Alkali promotion of iron oxide based catalyst for water gas shift reaction

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Abstract: An alkali-promotion was effective for an improvement of the WGS activity of a Ni-FeOx structured catalyst. High activity was especially obtained by addition of Cs component. The XPS spectra showed that a charge transfer was occurred from the alkali species to the active site of Ni, which enhanced the interaction between CO and Ni. The result of CO-TPR provided that the WGS reaction was progressed by the carbonate route at lower temperature side and by the formate route at medium temperature side.

Keywords: Structured catalyst, WGS, Alkali metal.

1. Introduction

The water gas shift (WGS, $CO + H_2O \rightleftarrows CO_2 + H_2$) is an effective reaction for removing carbon monoxide in a hydrogen production system[1]. The WGS reaction is an exothermic reaction, and the equilibrium conversion is a low at the higher temperature side due to thermodynamic limitations. Therefore, the reaction temperature should be lowered in order to achieve a high CO conversion, though the reaction rate is kinetically suppressed at the lower temperature side. Recently, a medium temperature shift (MTS, 250–400°C) was researched due to its more practical use. The MTS process could be performed for hydrogen purification in a single-stage[2]. An iron oxide-based material is one of the promising WGS catalyst for the MTS process, but this catalyst shows a low activity at medium temperature range around 300°C. We previously developed a nickel-doping iron oxide (Ni-FeOx) structured catalyst, which enables an effective heat exchange in the reaction field by conductive heat transfer[3]. The structured catalyst displayed a high performance for the WGS at a medium temperature. Furthermore, the WGS activity was enhanced by the potassium addition.

The aim of this study was to investigate the addition effect of the alkali metals (Li, Na, K, Cs) and the alkaline earth metals (Ca, Sr, Ba) to the Ni-FeOx structured catalyst on its WGS performance. The oxidation state of Ni over each catalyst was examined by X-ray Photoelectron Spectroscopy (XPS) for clarifying the reason for high activity over the alkali-promoted catalyst. The CO-TPR measurement was performed to obtain some clues for the reaction mechanism.

2. Experimental

The alkali-promoted catalyst was prepared as follows; the aluminum substrate was firstly activated by NaOH *aq*. and HCl *aq*. solutions. $FeCl_3$, urea and $Ni(NO_3)_2$ were then dissolved in a distillated water. The hydrothermal synthesis was then performed at 95ºC for 11 h. After hydrothermal synthesis, the prepared catalyst was calcined at 300ºC for 2 h. Subsequently, the prepared catalyst was immersed in an alkaline nitrate solution, and it was calcined at 500ºC for 2 h. In order to load an alkali component, the Ni-FeOx structured catalyst was immersed in alkali nitrate and/or alkaline earth nitrate solutions of $1.0\ mol{\cdot}L^{-1}$, then 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 were settled at the center of the reactor, and the catalyst was reduced by H_2 at 500ºC for 1 h. The flow rate was $CO/H_2O/He = 5/10/35\ ml{\cdot}min^{-1}$. The reaction temperature was carried out at 300ºC.

3. Results and discussion

Table 1 shows conversion and selectivity over the promoted Ni-FeOx structured catalyst at 300ºC. The alkali-promoted catalysts showed a superior activity to the bare Ni-FeOx structured catalyst. Especially, a high WGS activity was obtained over the Cs/Ni-FeOx structured catalyst. The addition of the alkali metal and alkaline earth metal also improved the selectivity to CO_2.

The XPS measurement was performed over the Ni-FeOx and M/Ni-FeOx (M: Li, Na, K, Cs) structured catalysts to investigate the electronic state of the Ni metal. The Ni_{2p} XPS spectra were shown in Fig 1. Before XPS measurements, the catalysts were reduced at 500°C for 1 h. In Fig. 1, the metallic Ni and the cationic Ni were observed at around 852 and 855 eV, respectively. As evident from the Ni metal peak, the clear shift in binding energy was observed. The energy shift to the lower binding energy for Ni metal peak was occurred by loading alkali metal with the low ionization energy. This result implied that there was the interaction between alkali metal and Ni, and a charge transfer occurred from alkali metal to Ni component on the catalyst. Such electron density of Ni might promote the interaction between CO and Ni, which produced a high performance for WGS reaction.

