

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/Co₃O₄. The measurements were made with a Q-Mass (**Model QGA; Hidden Analytical Ltd.**). It is noteworthy that K/Co₃O₄ shows no activity if it is not pre-reduced. Pre-reduction was conducted using H₂ or CO+H₂. The K/Co₃O₄ catalyst pre-reduced with syngas (CO+H₂) showed high and stable WGS activity. However, K/Co₃O₄ pre-reduced by H₂ showed not high WGS activity. K/Co₃O₄ pre-reduced by syngas (CO+H₂) also showed high selectivity to CO₂ and H₂ more than 99%, and carbon deposition was under the detection limit of a temperature programmed oxidation apparatus.

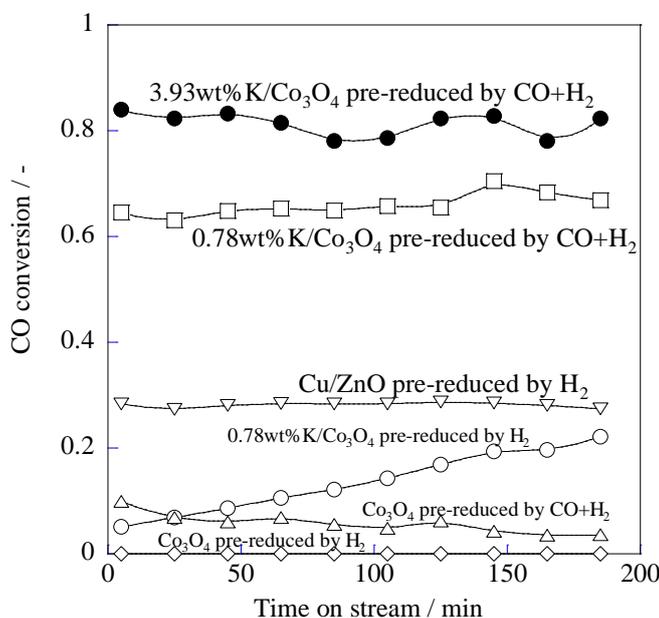


Figure 1. Catalytic activities over various K-loaded catalysts

Then, we investigated the effects of the loading amount of potassium on WGS catalytic activity. In addition to 0.78wt%K/Co₃O₄, we prepared 0.20 wt%, 3.93 wt%, and 5.89wt%K/Co₃O₄ catalysts, and conducted activity tests in the same conditions (CO+H₂ was used as pre-reduction gas). 0.20wt%K/Co₃O₄ 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/Co₃O₄ was lower than that of 3.93wt%K/Co₃O₄. 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, H₂, and CO+H₂. After H₂ reduction, all peaks were attributed to Co metal. However, after CO or CO+H₂ reduction, several peaks showing Co₂C were observed. The spectra after CO reduction also include some peaks that are attributed to CoO. Therefore, H₂ has too much of a strong reduction

property. CO pre-reduction for 3.93wt%K/Co₃O₄ 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, Co₂C 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/Co₃O₄ and 3.93wt%K/Co₃O₄. 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/Co₃O₄ 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 Co₂C as active sites more effectively than either CO or H₂ 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.

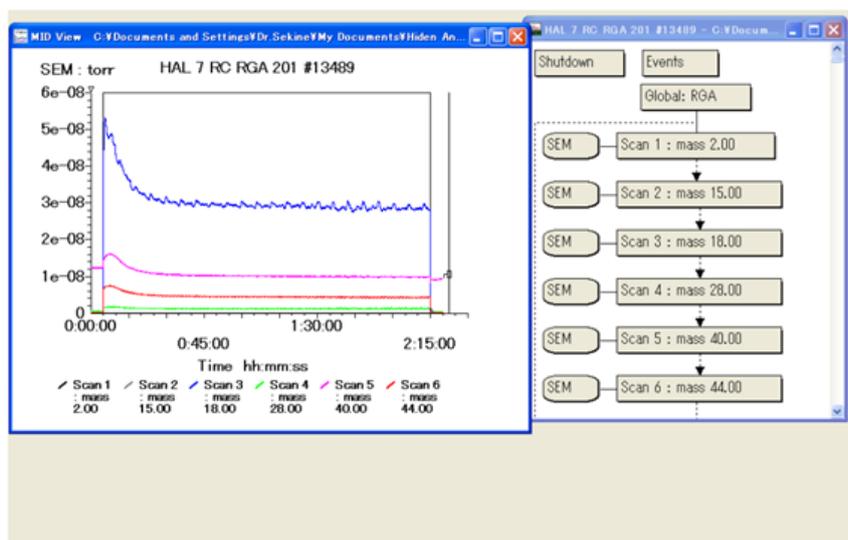


Figure 2. Analyses images using Q-Mass

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Paper Reference:

T. Majima, E. Kono, S. Ogo, Y. Sekine (2016) "Pre-reduction and K loading effects on noble metal free Co-system catalyst for water gas shift reaction", *Applied Catalysis A: General* **523**, 92-96

Hidden Product:

[QGA](#)