

A Comparison of Pt-Re and Rh-Re Catalysts in Oxidative Reforming

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Introduction

Bimetallic catalyst Pt-Re/Al₂O₃ is very active and stable for synthesis gas generation via oxidative reforming at very high space velocities (500,000 h⁻¹) and temperatures (up to 1000°C) [1, 2]. We ascribe the high activity of Pt to the formation of high-index crystal planes and the turn-over promotion by Re. Due to high oxygen affinity of Re, Pt in the Pt-Re alloy is freed from O occupancy for CH₄ activation. It activates C-H bonds much more effectively due to nearby O species provided by Re. This agrees with the findings published by Iglesia's group (a Pt-O* pair is much more effective for C-H bond activation) [3]. Higher stability of the catalyst is attributed to higher melting point of the Pt-Re alloy and an anchoring effect. Re in the Pt-Re alloy bounds with Al₂O₃ on the interface of the bimetallic particle and the support. In this study, we compare Pt-Re with Rh-Re and investigate the changes of Pt-Re and Rh-Re particles before and after partial oxidation of CH₄. The role each component plays and why Pt-Re is a better catalyst are discussed.

Materials and Methods

Catalyst preparation and testing details have been reported earlier [2]. TEM and STEM ADF images and EDX qualifications are obtained using a Tecnai G2 F20 TEM.

Results and Discussion

Rh catalyst sinters considerably at high temperatures. This is a problem for oxidative reforming since high temperatures are required in order to achieve high selectivity and conversion. Similar to Pt, Rh can alloy with Re. As expected, higher stability is observed on 0.5wt%Rh-2wt%Re/Al₂O₃ comparing to 2wt%Rh/Al₂O₃. However, the initial activity of Rh-Re is not as high as that of Rh or 0.5wt%Pt-2wt%Re/Al₂O₃ as plotted in Figure 1. TEM images disclose that unlike Pt-Re particles, which show high-index crystal planes after Re modification, Rh-Re crystals have low-index planes such as [11-1] and [010]. For C-H bond activation, Re's promotion effect on Rh is not as significant as on Pt. In addition, the stability of Rh-Re is not as good as that of Pt-Re.

The boiling point of Re₂O₇ is 360°C. In order for the Re bimetallic catalyst to work in oxidative reforming where O species is present, Re must be in the reduced form so that the alloy will not be destroyed and Re will be retained during the reaction. We randomly selected particles on the Pt-Re and Rh-Re catalyst before and after reaction and examined their compositions using TEM with an EDAX EDS spectrometer at STEM mode. As shown in Figure 2, on Pt-Re, significant numbers of particles contain only Re before reaction. More bimetallic particles are formed during reaction. On the spent catalyst, all Re-only particles disappear. The composition of the bimetallic particles peaks at the loading target. A small portion of Re could volatilize but by comparing the abundance of the particles, this portion should be small. On the other hand, Rh-Re forms bimetallic particles easier. Neither Rh-only nor Re-only particles are observed after reduction on Rh-Re. However, there is a significant

composition shift after reaction that indicates substantial Re loss during reaction. The loss of Re contributes to slow deactivation of Rh-Re. We believe that Pt does not form a stable oxide and it keeps Re staying in the reduced form. Therefore, formation of the volatile Re species is avoided. On the other hand, Rh has higher affinity to O. It is less effective for keeping Re in the reduced form. Therefore, Pt-Re is more stable than Rh-Re in oxidative reforming such as partial oxidation and autothermal reforming.

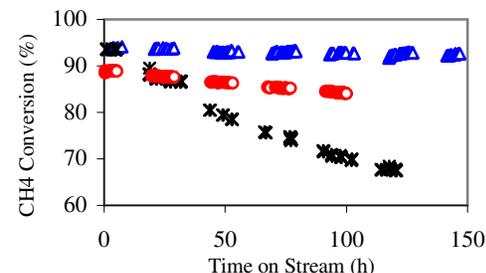


Figure 1. CH₄ conversion at 900°C, 500,000 h⁻¹, and CH₄/O₂=2. *: 2.0wt%Rh/Al₂O₃, Δ: 0.5wt%Pt-2.0wt%Re/Al₂O₃, and ○: 0.5wt%Rh-2.0wt%Re/Al₂O₃.

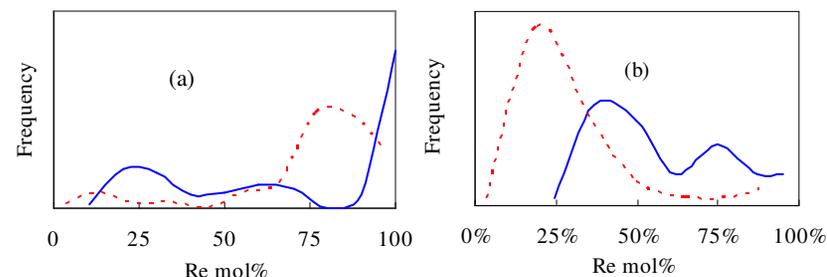


Figure 2. Distribution of bimetallic particle composition. (a) Pt-Re/Al₂O₃ and (b) Rh-Re/Al₂O₃. —: Fresh reduced and - -: After reaction

References

1. Zhao, S. and Ladebeck, J. 14th ICC Seoul, Korea July 13-18, 2008.
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3. Y. Chen, M. Li, E. Iglesia, 20th North American Catalysis Society Meeting, June 17-22, 2007, Houston.