

# Effect of alkali metal addition to iron oxide structured catalyst for water gas shift property

Ryo Watanabe, Kengo Tajima, Nozomu Hirata  
Kohno Yoshiumi and Choji Fukuhara  
Shizuoka University, Department of Applied  
Chemistry and Biochemical Engineering,  
Hamamatsu, Shizuoka, Japan  
\*E-mail: tfukuh@ipc.shizuoka.ac.jp

Water gas shift (WGS,  $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ ) is an effective approach for removing carbon monoxide from the reformed gas in a hydrogen production system. We have previously developed a Ni-including iron oxide structured catalyst (Ni-FeO<sub>x</sub>/Al) for WGS reaction [1]. In this study, in order to further enhance a WGS performance of the Ni-FeO<sub>x</sub> structured catalyst, we investigated the effect of alkaline metal (Li, Na, K, Cs) and alkali earth metal (Ca, Sr, Ba) addition to the catalyst on WGS property.

The alkali-promoted catalyst was prepared as follows; the aluminum substrate was firstly activated by NaOH *aq.* and HCl *aq.* solutions. The FeCl<sub>3</sub>, urea and Ni(NO<sub>3</sub>)<sub>2</sub> was then dissolved in a distilled water. The hydrothermal synthesis was then performed at 95°C for 11 h. After hydrothermal synthesis, the prepared catalyst was calcined at 300°C for 2 h. Subsequently, the prepared catalyst was immersed in an alkaline nitrate solution, and it was calcined at 500°C for 2 h. The WGS activity test was performed using a fixed bed reactor. The structured catalyst was firstly cut into square-shaped pieces (2.5 mm × 2.5 mm). The 80 pieces was settled at the center of the reactor, and the catalyst was reduced by H<sub>2</sub> at 500°C for 1 h. The flow rate of the feed gas was CO/H<sub>2</sub>O/He = 5/10/35 ml·min<sup>-1</sup>. The reaction temperature was at from 160 to 400°C. The outlet gas was analyzed by GC-FID.

Fig. 1(a) and 1(b) show a temperature dependence of a CO<sub>2</sub> yield over the alkali metal- and alkaline earth metal-promoted Ni-FeO<sub>x</sub> structured catalyst. From Fig. 1(a), the addition of alkali metal was positive effect for an enhancement of a WGS activity. The highest activity was obtained over the Cs promoted Ni-FeO<sub>x</sub> structured catalyst. Even at a low temperature of 225°C, the Cs-promoted

Ni-FeO<sub>x</sub> structured catalyst showed 18.5% yield. Similarly, the alkali earth metal addition gave a good result. The activity order of the promoted catalyst was a good coincidence with the first ionization energy order of the additional component. Thus, the high WGS activity might be due to one electron transfer from the promoted metal to active-site Ni [2].

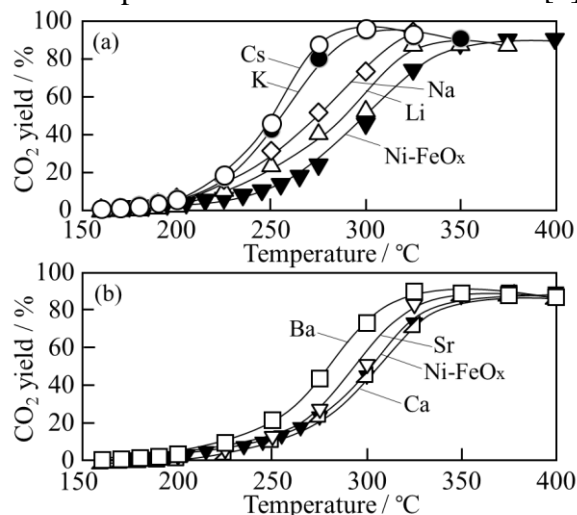


Fig.1 WGS over (a) M/Ni-FeO<sub>x</sub>/Al (M: Li, Na, K, Cs) and (b) M'/Ni-FeO<sub>x</sub>/Al (M': Ca, Sr, Ba) catalysts.

Table 1 shows conversion and selectivity over the promoted Ni-FeO<sub>x</sub> structured catalyst at 300°C. The addition of alkali metal and alkaline earth metal improved the selectivity to CO<sub>2</sub>. The disproportionation of CO and subsequent methanation of the carbon precursors were prevented by the strong adsorption of CO [3]. The addition of alkali metal and alkaline earth metal might promote an interaction between CO and Ni, which produced a high selectivity of CO<sub>2</sub>.

Table 1 Effect of alkali metal and alkaline earth metal on CO conversion and selectivity to CO<sub>2</sub>, CH<sub>4</sub> at 300°C.

Catalyst	CO conv.	CO <sub>2</sub> sel.	CH <sub>4</sub> sel.
Ni-FeO <sub>x</sub>	47.2	93.8	6.2
Li/Ni-FeO <sub>x</sub>	53.9	99.4	0.6
Na/Ni-FeO <sub>x</sub>	73.6	99.6	0.4
K/Ni-FeO <sub>x</sub>	95.9	99.0	1.0
Cs/Ni-FeO <sub>x</sub>	95.9	99.9	0.1
Ca/Ni-FeO <sub>x</sub>	46.4	99.4	0.6
Sr/Ni-FeO <sub>x</sub>	50.3	99.7	0.3
Ba/Ni-FeO <sub>x</sub>	74.6	98.4	1.6

## REFERENCES

- [1] R. Watanabe, S. Watanabe, N. Hirata and C. Fukuhara, *Catal. Lett.*, 146(12) (2016) 2478.
- [2] P.A. Zhdan, A.P. Shepelin, Z.G. Osipova and V.D. Sokolovskii, *J. Catal.*, 58(1) (1979) 8.
- [3] M.L. Ang, U. Oemar, Y. Kathiraser, E.T. Saw, C.H.K. Lew, Y. Du, A. Borgna and S. Kawi, *J. Catal.*, 329 (2015) 130.