

Optimization of CoMo-based Catalysts in the Sour Gas Shift Process

Justin X. Wang, Jason Spencer, Jamie Butler, Yeping Cai*
 Sud-Chemie Inc., 1600 W. Hill St., Louisville, KY 40210 USA
 *yeping.cai@sud-chemie.com

Introduction

Synthesis gas 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 Water Gas Shift (WGS) conversion. Catalysts used in this process are required to be physically rugged and highly active in sulfur containing, that is, sour gas stream. Cobalt-Molybdenum-based catalysts are exclusively used in industrial processes [1]. Conditions of three processes, i.e. pre-sulfidation, reaction and catalyst regeneration, are shown to influence catalytic performance significantly. It is well known that the active sites of CoMo-based catalysts are generated by pre-sulfidation. In the Sour Gas Shift (SGS) reaction, the presence of sulfur in the gas stream is required to maintain catalytic performance [2,3,4]. The deactivated catalyst can be regenerated by oxidation followed by re-sulfidation. Few investigations can be found in literature for sulfidation conditions, let alone for catalyst regeneration conditions. Literature citations determining the minimum amount of sulfur required to maintain catalytic performance in the SGS reaction are also rare. In this communication, pre-sulfidation conditions are optimized for the SGS reaction. Theoretical calculations and experimental verification are carried out to determine the effect of sulfur content on catalytic performance of oxide and sulfided CoMo-based catalysts. Performance of deactivated catalyst is shown to be fully restored by balancing reduction and sulfidation reaction rates.

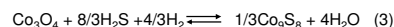
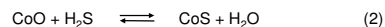
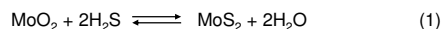
Materials and Methods

CoMo-based catalysts (oxide form) were prepared by co-impregnation with cobalt nitrate and ammonium heptamolybdate aqueous solutions. The oxide CoMo-based samples were sulfided with H₂S in H₂/N₂ at elevated temperatures. Kinetic tests were performed at pressures up to 200 psig, temperatures up to 510°C, and steam/carbon molar ratios ranging from 0.3 to 1.2. Inlet gas consisted of a mixture of CO, CO₂, N₂, H₂ and H₂S. The H₂S concentration was varied from 0 to 2000ppm. The catalysts were characterized with techniques of X-Ray diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), Temperature-Programmed-Reduction (TPR), BET surface area and pore volume measurement.

Results and Discussion

Pre-sulfidation: The current study shows that pre-sulfidation conditions have a strong impact on catalytic performance. With optimized sulfidation conditions for the SGS reaction, CoMo-based catalysts exhibit significantly higher activity than those sulfided at conventional conditions. This finding can be rationalized by understanding the competitive reactions of reduction and sulfidation.

Sulfur species required in the gas stream: The minimum amount of H₂S required in the SGS reaction is estimated with thermodynamic calculation of the following equations:



The relationship of $\ln K_p$ with temperature for the above Eq. 1 and Eqs. (2) and (3), the latter are related to the Co species, is illustrated in Figure 1.

At a specified reaction temperature, the minimum amount of sulfur required to maintain the sulfided states of Mo and Co can be calculated with the known amount of steam in the system.

Below the minimum amount of sulfur present in the stream, the SGS activity decreases with time-on-stream accompanied with S leaching which is detected at the outlet of the reactor. XPS studies reveal that oxysulfide species are generated by oxygen-sulfur exchange on the catalyst surface.

Catalyst Regeneration: In most cases of industrial regeneration/resulfidation process, catalyst performance can not be fully restored. Our study reveals that the performance can be fully restored by controlling the oxidation process and optimizing the two competitive reactions of reduction and sulfidation.

Significance

Many insights are provided to optimize process conditions to achieve higher activity of the CoMo-based catalyst in the SGS application.

References

1. K. Kochloefl, in "Handbook of Heterogeneous Catalysis" (ed. G. Ertl, H. Knozinger, J. Weitkamp), Wiley-VCH, 1997, p1831.
2. P. Hou, D. Meeker and H. Wise, J. Catal., 80 (1983) 280.
3. A.A. Andreev, V.J. Kafedjiysky and R.M. Edreva-Kardjieva, Appl. Catal. A, 179 (1999) 223.
4. M. Laniecki, M. Malecka-Grycz and F. Domka, Appl. Catal. A, 196 (2000) 293.

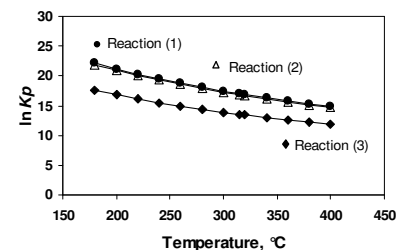


Figure 1 Function of $\ln K_p$ vs. Temperature