

PERFORMANCE AND CHARACTERIZATION OF A PLATE-TYPE CATALYST FOR STRUCTURED REFORMER AND CO SHIFT CONVERTER

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Summary

To construct structured methanol reformer and structured CO shift converter, a plate-type Cu-Fe/Zn catalyst was prepared by electroless plating technique on an aluminum substrate. The reforming and shift activities of the prepared catalyst were improved by oxidation than by reduction prior to reaction. The physicochemical properties of the catalyst were investigated so as to relate with such performances. For activity improvement, the oxidation caused the zinc component to migrate to the surface and form a CuZn alloy-like compound. The formation of such alloy accelerates the increase of monodentate-type formate group and contributes to the improvement of reforming and shift activities.

Keywords

Structured reactor, Electroless plating, Methanol steam reforming, CO shift reaction

Introduction

A wall-type reactor, in which metallic wall is catalyzed, enables an effective exchange of heat energy, a rapid response to load fluctuation and a downsizing of reactor dimension. Application of such reactor involving steam reformer and CO shift converter is expected, for an on-board or on-site type power generator system by fuel cells.

We have revealed that a plate-type copper-based catalyst prepared on an aluminum plate by electroless plating has high performances for methanol steam reforming and CO shift reaction[1,2], which offers the possibility of applying this catalyst in the wall-type reformer and shift converter. We also found that this plated catalyst was fairly improved in reforming and shift activities by reoxidation treatment prior to the reaction, and the activity is regenerated by oxidation treatment when declined. Such unique properties are very interesting and important from the views point of chemical engineering and catalytic chemistry.

In this study, the physicochemical properties of the plated copper-based catalyst were measured using various instruments so as to investigate the developing factor of reforming and CO shift properties for the plated catalyst.

1. Experimental

1.1 Preparation of Plate-Type Copper-Based Catalyst

The plate-type copper-based catalyst was prepared on an aluminum plate by electroless plating, which was the same technique as previous reports [1,2]. The plating process consisted of a displacement plating of zinc (20 °C, 20 min), an intermediate plating of iron (20 °C, 4.5 min),

and a chemical plating of copper with formaldehyde as a reducing agent (24 °C, 30 min). After being washed in a water bath, the plate was dried in air at room temperature for about 12h. In addition, in order to investigate the effect of the drying condition on catalytic performance of the plated Cu-Fe/Zn catalyst, the freshly plated catalyst was dried in a helium stream at 200°C for 1h.

1.2 Reaction and Characterization

The prepared Cu-Fe/Zn catalyst was placed in the flow reactor to examine its catalytic properties for steam reforming of methanol (LHSV:10.1 h⁻¹, S/C:1, p_{feed} :0.85 atm) and CO shift reaction (GHSV:2,120 h⁻¹, S/C:2, p_{feed} :1.0 atm). The catalyst was oxidized in an air stream (300 °C, 1 h) or reduced in a hydrogen stream (300 °C, 1h) prior to the reaction. Conversion and selectivity of products were calculated on the basis of carbon.

The physicochemical properties of the plated catalyst layer were characterized using XRD, SEM, EDX, FT-IR. The surface area of metallic copper component was measured by N₂O adsorption.

2. Result and discussion

2.1 Catalytic Properties of Prepared Catalyst

Table 1 shows the properties of methanol steam reforming (M.S.R.) and CO shift reaction (CO S.R.) for the Cu-Fe/Zn catalyst with different pre-treatment prior to the reaction. The activities for both reactions of the Cu-Fe/Zn catalyst are improved by oxidation treatment rather than that by the reduction treatment, and the selectivity is kept high for both reactions in each treatment. But the activity of the catalyst subjected to forced drying in helium

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after plating was considerably decreased, although the catalyst was oxidized. It was found that the oxidation treatment and the drying in an air after plating are very important factors for developing the reforming and shift performances.

