Real Feed Studies Of Unsupported TMS (Transition Metal Sulfide) Catalytic Material

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Abstract— In this report we describe the structure and composition of TMS (Transition Metal Sulfide) catalysts that have been stabilized in an HDS (HydroDeSulfurization) environment. Catalytic activity is predicted through the use of commercial software which develops a fundamental understanding of the catalytic materials. Catalytic activity is then systematically measured using the model reaction HDS of DBT (DiBenzoThiophene) under moderate pressure and temperature. The DBT results are then extended to Real Petroleum Feeds. New TMS catalysts are developed through theory, synthesis, characterization and then the use of model reactions as described above. The use the HDS of DBT as our model reaction predicts accurately behavior in real petroleum feeds and rapidly screens catalysts for real feed tests. Behavior in real feeds is required to move closer to commercialization. In the case of the TMS we have three different exciting real feed results to report.

Keywords—Transition Metal Sulphide (TMS) Catalysts, HydroDeSulfurization (HDS), and Commercialization.

I. INTRODUCTION

Our recent studies have provided the structure and composition of TMS (Transition Metal Sulfide) catalysts that have been stabilized in an HDS (HydroDeSulfurization) environment [1]. The recent development of commercial software able to determine or predict catalytic activity, has led to commercialization and potential commercialization of the TMS catalytic materials as described in reference [2]. Additionally, we have developed a fundamental understanding of the catalytic materials as described in reference [3]. This progress has led to outstanding activity improvements using the model reaction HDS of DBT (DiBenzoThiophene) under moderate pressure and temperature (450 psi hydrogen, 350ºC) see Fig 1. In this report we extend the DBT results to Real Petroleum Feeds. New TMS catalysts are developed through theory, synthesis, characterization and then

the use of model reactions as described above. The use the HDS of DBT as our model reaction over the years has predicted accurately behavior in real petroleum feeds and rapidly screens catalysts for real feed tests. Behavior in real feeds is required to move closer to commercialization. In the case of the TMS, we have three different exciting real feed results and our catalyst are being commercialized.
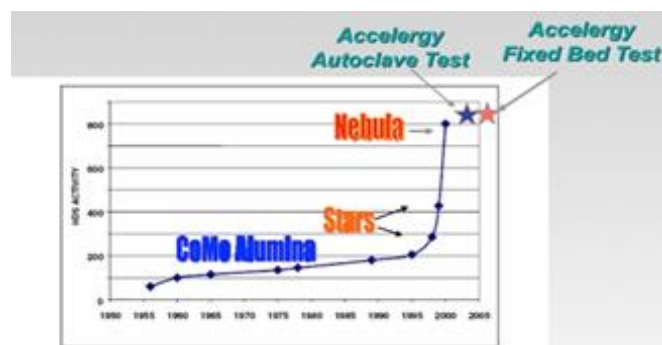

Fig 1. Development of HDS Catalysts with time.

II. CATALYST SYNTHESIS

All catalysts described below where prepared using the hydrothermal technique as described in U.S. Patent 7,223,713 [4]. The process begins with the synthesis of the ammonium thiomolybdate precursor (ATM).

Synthesis of B1 Catalyst by hydrothermal method: 25 grams of heptamolybdate are dissolved in 120 ml of deionized water, then 200 ml of $(NH_4)_2S$ are added. This mix is kept under stirring for 30 min at 55ºC, and then it has to be refrigerated in the original solution in order to crystallize the ATM. The crystals in the original solution are always refrigerated. The process continues reacting water solutions of ATM and cobalt chloride (CoC_{l2} $6H_2O$). Weigh the desired amount of ATM and disperse it in 10 ml of water per every gram of ATM used. Continue preparing cobalt chloride (CoC_{l2} $6H_2O$) solution, use 0.44g per every gram of ATM used. Finish with reaction between the two solutions, forming a dense black solution of $Co_{0.5}/[(NH_4)_2MoS_4]$ according to the equation below:

$$2(NH_4)_2MoS_4 + 0.5CoCl_2 \rightarrow Co_{0.5}/[(NH_4)_2MoS_4]_2 + 2NH_4Cl \ (1)$$
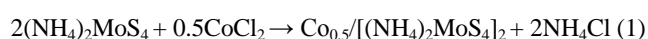
The resulting black solution is placed into a borosilicate liner, then introduce the liner into the vessel of the PARR reactor. The decomposition reaction is run under the following conditions: 300ºC and 1300psi during two hours. The time starts to count once the temperature has been reached. Once the reaction is finished, the reactor is cooled down to below 70ºC, the reactor can be opened and the catalyst recovered and washed with isopropanol, then let it be dried at room temperature for one day.

