

Acid-Mediated Strategy to Construct Oxygen-free Ir-Re Coordination for Matching Configuration of Glycerol to Selective Hydrogenolysis

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Highlights

- This work proposes an acid-mediation approach to construct oxide-free Ir-Re bimetallic sites with direct Ir-Re coordination (IrRe-H).
- The high-valence Re species is removed on the IrRe-H catalyst achieved by the acid-mediation strategy as compared with that prepared with the conventional method.
- The acid-mediated IrRe catalyst shows much higher selectivity to the target 1,3-propanediol (1,3-PDO) as compared with the conventional IrRe-IM catalyst without being mediated by acid.

1. Introduction

Conversion of biomass-derived glycerol into 1,3-propanediol (1,3-PDO) is widely considered as a promising strategy for addressing the depletion of fossil resources and valorizing biodiesel prices. However, the hydrogenolysis of glycerol to 1,3-PDO remains a great challenge due to the steric hindrance and the thermodynamic advantages of 1,2-propanediol (1,2-PDO) formation relative to 1,3-PDO formation. Excessive study has focused on kinetic control to attain high 1,3-PDO selectivity via manipulating the interface of Ir and oxophilic metal Re, in which metallic Ir is responsible for activating molecular H₂ and Re species is thought to cleavage the central C-OH bond [1]. However, pronounced high-valence ReO_x species will accumulate on the support due to the strong oxygen affinity of Re, which lead to side reactions. Here, we propose an acid-mediation strategy for constructing oxygen-free Ir-Re bimetallic active sites featured with direct Ir-Re coordination. Catalytic performance tests demonstrate that the acid-mediated IrRe catalyst shows much higher selectivity to the target 1,3-propanediol (1,3-PDO) as compared with the conventional IrRe catalyst without mediated by acid.

2. Methods

The IrRe-H catalyst supported on silica (KIT-6) was prepared via simple impregnation method and subsequent mediation by HNO₃ (0.1M) solution for 60 minutes, then washed by deionized water and dried. For comparison, bimetallic IrRe/KIT-6 catalysts with the similar metal loadings as the actual loading of IrRe-H catalyst were also controllably prepared by incipient wetness impregnation described in the literature [2], and the obtained catalyst are denoted as IrRe-IM. 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. The reaction of glycerol hydrogenolysis was conducted under 393K and 8 MPa H₂.

3. Results and discussion

The detailed microstructures of the IrRe-IM and IrRe-H catalysts were investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy. As shown in Figure 1a, the k²-weighted Fourier transformed EXAFS (FT-EXAFS) at the Re L₃-edge of the IrRe-IM catalyst shows an obvious coordination peak at 1.8 Å assigned to the Re=O bond. This can be rationalized by the high oxophilicity for Re atom, which cannot be fully reduced to metallic state from NH₄ReO₄ during H₂ flow at 773K, thus contributing to the remained coordinated O atoms nearby Re atoms. Notably, a new distinct peak

at 2.3 Å assigned to the Ir-Re coordination is observed at Re L3-edge of the IrRe-H catalyst. As demonstrated in Figure 1b, as compared with those of the IrRe-IM catalyst, the intensities of high-valence Re species (i.e., Re^{VI} and Re^{VII}) decreases significantly on the IrRe-H catalyst whereas those of low-valence Re specie increases remarkably. These spectroscopic results reveal that the acid-mediation process removes oxygen-containing species from the IrRe alloy surfaces and thus successfully constructs the direct Ir-Re coordination without the interference of oxygen (Figure 1c).

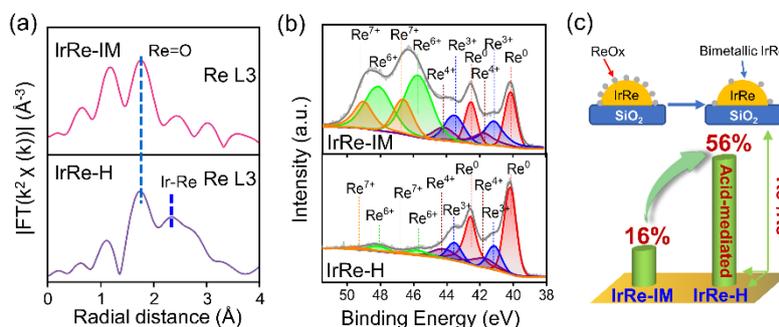


Figure 1. (a) FT-EXAFS spectra at Re L3 edge of IrRe-IM and IrRe-H. (b) Re 4f XPS spectra of the IrRe-IM and IrRe-H catalysts. (c) Schematic diagram of acid-mediated engineering on bimetallic IrRe surface.

Figure 2 shows the conversion of glycerol and product selectivity for the hydrogenolysis over the IrRe-IM and IrRe-H catalysts at various reaction times. On the IrRe-IM catalyst, the ratio of the 1,3-PDO selectivity to 1,2-PDO selectivity remains unchanged with the increasing glycerol conversion, and approximately keeps at 1.4, indicating that the formation of 1,3-PDO and 1,2-PDO are similarly competitive on the IrRe-IM catalyst (Figure 2a). As shown in Figure 2b, the ratio of 1,3-PDO selectivity to 1,2-PDO selectivity on the IrRe-H catalyst keeps at around 3.2, which is much higher than that for the IrRe-IM catalyst, suggesting that the formation of 1,3-PDO is clearly predominant over that of 1,2-PDO on the IrRe-H catalyst.

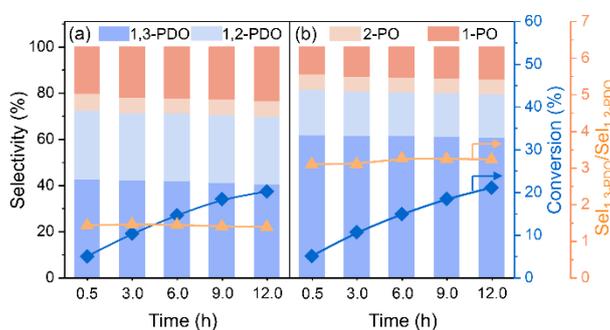


Figure 2. Conversion of glycerol, selectivities to products and the ratio of 1,3-PDO selectivity to 1,2-PDO selectivity versus reaction time on (a) IrRe-IM and (b) IrRe-H catalysts.

4. Conclusions

In summary, an acid-mediation strategy has been proposed here for constructing Ir-Re bimetallic active sites featured with direct Ir-Re coordination without high-valence Re species. Such direct Ir-Re coordination shows much higher selectivity for the hydrogenolysis of the central C–OH bond of glycerol to 1,3-PDO.

References

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Keywords

Ir-Re coordination; glycerol hydrogenolysis; 1,3-propanediol