

Cobalt-Molybdenum Carbides for Hydrogen Deuterium Exchange Reaction

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Highlights

- Hydrogen activation of cobalt-molybdenum carbides
- Deuterium disappearance rate for hydrogen-deuterium exchange reaction at 200 K
- The 873K-carburized Co(0.75)Mo(0.25) catalyst has the highest activity.
- The active species is CoMo carbide with excess Co metal and beta-molybdenum carbide.

1. Introduction

Many industrial processes involve hydrogen activation reaction, such as hydrogenolysis, anode reaction of a fuel cell, ammonia synthesis and water-gas shift reaction. In these reactions, the catalyst is needed to activate hydrogen for dissociative adsorption. The hydrogen activation was estimated by the dissociation of hydrogen based on the D₂ disappearance rate during the H₂-D₂ exchange equilibrium reaction [3]. The exchange reaction involves the splitting the bond of hydrogen of hydrogen molecule to form hydrogen atom and the dissociative adsorption on the surface. The cobalt molybdenum carbide of non-noble metal is known to be highly active in hydrogenation, hydrogenolysis, oxygen reduction reaction [2] and water-gas shift reaction [3]. The cobalt molybdenum carbides were subjected to the H₂-D₂ exchange equilibrium reaction for a fully understanding of the hydrogen activation. The active sites of cobalt molybdenum carbide for the hydrogen activation were studied in combination with the XRD and TPR and XPS.

2. Methods

The CoMo catalysts with various Co/(Co+Mo) ratios were prepared by oxidation process, hydrogen reduction process, or carburization process. The activity of the prepared catalysts was evaluated by D₂ disappearance rate during hydrogen activation for hydrogen-deuterium (H₂-D₂) equilibrium reaction. The CoMo catalysts were oxidized at 723 K for 1 h (oxidized catalyst), reduced at 673 K for 2 h (reduced catalyst), and carburized from 573 K to 773 K (or 873 K) at 1 K/min and maintained at the temperatures of 773-873 K for 2 h (carburized catalyst). The H₂-D₂ reaction was carried out at the reaction temperatures of 200-373 K using a flow microreactor and at atmospheric pressure. The catalysts were characterized by the XRD, TPR and XPS.

3. Results and discussion

The Co(0.25)Mo and Co(0.75)Mo catalysts carburized at 823-873 K, showed higher activities at 273-373K than the oxidized and reduced catalysts, even at 200 K. The 873 K-carburized Co(0.75)Mo catalyst was the highest activity for the H₂-D₂ reaction even at 200 K, which contained CoMo carbide and Co metal, but no Co carbide was formed. The second active catalyst was the 873 K-carburized Co(0.25)Mo catalyst. In addition, the oxidized CoMo catalyst contained CoMoO₄ as a precursor. The reduced Co(0.75)Mo had Co metal. The temperature-programmed reduction of the carburized CoMo catalysts was carried out at 10 K/min from 298 to 1123 K with mass spectrometer to detect methane.

The carburized CoMo catalyst contained β-Mo₂C and Co metal, leading to a high activity for the H₂-D₂ reaction. Therefore, the catalysts with a high activity for hydrogen activation consisted of CoMo carbide. The XRD and TPR analyses showed that the 873 K-carburized catalysts contained CoMo carbide together with Co metal (Co⁰) and β-Mo₂C (Mo^{δ+}) for excess cobalt and with β-Mo₂C for excess Mo atoms of the constituent.

4. Conclusions

The 873 K-carburized Co(0.75)Mo catalyst was the highest activity for the H₂-D₂ reaction even at 200 K. The catalyst contained CoMo carbide with excess Co metal and beta-Mo₂C. No Co carbide was formed.

References

- [1] E. J. M. Hensen, G. M. H. . Lardinois, V. H. J. de Beer, J. A. R. van Veen, R.A. van Santten, J. Catal. 187 (1999) 95–108.
- [2] S. Izuhar, M. Nagai, J. Power Source, 182 (2008) 52–60.
- [3] M. Nagai, K. Matsuda, J. Catal. 238 (2006) 489–496.

Keywords

“Hydrogen activation”, “H₂-D₂ exchange reaction”, “CoMo carbide”, “Active species ”