Synthesis of B3 Catalyst by hydrothermal method: The B3 catalyst follows the first two steps for B1 described above. In the B3 process the complex ATM/EDA

(AmmoniumThiomolybdate/Ethylenediamine)

precursor is used: One gram of ATM requires 2ml of Ethylenediamine, mixed into a paste and then heated at 400ºC until a powder is formed. The ATM/EDA complex is then mixed with cobalt nitrate $(CoNO_3)^2$. Weigh the desired amount of ATM /EDA and disperse it in 10 ml of water per every gram of ATM/EDA used. Continue by preparing an aqueous cobalt nitrate $(CoNO_3)^2$ solution; use 0.55g per every gram of ATM/EDA used. The reaction between these two solutions, forms a dense black solution of $Co_{.05}/[(NH_4)_2MoS_4]_2$.

$$2(NH_4)_2MoS_4 + Co_{0.5}(NO_3) \rightarrow Co_{.5}/[(NH_4)_2MoS_4]_2 + NH_4NO + NH_3 + \frac{1}{2}H2 \qquad (2)$$
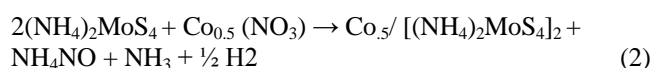
Synthesis of B5 Catalyst by hydrothermal method: The process continues reacting water solutions of ATM and cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O)$. Weigh the desired amount of ATM and disperse it in 10 ml of water per every gram of ATM used. Continue preparing cobalt nitrate solution, use 0.786g (in minimum amount of water) per every gram of ATM used. Finish with reaction between the two solutions, forming a dense black solution of Co $0.7/[(NH_4)_2MoS_4]_2$ according to the equation below:

$$2(NH_4)_2MoS_4 + Co(NO_3)_2 \rightarrow Co_{0.7}/[(NH_4)_2MoS_4]_2 + 2NH_4NO_3 \qquad (3)$$
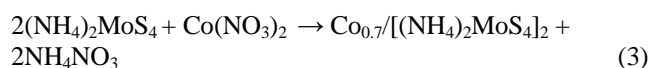
III. CATALYTIC TESTS

Accelergy Corporation Tests: Catalysts were tested using a refinery diesel hydrotreater feed under various conditions. The feed blend contained 35vol% LCCO (Light Catalytic Cycle Oil) from a FCC (Fluid Catalytic Cracker) Unit (increase of 2 CN for 200 scf/bbl). Increasing percentages of a sweet syncrude based straight run diesel were tested at a constant LCCO percentage. Figure 2 shows the results of two catalysts run under identical conditions: Al2O3 Supported Commercial KF-757 and Unsupported Catalyst (Brenda–described above). Brenda was run at two LHSV (Liquid Hourly Space Velocities): 2.8h[-1] and 2.3[-1]. The unsupported catalyst showed 2.0 to 2.8 times the activity of the commercial catalysts, validating earlier autoclave screening tests. An ultra-low 5 ppm sulfur target was met and two temperatures and

multiple feeds where explored. Additionally, a 40+ day accelerated deactivation test was performed.
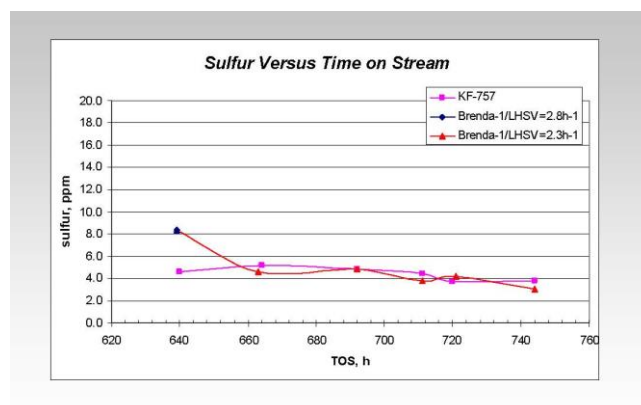

Fig 2. LCCO Catalyst Results

IV. OXFORD CATALYSTS TESTS

Three Unsupported Catalysts (B1A, B1A3 and B1A5–described above) where tested against an Al_2O_3 Supported Commercial KF-767. The results for sulfur removal and nitrogen removal are shown in Table 1. The results for B1A5 are exceptional against the Commercial Catalyst. B1A5 was tested a particle size of 0.5 to 1.0 mm. This particle size is standard in these tests.

Sample	Residual S (wppm)	Residual N (wppm)
B1A	38	0.2
B1A3	118	11.5
B1A5	5	0.3
KF767	123	4.2

a. Oxford Catalyst Tests

REFERENCES

For papers published in translation journals, please give the English citation first, followed by the original foreign-language citation [6].

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