In order to clarify the role of alkali metal, the temperature programmed reaction with CO (CO-TPR) was performed over the K/Ni-FeOx structured catalyst. Before CO-TPR measurement, H_2O was adequately supplied to the catalyst to form OH-group on the catalyst surface. Fig. 2 shows CO_2 production flow rate in the CO-TPR profile over the K/Ni-FeOx structured catalyst. Based on the mass balance and the H_2 production profile (not shown), CO_2 production profile was separated with the three regions contributed by the carbonate species, the formate species and CO disproportionation. The detection of CO_2 without H_2 formation at lower temperature side indicated that the CO oxidation by lattice oxygen ($CO + O^{2-}_{lat} \rightarrow CO_2 + 2e^- + Vox$) was progressed on the catalyst. By increasing temperature, the CO_2 was produced with H_2. The formation of CO_2 with H_2 indicated that the WGS reaction mainly proceeded by the formate intermediate route at the medium temperature. At further high temperature, CO_2 was produced by the CO disproportionation. By loading the alkali species, the redox property of the Ni-FeOx might be enhanced due to charge transfer from the alkali component to Ni-FeOx as shown in Fig. 1. Thereby, the CO_2 was probably detected without the formation of H_2 at the lower temperature side.

Table 1. Effect of alkali metal and alkaline earth metal on CO conversion and selectivity to CO_2, CH_4 at 300°C.

Catalyst	CO conv.	CO_2 sel.	CH_4 sel.
Ni-FeOx	47.2	93.8	6.2
Li/Ni-FeOx	53.9	99.4	0.6
Na/Ni-FeOx	73.6	99.6	0.4
K/Ni-FeOx	95.9	99.0	1.0
Cs/Ni-FeOx	95.9	99.9	0.1
Ca/Ni-FeOx	46.4	99.4	0.6
Ba/Ni-FeOx	74.6	98.4	1.6

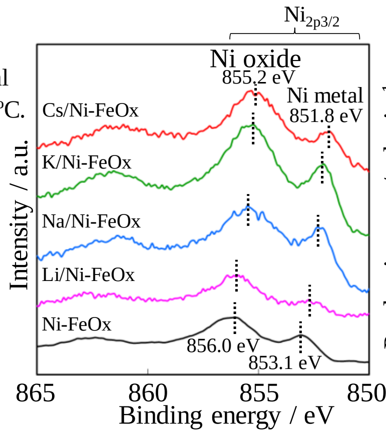

Figure 1. Ni_{2p} XPS spectra for the Ni-FeOx and M/Ni-FeOx (M: Li, Na, K, Cs) catalysts.

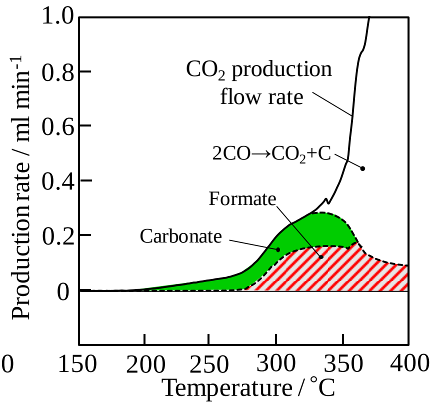

Figure 2. CO-TPR profile of the K/Ni-FeOx structured catalyst.

4. Conclusions

We investigated the role of alkali metal (Li, Na, K, Cs) and alkaline earth metal (Ca, Sr, Ba) on the Ni-FeOx structured catalyst for the WGS reaction. The addition of these promoters improved the WGS performance of the Ni-FeOx structured catalyst. The Cs addition was the most effective for an enhancement of the WGS performance. The XPS spectra showed that an electron was transferred from the alkali species to the active site of Ni. Such effect enhanced an interaction between CO and Ni, which might improve a redox performance of the catalyst.

References

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