Table 1 Effect of pre-treatment condition on M.S.R. and CO S.R. performances for the plate-type Cu-Fe/Zn catalyst

Reaction	Pre-treatment condition	React. temp.(°C)	Conversion [%]	Selectivity of CO ₂ [%]
M.S.R	Reduced in H ₂ at 300°C	250	14.3	97.9
		300	59.6	95.4
	Oxidized in air at 300°C	250	45.2	98.7
		300	92.9	93.0
	Oxidized after drying in He	250	12.0	98.1
	300	39.7	96.1	
CO S.R	Reduced in H ₂ at 300°C	250	53.7	100
		300	85.4	100
	Oxidized in air at 300°C	250	95.0	100
		300	98.8	100
	Oxidized after drying in He	250	37.6	100
	300	63.3	100	

2.2 Physicochemical Properties of Prepared Catalyst

Fig.1 shows the XRD profiles for the surface layer of each plated catalysts with different pre-treatment. For the oxidized catalyst, a peak of a CuZn alloy is distinctly observed near $2\theta=42.3^\circ$. While, for the reduced catalyst, such peak is rather weak, and no peak is observed for the catalyst dried in helium. From the elemental profiles

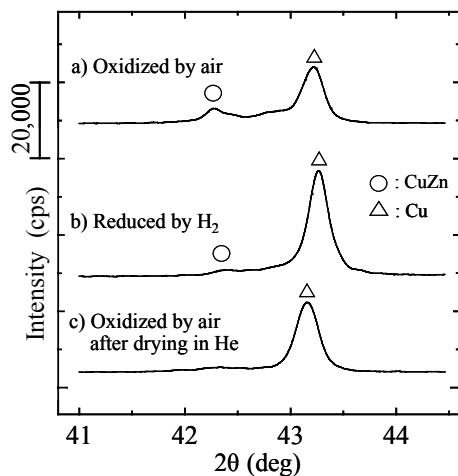


Fig.1 XRD profiles of the Cu-Fe/Zn catalyst with different pre-treatment.

measured by EDX in a section of the plated layer with different treatment, it was observed that zinc component in the plated layer migrated to the surface by oxidation treatment [2]. Thus, the zinc component migrated to the surface layer would formed a CuZn alloy-like component with copper component. Such alloy-like species in the surface layer might be a factor related to reforming and shift activities. It was also obvious that there is no

correlation between the catalytic activity and the surface area of metallic copper component. The contribution of metallic copper acting as an active site was small.

Fig.2 shows IR spectra for formate groups, which are considered as the intermediate species of reforming and shift reaction [3,4], on the Cu-Fe/Zn catalyst with different pre-treatment. The peak at $1570\text{--}1650\text{ cm}^{-1}$ is attributed to asymmetric stretching vibration of O-C-O, and the peak at $1340\text{--}1360\text{ cm}^{-1}$ is to symmetric stretching vibration of O-C-O. Of these peaks, the peak of the monodentate-type (1650 cm^{-1}) is the largest for the oxidized catalyst, followed by the reduced catalyst and the catalyst oxidized after being dried in helium in the order of absorbance. This order corresponds to that of reforming and shift activities shown in Table 1. The formation of the CuZn alloy-like compound accelerated the increase of forming highly reactive formate group and contributed to the improvement of activity.

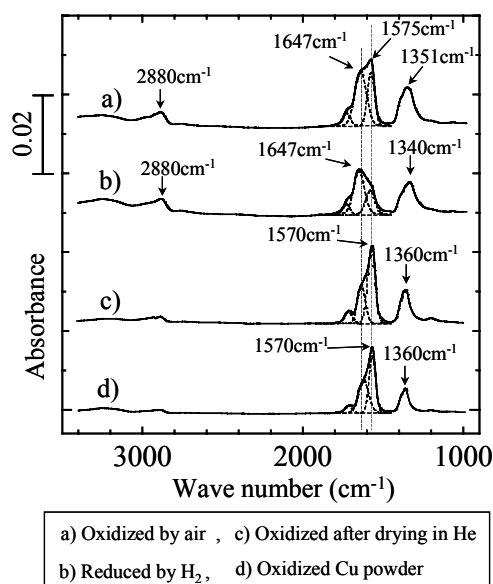


Fig.2 IR spectra of formate groups in the Cu-Fe/Zn catalyst with different pre-treatment.

3. Conclusion

The reforming and CO shift properties of the Cu-Fe/Zn catalyst related to the formation of CuZn alloy-like compound. Such formation accelerated the increase of forming highly reactive formate group (monodentate-type) and contributed to the improvement of reforming and shift activities.

References

- (1) C. Fukuhara, H. Ohkura, Yoshiyuki Kamata, Yuji Murakami, A. Igarashi, *Appl. Catal. A: Gen.*, **2004**, 273, 125.
- (2) C. Fukuhara, H. Ohkura, K. Gonohe and A. Igarashi, *Appl. Catal. A: Gen.*, **2005**, 279, 195.
- (3) T. V. Herwijnen, W. A. de Jong, *J. Catalysis*, **1980**, 63, 83.
- (4) C. T. Campbell, K. A. Daube, *J. Catalysis*, **1987**, 104, 109.