# Support effect on the bimetallic structure of Ir–Re catalysts and their performances in glycerol hydrogenolysis

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### A B S T R A C T

Comparative study was made between the bimetallic Ir–Re catalyst supported on amorphous silica-alumina (ASA) and the ones supported on de-aluminated ASA (D-ASA) to elucidate the effects of surface Al in the support on the Ir–Re structure and their catalytic behavior in glycerol hydrogenolysis. The Ir–Re interaction is greatly inhibited because of the stronger interaction between Re species and (Si-)Al-OH sites on ASA surface, resulting in the appearance of highly dispersed Re clusters and large Ir crystals after reduction. The barely synergy between the isolated Ir and Re metals in addition to the decreased metal dispersion restrains the glycerol hydrogenolysis reaction over Ir–Re/ASA. On the other hand, the retained mobility of Re species on 'inert' D-ASA supports offers the intimate contact between Ir and Re species and hence the formation of Ir–Re alloy catalysts after reduction, promoting greatly the synergy between Ir and Re species in glycerol hydrogenolysis.

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## 1. Introduction

Reduction of the oxygen content and the length of the carbon chain via C–O or C–C hydrogenolysis is of great importance in catalysis. Especially in the area of biomass transformation, the much higher oxygen content in the biomass derivatives than fossil resources motivates the researches of selective cleavage of C—OH bond to obtain desired chemicals. Hydrogenolysis of glycerol, which is a main product in biodiesel industry, is considered as the model reaction for reducing the oxygen content of more complicated biomass molecules, e.g., sorbitol and xylitol [1]. On the other hand, hydrogenolysis of glycerol can produce several value-added chemicals such as propanediols and propanols (Scheme 1), and the most challenging target product is 1,3-propanediol (1,3-PD) [1–13]. Up to now, the most efficient catalysts [7,9–12,14–16] for hydrogenolysis of the central C—OH group of glycerol are mainly composed of a highly reducible metal (e.g., Pt, Ir) and species of rhenium or tungsten. The Re-modified Ir/SiO$_2$ catalyst is a promising candidate, exhibiting both excellent 1,3-PD selectivity and high activity [8,9]. The interplay between Ir and Re is suggested to be responsible for its superior performance. It is generally accepted that Ir activates H$_2$, while surface Re–OH group formed during reac-
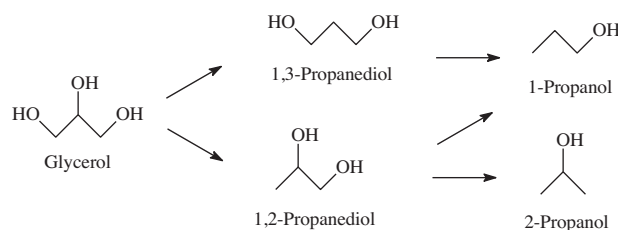


**Scheme 1.** Reaction pathway for glycerol hydrogenolysis.

tion is likely to act as the adsorption site for glycerol [14]. However, the necessity of possessing Ir–Re vicinity has not been verified.

It is known that hydrogenolysis of glycerol over bimetallic Ir–Re catalysts is a structure-sensitive reaction [8,11]. Our previous study has shown that the catalytic behavior is closely related to the bimetallic Ir–Re structure, i.e., Ir–Re alloy or Ir–ReO$_x$ structures [8]. The degree of Re reduction and the resulting bimetallic Ir–Re structure depends largely on the thermal processing procedures. Calcination of the Re precursor will expedite the formation of strong Re$^{7+}$—O-support/IrO$_2$ bonds, thus making it difficult to be reduced [14–16]. Moreover, the strength of Re$^{7+}$—O-support bonds formed during calcination step depends on the nature of supports (e.g., Al$_2$O$_3$ and SiO$_2$) [15,16]. On the other hand, when catalysts are directly activated before calcination, Re species in form of ReO$_4^-$ after drying can be easily reduced, independent of the nature of supports [16]. However, there remains a question

to be addressed regarding the possible influence of the support on the bimetallic structure of catalysts prepared by direct reduction method. Although the Re species is fully reduced, regardless of the support, the formed bimetallic structure with Ir, which has great influences on the performance of the catalyst, may strongly depend on the nature of support, because of the different strength of metal-support interaction and mobility of metal species on support [17–21].

Moreover, silica-alumina was used as an acid additive in glycerol hydrogenolysis over bimetallic Ir–Re catalysts to maximize the activity [23]. Interestingly, the direct employment of silica-alumina as support for bimetallic Ir–Re to form a multi-functional catalyst exhibited low activity than that on silica, which was preliminarily ascribed to the presence of trace Fe on support surface by Nakagawa et al. because the performance can be improved upon HNO₃ treatment [23]. Yet, the surface chemistry of silica-alumina, especially Al content, could be significantly changed during acid treatment [22]. In this context, a knowledge about the possible effect of surface Al on the structure of Ir–Re catalyst prepared by direct reduction method is desired.

