DEACTIVATION OF IR-RE ALLOY CATALYST IN GLYCEROL HYDROGENOLYSIS

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Abstract

Ir-Re alloy catalysts supported on silica were prepared and reused in glycerol hydrogenolysis to 1,3-propanediol with the aid of Amberlyst-15. The catalyst stability was systematically investigated by extensive characterization of the fresh and used catalysts. The results indicated that the Ir-Re alloy gradually deactivated in the reaction mainly because the strong oxophilicity of Re species resulted in its migration onto the catalyst surface and thus the segregation of Re from alloy.

Keywords

Glycerol hydrogenolysis, Ir-Re alloy, Catalyst stability.

Introduction

Hydrogenolysis of biomass-derived glycerol to 1,3-propanediol (1,3-PD), a route alternative to petroleum based processes, has attracted much attention because of its sustainability feature and the highly added value of 1,3-PD. Among the catalysts for this selective hydrogenolysis, Ir-Re based catalyst exhibits superior performance owing to the snergy between Ir and Re (Amada, 2011).

Recently, we have proposed an exceptionally active Ir-Re alloy catalyst by direct reduction method for glycerol hydrogenolysis, exhibiting the highest reported 1,3-PD formation rate of 25.6 $mol_{1,3-PD}mol_{Ir}^{-1}h^{-1}$ at 63% of glycerol conversion with the aid of amberlyst-15 (Deng, 2015). However, the stability of Ir-Re alloy, which is critically important for its potential industrial application, has not been addressed so far.

Herein we investigated the behavior of Ir-Re alloy in its cycling use for glycerol hydrogenolysis in a batch reactor in this work. Extensive characterizations of the fresh and used catalysts have been conducted to explore the deactivation mechanism of Ir-Re catalyst, aiming at better design and optimization of highly active catalyst for glycerol hydrogenolysis.

Methodology

Ir-Re alloy catalyst was prepared by impregnation the silica support (G-6, Fuji Silysia Chemical Ltd.) with H_2IrCl_6 and NH_4ReO_4 solutions using direct reduction method as reported in our previous paper (Deng, 2015), denoting as Ir-Re/G-6. The actual loadings of Ir and Re determined by ICP are 5.0wt% and 4.8wt%, respectively. 20 g aqueous glycerol solution (20 wt%) and 150 mg catalyst were charged into a 100 mL autoclave (Parr Instruments) with 50 mg Amberlyst-15 as an additive. The hydrogenolysis reaction was conducted under 393K and 8 MPa H_2 for 12h. The used catalyst was reused without any other special treatments. In each reuse run, additional 15 mg fresh catalyst (10 wt% of the total catalyst amount) and 20 mg Amberlyst-15 were added into the reactor to compensate the catalyst loss during the transfer process. The liquid products were analyzed by an HPLC (Waters) with an RID detector and a C18 column. CO-DRIFT was conducted on a Perkin Elmer Spectrum 100 spectrometer with a MCT detector and an in-situ cell. ICP-AES was

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conducted on a Vanan 710. TEM images were taken on JEOL JEM 2100F. TGA was carried out on a TA SDT-Q600 thermobalance in an air flow. FTIR was conducted on a Nicolet 6700.

Results and Discussion

The Ir-Re/G-6 catalyst was reused for 4 times in glycerol hydrogenolysis and their catalytic performance is shown in the Table 1. It can be seen that the activity of the recycling catalysts declined significantly after first use and then slowly with the increasing cycling times. The fresh catalyst presented much higher glycerol conversion than the used ones. It is evident that the Ir-Re alloy tends to deactivate during the glycerol hydrogenolysis.

Table 1. Reusability of Ir-Re/G-6

Usage time	Conv. /%	Selectivity/%			
		1,3-PD	1,2-PD	1-PO	2-PO
1st	67.8	29.6	14.9	47.6	9.0
2nd	50.9	32.0	23.4	36.3	8.3
3rd	48.6	31.7	26.4	33.8	8.1
4th	42.2	31.9	29.1	31.8	7.2

Note: 1,2-PD: 1,2-propanediol; 1-PO: 1-propanol; 2-PO: 2-propanol

The fresh and used catalysts were extensively characterized to explore the possible causes for the deactivation during hydrogenolysis. The ratios of Ir and Re leaching into the product mixture solution after first run were only 0.14% and 0.38% as determined by ICP-AES, indicating that loss of active metals resulting from leaching did not account for the deactivation of Ir-Re catalyst. The TG analysis combined with FTIR spectra revealed that coking or fouling were not the main cause for the deactivation. TEM images of fresh and spent catalysts after 4 uses showed average particle diameter of 2.8nm and 3.4nm, which means the particle size of Ir-Re alloy was slightly increased after each run and could be part of the reason that the activity declined.

CO-DRIFTs, as a sensitive technique to probe the interaction between the metals for bimetallic catalysts, is used to detect the structural alterations of Ir-Re alloy catalyst during the cycling use. As shown in Fig.1, the CO adsorption band of the fresh catalyst appears at 2059 cm^{-1}, an intermediate position between the band position for Ir/G-6 of 2080 cm^{-1} and Re/G-6 of 2035 cm^{-1}, suggesting the formation of Ir-Re alloy. After cycling run, the CO adsorption band of the used catalyst gradually split into two peaks attributed to separate metallic Ir and Re, indicating the segregation of two metals from the Ir-Re alloy. We have known that both monometallic Ir or Re catalysts were inactive for glycerol hydrogenolysis and the Ir-Re-OH sites produced by the interaction between Ir and Re are acidic sites for glycerol absorption, while H$_2$ is activated by Ir (Deng, 2015; Nakagawa, 2012). As the activity of Ir-Re alloy is dependent on the close contact of

the two metals, the segregation of alloy would definitely result in deactivation. Re species in the Ir-Re alloy tend to migrate to the catalyst surface when contacting with aqueous glycerol solution during the cycling use because of its strong oxophilicity, which finally leads to segregation of Ir and Re from the alloy and deteriorates significantly the catalytic performance.
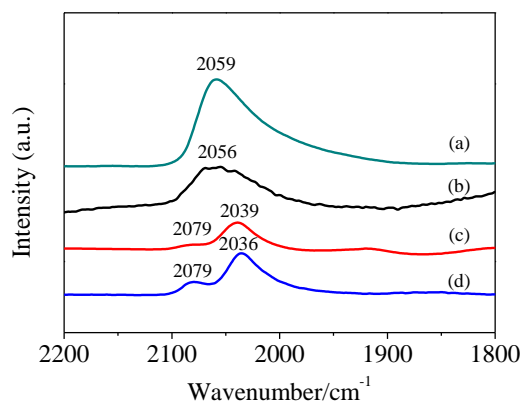

Fig 1. CO-DRIFTs of fresh (a) and used Ir-Re/G-6 after 1(b), 2(c) and 3(d) runs

Conclusions

The Ir-Re/G-6 alloy catalyst gradually deactivated in the glycerol hydrogenolysis mainly owing to the segregation of alloy. These findings could provide useful knowledge for the rational design of highly efficient and stable catalysts for selective hydrogenolysis of glycerol or other polyols in view of biomass transformation into value-added chemicals.

Acknowledgments

References

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