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Pre-reduction and K loading effects on noble metal free Co-system catalyst for water gas shift reaction

Water gas shift (WGS) reaction is an important reaction for carbon monoxide removal, and the catalysts for the reaction have been investigated over the past three decades. Although many researches have revealed that noble metals enhance the activity of WGS catalysts, the price of these metals creates concerns. This is why noble metal free catalyst is required for water gas shift reaction.

We examined activity tests with various pre-reduction conditions using K/Co_3O_4. The measurements were made with a Q-Mass (**Model QGA; Hiden Analytical Ltd**.). It is noteworthy that K/Co_3O_4 shows no activity if it is not pre-reduced. Pre-reduction was conducted using H_2 or $CO+H_2$. The K/Co_3O_4 catalyst pre-reduced with syngas ($CO+H_2$) showed high and stable WGS activity. However, K/Co_3O_4 pre-reduced by H_2 showed not high WGS activity. K/Co_3O_4 pre-reduced by syngas ($CO+H_2$) also showed high selectivity to CO_2 and H_2 more than 99%, and carbon deposition was under the detection limit of a temperature programmed oxidation apparatus.

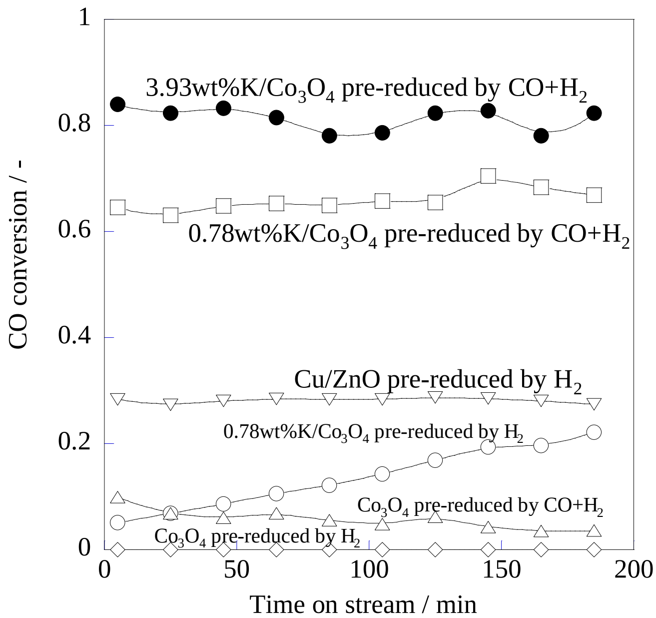

Figure 1. Catalytic activities over various K-loaded catalysts

Then, we investigated the effects of the loading amount of potassium on WGS catalytic activity. In addition to 0.78wt%K/Co_3O_4, we prepared 0.20 wt%, 3.93 wt%, and 5.89wt%K/Co_3O_4 catalysts, and conducted activity tests in the same conditions ($CO+H_2$ was used as pre-reduction gas). 0.20wt%K/Co_3O_4 showed lower activity than those of the others. Apparently, a threshold to the loading amount of potassium exists, but increasing the loading amount to 3.93 wt% improved the CO conversion from about 65% (0.78 wt%K) to >80%. However, the activity of 5.89wt%K/Co_3O_4 was lower than that of 3.93wt%K/Co_3O_4. Therefore, we inferred that the optimum loading amount of potassium for this catalyst to show high WGS activity was 0.78–3.93 wt%K.

XRD measurements were conducted to analyze the structure of the support after reduction by CO, H_2, and $CO+H_2$. After H_2 reduction, all peaks were attributed to Co metal. However, after CO or $CO+H_2$ reduction, several peaks showing Co_2C were observed. The spectra after CO reduction also include some peaks that are attributed to CoO. Therefore, H_2 has too much of a strong reduction property. CO pre-reduction for 3.93wt%K/Co_3O_4 caused the low initial activity. Pre-treatment by syngas is more favorable than pre-treatment by CO. Moreover, to clarify whether CoO shows WGS activity or not, we conducted activation tests using K/CoO without pre-reduction. However, it showed no WGS activity at all. Considering these results, Co_2C is apparently an important active species to proceed with WGS reaction.

To clarify the fine structure of Co, EXAFS measurements were investigated. Co foil was used as a reference sample. The most noticeable peak on Co foil shows that the Co–Co bond is near 0.2 nm. The same peak appeared both for 0.78wt%K/Co_3O_4 and 3.93wt%K/Co_3O_4. The peak, however, was stronger with lower loading amount of K. This trend is the same as that of results shown in XPS spectra for Co2p3. When the loading amount of K is lower, the bulk structure is also reduced to Co metal, and carbide formation is difficult.

In conclusion, we investigated the activity of a noble metal free Co-system catalyst for a water gas shift (WGS) reaction. K/Co_3O_4 catalyst shows no WGS activity without pre-treatment, but it shows high stable activity after pre-reduction with syngas for 200 min. Pre-reduction by syngas can form Co_2C as active sites more effectively than either CO or H_2 reduction. Potassium loading stabilizes the catalyst structure in a reduction atmosphere, and has an electron-donating effect. Loading potassium suppresses excess reduction of Co-oxide to metallic Co.

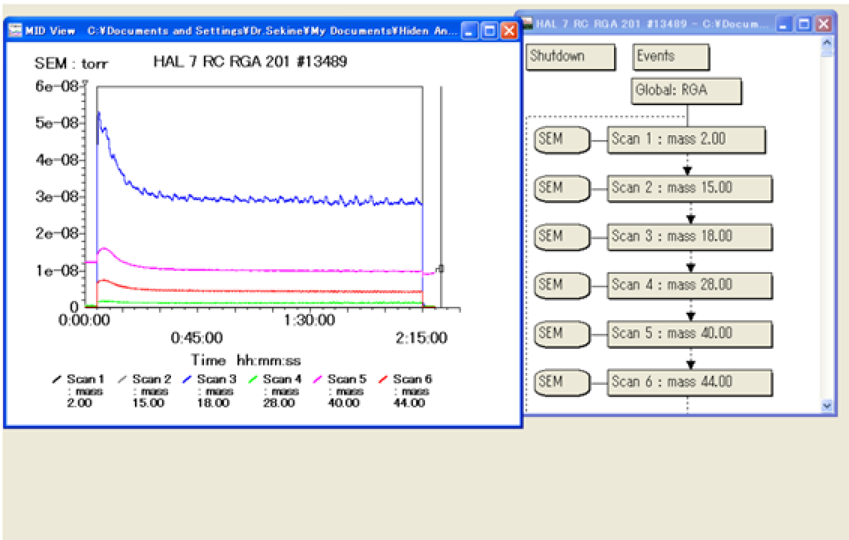

Figure 2. Analyses images using Q-Mass

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