In this work, a comparative study on structure and performance of catalysts between the Ir–Re supported on alumina-silica material (ASA) and the one supported on de-alumina ASA(D-ASA) was made, aiming at revealing the influence of the Al in supports on the Ir–Re alloy structure. Furthermore, an in-depth knowledge into the manipulation of Ir–Re alloy structure as well as the reaction mechanism of glycerol hydrogenolysis over bimetallic Ir–Re of different structures could be obtained.

## 2. Experimental

### 2.1. Catalyst preparation

ASA material (Aldrich, surface area = 474 m²/g, pore volume = 0.67 cm³/g) was used as received, while the D-ASA materials were obtained by treating the as-received ASA with HNO₃ aqueous solution. The D-ASA-0.5 represents the ASA treated with HNO₃ (0.05 M) at room temperature for 0.17 h, while the D-ASA-2.0 represents the ASA treated with HNO₃ (0.5 M) for 2 h. Bimetallic Ir–Re catalysts were prepared by sequential incipient wetness impregnation of the support with H₂IrCl₆ (Sigma–Aldrich, 99.9%) and then NH₄ReO₄ (Sigma–Aldrich, 99.0%) aqueous solutions, as described elsewhere [8]. The impregnated samples were dried at 120 °C for 12 h after each impregnation procedure. The resulting bimetallic Ir–Re catalysts were directly reduced at 500 °C in pure hydrogen (70 mL/min) for 3 h and subsequently passivated after cooling to room temperature in 1% O₂/Ar flow (30 mL/min) for 20 min. The loading amount of Ir was 4.0 wt% and the molar ratio of Re to Ir was 1.0.

### 2.2. Glycerol hydrogenolysis

Hydrogenolysis of glycerol was carried out in a 100 mL stainless steel autoclave (Parr Instruments) equipped with an electronic temperature controller and a magnetic stirrer. In a standard procedure, 20 g of 20 wt% glycerol aqueous solution, 150 mg of reduced bimetallic Ir–Re catalyst and 50 mg of amberlyst-15 were loaded into the autoclave. The pH value in each run was 3–4. 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 reaction, the resulting reaction mixture was centrifuged, filtered and analyzed by UPLC (Waters 2414) equipped with an RI detector and a C18 AQ column. The study on the effect of acid (i.e., amberlyst-15) loading was conducted over silica (i.e., KIT-6) supported Ir–Re catalysts at the same reaction conditions. Carbon balance of liquid phase in all tests was greater than 95%. The possible gaseous product was also examined by using GC–MS, in which only trace propane was found.

Conversion and selectivity were calculated as follows:

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

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

### 2.3. Characterization

The aluminum contents of ASA supports 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 Cu Kα radiation. N₂ physisorption measurements were performed at −196 °C on an ASAP 2010C (Micromeritics, USA), after out-gassing the samples at 300 °C and 133.3 Pa for 6 h. Transmission electron microscope (TEM) characterization was carried out for the reduced bimetallic Ir–Re catalysts using JEOL JEM 2100F with accelerating voltage of 200 kV and a point resolution of 0.18 nm. Mean particle sizes and distributions were determined by measuring over 200 randomly selected metal particles. EDX scanning for areas with large aggregates in Ir–Re/ASA was also performed. Moreover, STEM mode was employed for elemental analysis of single metal particles of Ir–Re/D-ASA-0.5 and Ir–Re/D-ASA-2.0. X-ray photoelectron spectroscopy (XPS) was conducted on a Multilab 2000 spectrometer (Thermo VH Scientific) using Al Kα radiation (1486.6 eV). Binding energy was calibrated using the binding energy of the C 1 s peak (284.6 eV) as a reference.

H₂ temperature-programmed reduction (H₂-TPR) was carried out in a U-shaped quartz tube with 5% H₂/Ar (30 mL/min) using a Micromeritics AutoChem 2920 equipped with a thermal conductivity detector. The amount of sample used was 40–70 mg, and the temperature was increased from room temperature to 800 °C at a heating rate of 10 °C/min.

IR spectra of CO adsorption were recorded on a Nicolet 6700 FTIR spectrophotometer in diffuse reflectance mode, using an in-situ cell equipped with a sample cup, heater and ZnSe windows. Pre-reduced or passivated samples were placed into the sample cup, and then reduced in-situ at 350 °C in flowing H₂ for 1 h. The sample was cooled to room temperature, then 2% CO/Ar was introduced. After the CO coverage reached its saturation level, IR spectra were collected at 25 °C.

## 3. Results and discussion

### 3.1. Physicochemical properties of supports

The physicochemical properties of ASA, D-ASA-0.5 and D-ASA-2.0 are shown in Table 1. As can be seen, the bulk Si/Al ratio of supports increases in the order of D-ASA-2.0 > D-ASA-0.5 > ASA. This indicates the de-alumination happens when treating ASA with HNO₃ acid. The surface Si/Al ratio was further investigated by XPS characterization, which is higher than the bulk Si/Al ratio. Namely, the surface Al content is lower than the bulk, which is more remarkable in the de-aluminated ASA because the surface Al is very likely to be removed firstly. Notably, the D-ASA-2.0 shows trace Al on the surface, exhibiting structure of ASA encapsulated by a silica layer [22].

Moreover, the surface area of supports increases with the decrease of Al content by HNO₃ treatment, which can be attributed