Low Temperature Water Gas Shift Reaction over Cu/Zn/Al Catalysts

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Introduction
The water gas shift reaction plays an important role in manufacturing hydrogen, ammonia, methanol and other chemicals [1]. There has recently been renewed interest in studying water gas shift catalysts due to their importance in PEM fuel cell application [2, 3]. Since water-gas-shift is an exothermic reaction, low temperature thermodynamically favors higher CO conversion. For maximum efficiency and economy of operation, many plants contain a high temperature stage (350 - 400 °C) and a low temperature stage (180 - 240 °C). The high temperature reactor converts bulk carbon monoxide from ~15% to ~3% and the low temperature unit further reduces CO level to less than 0.4%. Although Cu-based catalysts have been used as commercial low temperature shift (LTS) catalysts since the 1960's, controversy remains in literature in terms of oxidation state of Cu, the role of ZnO, the active site for the reaction and the role of the support (Al_2O_3) [4]. Our current investigation is aimed to develop an understanding of the Cu/Zn system under LTS reaction conditions. By understanding the fundamental chemistry of the catalyst system, significant improvement in activity has been made.

Experimental
Catalysts were precipitated by various techniques. A typical method involves co-precipitation of respective metal nitrates with soda ash at a constant pH. The obtained precipitate was aged and washed to remove sodium. After drying, the resulting precursors were analyzed by XRD and TGA/DSC coupled with MS. In-situ XRD was performed on precursors by heating in air at a rate of 10 °C/min, which identifies the disappearance of hydroxy-carbonate precursors and simultaneous evolution of crystalline oxides as a function of temperature. TPR experiments were performed at a heating rate of 10 °C/min up to 500 °C in a 20 sccm flow of 5%H_2/Ar stream. Cu surface area was measured on reduced catalyst by pulsing N_2O at room temperature according to the following equation.

$$N_2O + 2\,Cu° \rightarrow N_2 + Cu_2O$$
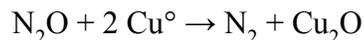
The amount of N_2 formed was used to compute the copper surface area, assuming that the number of copper atoms present in a square meter is about 1.41×10^{19} [5]. Water gas shift reaction was performed in a ¼"quartz reactor at inlet CO concentration of 2%. Space velocity was chosen so that CO conversion is far away from equilibrium. Reaction temperature was varied from 170 to 230 °C.

Results and Discussions

Figure 1 shows LTS activity as a function of Cu surface area for six Cu/Zn/Al catalysts with similar composition but various preparation techniques. Their LTS activity was obtained at a reaction temperature of 170 °C with 2% CO and 33% steam. A catalyst was first reduced in a 2% H_2/N_2 stream at 204 °C. The Cu surface area was then measured, and followed by LTS reaction. The highest LTS activity was obtained on Cat.A and Cat.D. However, their Cu surface area differs almost 100% (13.8 vs. 25.4 m^2/g). On the other hand, Cat.B and Cat.C, both have the lowest Cu surface area at ~12 m^2/g, exhibit much higher CO conversion activity than Cat.E (22.3 m^2/g) and Cat.F (19.9 m^2/g). There appears no relationship between metallic Cu surface area and water gas shift reaction activity.

The Cu S.A. and activity data suggest that partially oxidized Cu is responsible for activity. Although the nature of such partially oxidized Cu is still under investigation, maximizing the amount of active sites can guide the development of an LTS catalyst exhibiting much higher activity than any known Cu/Zn/Al LTS catalyst. The function of ZnO and Al_2O_3 to facilitate the water gas shift reaction will be discussed.
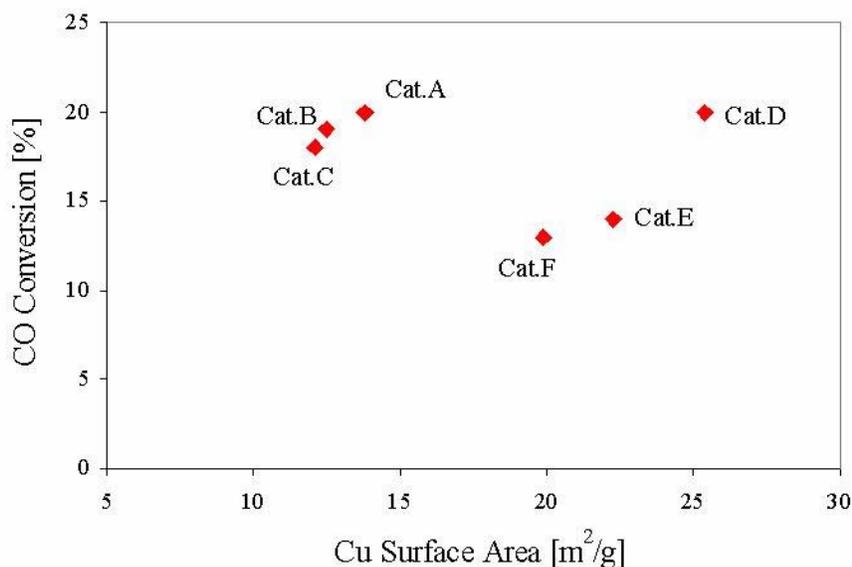

Figure 1. Correlation between CO conversion and Cu S.A.

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