Sulfur deactivation of high-temperature water-gas shift catalysts

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Introduction

Hydrogen production has been the focus of increased interest due to its promise for providing the absolute clean fuel and its potential use in fuel cells. Hydrogen production from coal has attracted great attention with the current energy demands. The water-gas shift (WGS) reaction is of central significance to concentrate hydrogen from coal derived synthesis gas. Development of Fe-Cr catalysts to improve their activity and stability has been pursued in the last two decades. However, this formulation is not commercially viable for use in coal-based fuel processors due to its sensitivity to sulfur poisoning. The commercial high temperature Fe-Cr catalyst deactivates in H_2S or COS at concentrations above 50 ppm [1]. Understanding the sulfur deactivation of high temperature water-gas shift catalysts will play an important role in designing sulfur tolerant catalysts for hydrogen from coal. Research on deactivation mechanism for WGS catalysts in the presence of sulfur received little attention in literature.

Materials and Methods

Catalyst precursors were iron (III) acetylacetonate $(C_5H_8O_2)_3Fe$, aluminum nitrate $(Al(NO_3)_3.9H_2O)$, copper nitrate $(Cu(NO_3)_2.3H_2O)$. All precursors are purchased from Aldrich. Ethanol (200 proof, Aldrich) was used as the organic solvent. Initially, iron (III) acetylacetonate was dissolved in ethanol at 60 °C. The aqueous solutions of aluminum and copper nitrates were added dropwise into the iron (III) acetylacetonate-ethanol mixture. After this step, the gelation pH value was adjusted with a diluted 0.5M NaOH solution. Catalysts were aged under continuous stirring at 60 ºC for 30 min after a desired pH value was reached. This was followed by a room temperature aging for another 30 min. Then a filtration system was used to wash the catalysts several times to remove Na+ ions brought in during pH adjustment. The filter cake formed was dried overnight in an oven at 110 ºC. Dry samples were ground to fine powder and were calcined under air at 450 ºC (ramp rate = 5.0 ºC /min) for 4 h.

Reaction experiments were performed using a reaction system described in a previous publication [2].

X-ray photoelectron spectroscopy analysis (XPS) was performed using an AXIS Ultra XPS spectrometer, operated at 13 kV and 10 mA with Al Kα radiation (1486.6 eV). Reduced samples were treated with simulated clean coal gas (10% CO, 5% CO_2, 7.5% H_2, 10% H_2O and 67.5% N_2) at 350 ºC for 2 h. Sulfur poisoned samples are obtained by using the same catalysts under different sulfur concentrations at 400 ºC. All samples are transferred to the XPS chamber using an inert-atmosphere transfer chamber without exposing them to the atmosphere. All binding energies were referenced to C 1s binding energy of 284.5 eV.

Results and Discussion

From reaction testing, Fe-Al-Cu catalyst prepared by sol-gel technique is highly active in WGS reaction when there is no sulfur present in the feed. With sulfur, the activity decreased to different extents depending on the composition. The deactivation is closely related to interaction between H_2S and the catalyst. Deactivation mechanisms have been investigated by examining the changes taking place on the sulfur-poisoned catalysts through temperature-programmed reduction, temperature-programmed reaction, in-situ diffuse reflectance infrared Fourier transformed spectroscopy, and X-ray photoelectron spectroscopy. A comparison of the Fe 2p regions of the X-ray photoelectron spectra of freshly reduced samples and sulfur exposed samples is presented in Figure 1. After reduction, Fe species existed as Fe_3O_4 on the surface. If Fe-Al-Cu was exposed to 50 ppm H_2S before reduction, H_2S was found to reduce Fe_2O_3 in the original sample to Fe_3O_4. From S2p region of this sample (result not shown), a sulfide phase was observed. When Fe-Al-Cu was exposed to harsher sulfur environment (1000 ppm H_2S), a clear FeS_2 phase was observed on the surface together with Fe_3O_4 phase. Formation of FeS_2 is closely related to a decline in reaction activity. From other characterization studies, reactant molecules adsorption properties changed as well. In spite of the decline in activity, the sulfur-poisoned catalysts still remained more active compared to commercial Fe-Cr catalysts.

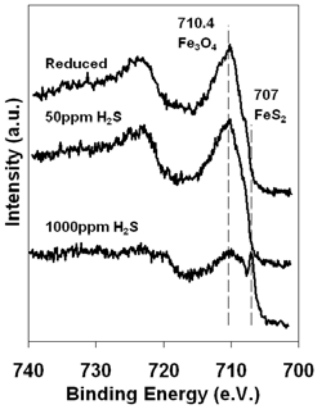

Figure 1 Fe 2p region of Fe-Al-Cu catalysts after different treatment

Significance

Studies on deactivation mechanisms are essential for understanding the factors that govern these processes. The insight to be gained through these studies will help development of sulfur tolerant catalysts for application in hydrogen production from coal.

References

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