. Catal., 2014, 315, 48.
- 10 16 F. Kleitz, S. H. Choi and R. Ryoo, Chem. Commun., 2003, 2136.
 - 17 T. W. Kim, F. Kleitz, B. Paul and R. Ryoo, J. Am. Chem. Soc., 2005, 127, 7601.
 - 18 L. E. S. Rygh and C. J. Nielsen, J. Catal., 2000, 194, 401.
- 19 a) T. Marzialetti, M. Oportus, D. Ruiz, J. L. G. Fierro and P. Reyes,
- *Catal. Today*, 2008, **133-135**, 711; b) W. T. Tysoe, F. Zaera and G. A. Somorjai, *Surf. Sci.*, 1988, **200**, 1.
- 20 H. I. Karan, K. Sasaki, K. Kuttiyiel, C. A. Farberow, M. Mavrikakis and R. R. Adzic, ACS Catal., 2012, 2, 817.
- S. Hirasawa, H. Watanabe, T. Kizuka, Y. Nakagawa and K. Tomishige, *J. Catal.*, 2013, **300**, 205.
- 22 B. Hammer, L. B. Hansen and J. K. Nørskov, *Phys. Rev. B*, 1999, **59**, 7413.
- 23 M. Haneda, H. Kudo, Y. Nagao, T. Fujitani and H. Hamada, *Catal. Commun.*, 2006, 7, 423.
- 25 24 B. Pholjaroen, N. Li, Y. Huang, L. Li, A. Wang, T. Zhang, *Catal. Today*, 2014, DOI: 10.1016/j.cattod.2014.08.011.
 - 25 L. Zhang, A. M. Karim, M. H. Engelhard, Z. H. Wei, D. L. King and Y. Wang, *J. Catal.*, 2012, **287**, 37.
- 26 G. Borda, H. Rojas, J. Murcia, J. L. G. Fierro, P. Reyes and M.
 Oportus, *React. Kinet. Catal. Lett.*, 2007, 92, 369.
- 27 K. Chen, K. Mori, H. Watanabe, Y. Nakagawa and K. Tomishige, *J. Catal.*, 2012, **294**, 171.
- 28 Y. Nakagawa, K. Mori, K. Chen, Y. Amada, M. Tamura and K. Tomishige, *Appl. Catal. A.*, 2013, 468, 418.
- a) Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa and K. Tomishige, *Appl. Catal. B*, 2010, **94**, 318; b) K. Chen, S. Koso, T. Kubota, Y. Nakagawa and K. Tomishige, *ChemCatChem*, 2010, **2**, 547.
 - 30 T. Ebashi, Y. Ishida, Y. Nakagawa, S. Ito, T. Kubota and K. Tomishige, J. Phy. Chem. C, 2010, 114, 6518.
- ⁴⁰ 31 a) S. Liu, M. Tamura, Y. Nakagawa and K. Tomishige, ACS Sustainable Chem. Eng., 2014, 2, 1819; b) S. Liu, Y. Amada, M. Tamura, Y. Nakagawa and K. Tomishige, Catal. Sci. Technol., 2014, 4, 2535; c) S. Liu, Y. Amada, M. Tamura, Y. Nakagawa and K. Tomishige, Green Chem., 2014, 16, 617; d) K. Chen, M. Tamura, Z.
- 45 Yuan, Y. Nakagawa and K. Tomishige, *ChemSusChem*, 2013, 6, 613; e) M. Tamura, K. Tokonami, Y. Nakagawa and K. Tomishige, *Chem. Commun*, 2013, 49, 7034.

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

Table of Contents graphic:



The first synthesis of supported Ir-Re alloy catalyst, which exhibits significantly improved activity in glycerol hydrogenolysis and enhanced resistance against particle sintering compared with bimetallic Ir-Re catalyst with Ir-ReO_x structure.