The Insight of Active Sites: Reduced and Sulfided CoMo Catalysts

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Introduction

Technology for syngas production from gasification of crude oil or coal and from biomass pyrolysis is a continually improving process. One particular operation of every commercial process that has received a great deal of attention is the Water Gas Shift (WGS) conversion. Catalyst used in this process is required to be physically rugged and highly active in sulfur containing or sour gas stream. Molybdenum-based catalysts are exclusively used in industrial processes [1]. Molybdenum-based catalysts are also primary catalysts for hydro-treating processes. It is well-known that Mo-based catalysts need to be sulfide as effective catalysts. It is also proposed that reduced Mo-based catalysts might exhibit a behavior analogous to that of sulfide form [2-3]. However, no literature can be found to study reduced Mo-based catalyst for WGS reaction. In this communication, WGS reaction over reduced and sulfided CoMo/Al$_2$O$_3$ catalyst was investigated. Effect of sulfur in feed was tested. Mechanisms and active sites were discussed for WGS and hydro-treating processes.

Materials and Methods

CoMo-based catalysts (oxide form) were prepared by impregnation with cobalt nitrate and ammonium heptamolybdate aqueous solutions. Reduced and sulfided catalysts were made by in-situ reducing or sulfiding oxide form at elevated temperature. Kinetic tests were performed at 200 psig, temperatures up to 450°C, and steam/gas molar ratio of 1.0. Inlet gas consisted of a mixture of CO, CO$_2$, N$_2$, H$_2$ with or without H$_2$S. The catalysts were characterized with techniques of XRD, XPS, Temperature-Programmed-Reaction (H$_2$O, CO).

Results and Discussion

Figure-1 shows that both reduced and sulfide CoMo/Al$_2$O$_3$ catalysts are active for WGS reaction. However, reduced catalyst has lower activity than sulfide catalyst. The presence of H$_2$S in the syngas feed leaded to an increase in water gas shift activity. The results are contrary to the finding from hydrogenation of aldehyde to alcohol [4], which indicated higher activity over reduced catalyst and H$_2$S in feed suppressed hydrogenation activity.

XPS study showed that majority of Mo species exists as Mo$^{4+}$ over both reduced and sulfide catalysts. Upon exposed to H$_2$S under WGS reaction conditions, reduced catalyst was converted to oxi-sulfide species by sulfur-oxygen exchange on active phase surface. Temperature–programming-reaction of H$_2$O and CO showed that WGS reaction proceeds through redox mechanism (equation I and II) over both reduced and sulfide catalysts, which is different from hydrogenation of aldehyde (equation III and IV). In WGS reaction, surface reaction of CO with activated O (equation II) or CO$_2$ desorption were assumed to be rate-determining step. When oxygen (site A) is replaced by sulfur (site B or C) on the active surface, bonding of activated O and Mo site (from equation I) is weakened due to less electronegative of sulfur than oxygen, which benefits formation of CO$_2$ (equation II), the rate determining step. Contrarily, the weaker bonding of adsorbed O in the aldehyde molecule and Mo site weakens activating O=C double bond that impairs hydrogenation reaction, the rate determining step (equation IV).

Significance

Active sites of reduced and sulfide CoMo catalysts are the same for WGS and hydro-treating reactions. However, reaction mechanisms are different. Therefore, the presence of sulfur in the feed affects reaction results differently.

References