Towards efficient Ir-Re/KIT-6 catalysts for glycerol hydrogenolysis to 1,3-propanediol by controlling the thermal pretreatment

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Introduction

Hydrogenolysis of biomass-derived glycerol to 1,3-propanediol, providing route to relieve the reliance on petroleum processes and to meet the sustainable goals, has attracted much attention. Ir-Re based catalyst is a promising candidate for the selective production of 1,3-propanediol from glycerol due to the synergistic effect between Ir and Re[1]. Attention is therefore paid to modify the degree of Ir-Re interaction and hence their catalytic performance. Since Re-support interaction is known to be a function of thermal treatment[2], we speculated that the degree of Ir-Re interaction, as well as the interaction between both metals and the support, may be modified by controlling the thermal pretreatment.

Materials and Methods

A series of Ir-Re/KIT-6 catalysts was prepared by sequential impregnation of the KIT-6 support (an ordered mesoporous silica with a cubic arrangement of interconnected pores) with aqueous solutions of H_2IrCl_6 and NH_4ReO_4. The impregnated samples (denoted as Ir-Re/KIT-6) were thermally treated as shown in **Figure 1**. Glycerol hydrogenolysis test was performed in 100-mL batch reactor with standard reaction conditions: 120 °C, 8 MPa, 20 wt% glycerol aqueous solution (20 g), 150 mg catalyst.

Results and Discussion

Figure 1 shows the the preparation approach for Ir-Re/KIT-6 catalysts. In the case of Ir-Re/KIT-6-C, the mean valence of Re after TPR is estimated to be 2.4, determined by H_2 consumption, while for Ir-Re/KIT-6, the Re species is completely reduced to metallic state. The lower reduction degree of Re for calcined sample is possibly due to the formation of Si-O-Re bond, which exhibits lower reducibility compared with physisorbed Re species.

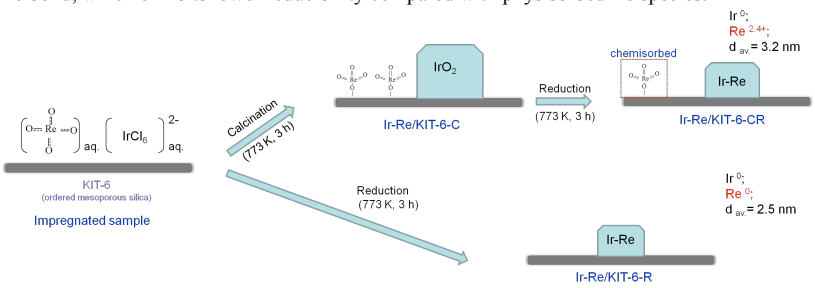

Figure 1. Scheme of the preparation approach for bimetallic Ir-Re/KIT-6 catalysts.

Figure 2A shows the catalytic performance of the two catalysts for glycerol hydrogenolysis. The Ir-Re/KIT-6-R catalyst exhibited a much higher rate of 1,3-propanediol formation compared to Ir-Re/KIT-6-CR. The average 1,3-propanediol formation rate in 2 h reaction was 67.3 $mol_{1,3\text{-PD}}\, mol_{Pt}^{-1}\, h^{-1}$ for Ir-Re/KIT-6-R, which is 2.4-times that of Ir-Re/KIT-6-CR and about 3 times higher than the best literature results at the same reaction conditions (14.9 $mol_{1,3\text{-PD}}\, mol_{Ir}^{-1}\, h^{-1}$ in 4 h) [1]. The remarkably enhanced activity is attributed to the higher extent of Ir-Re interaction for Ir-Re/KIT-6-R, since the extent of Re reduction is higher compared to Ir-Re/KIT-6-CR. With the aid of TPR-TPO-TPR, the Re species present is classified qualitatively and quantitatively into different types, according to their reducibility.

In order to explore the role of Re oxidation state, Ir-Re/KIT-6-R catalysts with different degrees of Re reduction (**Figure 2B inset**) were prepared by reducing the catalyst at three different temperatures (400, 500 and 600 °C), followed by testing in glycerol hydrogenolysis. The activity is monotonously increases with Re reduction degree, while the particle size are similar as determined by TEM observation.

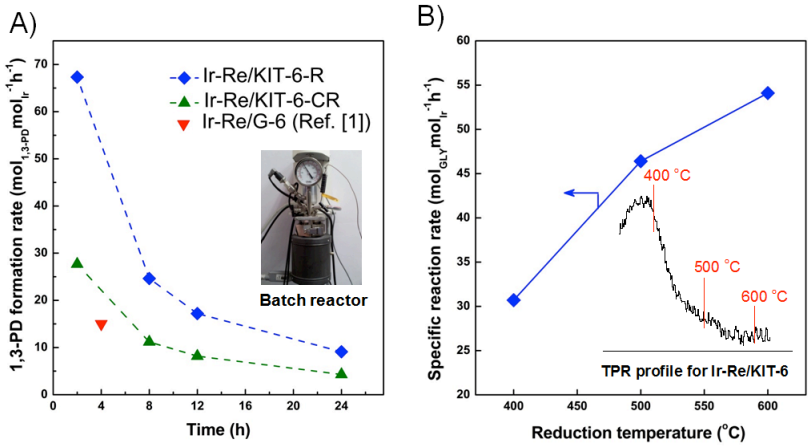

Figure 2. A) Hydrogenolysis of glycerol catalyzed by Ir-Re/KIT-6-R and Ir-Re/KIT-6-CR; B) Effect of reduction temperature on the average rate of glycerol hydrogenolysis catalysed by Ir-Re/KIT-6-R. The inset is the TPR profile for Ir-Re/KIT-6-R.

Significance

Our results demonstrated that the Re reduction degree and the extent of Ir-Re interaction is a function of thermal treatment, and plays a critical role in glycerol hydrogenolysis. With the aid of TPR-TPO-TPR, three types of Re with different reducibilities are identified and quantified, which may help in further understanding the role of Re in future studies.

References

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2. Kim, D. S.; Wachs, I. E. *Journal of Catalysis* **1993**, *141*, 419.