

PILOT PLANT STUDY OF THE PERFORMANCE OF AN INDUSTRIAL $\text{MoO}_3/\text{Al}_2\text{O}_3$ CATALYST IN HYDROTREATMENT OF KUWAIT ATMOSPHERIC RESIDUE

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INTRODUCTION

Graded catalyst systems with two or more types of catalysts are used in recent years in multiple reactor fixed-bed residue hydrotreaters to achieve demetallation (HDM), desulfurization (HDS) and denitrogenation (HDN) together with conversion of residues to distillates at desired levels(1,2). Rapid catalyst deactivation is reduced and the on-stream efficiency is increased with such multiple catalyst systems. Since the overall performance of the process with regard to various conversions and catalyst life is strongly tied up with the performance of the catalysts in different reactors, information on the activity, selectivity and deactivation rate of individual catalysts is highly desirable for optimizing reactor loading with such multiple catalyst systems. In the present work, we have examined the performance of an industrial HDM catalyst containing MoO_3 alone on alumina in hydrotreating Kuwait atmospheric residue in a fixed-bed pilot plant. Systematic studies were conducted to assess the activity and selectivity of the catalyst for various reactions such as HDM, HDS, HDN, asphaltenes conversion and hydroconversion of the residual oil feed to distillates. The reaction kinetics in residual oil hydrotreating was also investigated as part of the study.

EXPERIMENTAL

The hydrotreating experiments were conducted in a fixed-bed reactor unit (manufactured by Vinci Technologies) using Kuwait atmospheric residue as feed. The feedstock contained 4.3 wt% sulfur, 69 wtppm vanadium, 22 wtppm nickel, 0.31 wt% nitrogen, 3.6 wt% asphaltenes and 12.2 wt% CCR. A commercial HDM catalyst containing 4.3 wt% MoO_3 on alumina (surface area = 200 m^2/g ; pore volume = 0.67 ml/g) was used in all experiments. 50 ml catalyst charge diluted with an equal amount of carborundum was used for each run. The catalyst was presulfided using straight run gas oil containing 3 wt% dimethyl disulfide (DMDS) by a standard procedure before injecting the feed. The run conditions used for different studies are summarized in Table 1. During the course of each run, product samples were collected every 12 hours and analyzed for sulfur, metals (V and Ni), nitrogen, asphaltenes, CCR, viscosity, density and distillates yield.

Table 1. Run Conditions for Temperature and LHSV Effect Studies

Process Parameter	Range	
	Temperature Effect Study	LHSV Effect Study
Temperature ($^{\circ}\text{C}$)	360 - 420	380
Pressure (bar)	120	120
LHSV (h^{-1})	1	0.5 - 4.0
H_2/Oil Ratio (ml/ml)	570	570
Time-on-stream(h)	120	120

RESULTS AND DISCUSSION

In the first set of experiments reactor temperatures were varied in the range 380 – 420 °C to investigate the performance of the HDM catalyst in promoting various reactions such as HDM, HDS, HDN, asphaltenes conversion, CCR reduction and hydrocracking of residues to distillates as well as to examine the deactivation behavior of the catalyst at different temperatures.

In Fig. 1 the desulfurization data for different temperatures are plotted as a function of time-on-stream. It is seen that the extent of desulfurization is very low (around 20%) at 360 °C and increases substantially with increasing temperature reaching about 65% at 420 °C. An interesting observation that can be made in the results presented in Fig. 1 is a gradual increase in the degree of HDS with increasing time-on-stream. The HDS activity is usually expected to decrease with time during the early period of operation due to rapid initial deactivation of the catalyst. But in the present study the HDS activity shows an increase with increasing run time, probably because of the accelerating effect of nickel deposited on the catalyst surface.

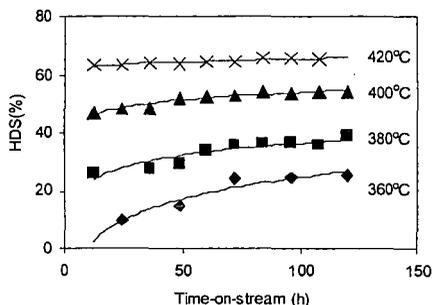


Fig. 1 Sulfur removal vs time-on-stream at different reactor temperatures

The data presented in Fig. 2, which compares the catalysts activity for various reactions such as HDS, HDV, HDNi, HDN and asphaltenes conversion that occur during residual oil hydrotreating shows the following order:



The low activity catalyst containing unsupported MoS_2 on alumina with large pores used in the present study appears to favor HDM and asphaltenes cracking reactions which are more diffusion limited than other reactions. The higher activity of the catalyst for HDM and asphaltenes conversion reactions can, thus, be attributed to the large pores in the catalyst which facilitates the diffusion of large metal containing molecules and asphaltenes into the catalyst pellet. The enhanced reactivity of vanadium relative to nickel may be attributed to a combination of factors resulting from the chemistry of oxygen ligand in vanadyl (VO^{2+}) group(3).

In the second set of experiments, the liquid hourly space velocity (LHSV) of the feed was varied in order to investigate the kinetics of various reactions in residual oil hydrotreating. The kinetics of petroleum residue hydrotreating is highly complicated due to the complex composition of the residues which includes high concentrations of asphaltenes, sulfur, nitrogen and metals (V and Ni). The low diffusivities and reactivities for these large molecular species make the kinetics of the process further complicated.

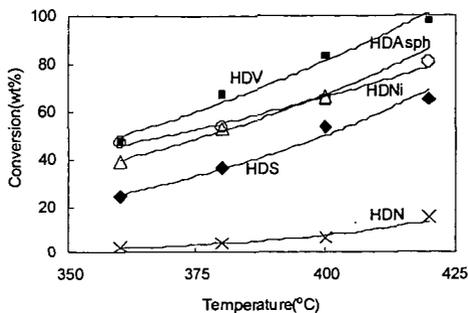


Fig. 2 Comparison of catalyst's activity for various reactions in hydrotreating of Kuwait atmospheric residue

In the present studies, the conversion data generated for various reactions at different space velocities were used to determine the reaction order for different reactions such as HDS, HDV, HDNi and asphaltenes cracking that occur during residual oil hydrotreating. The results presented in Fig. 3 show that HDS and asphaltenes cracking reactions obey second order kinetics. The activation energies calculated from the Arrhenius plots in Fig. 4 are 26.1 kcal/mole for HDS and 23.6 kcal/mole for asphaltenes eracking reactions.

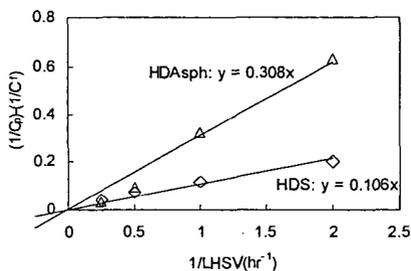


Fig. 3 Second-order plot of kinetic data for HDS and HDAsph of Kuwait atmospheric residue

The plots of kinetic data for vanadium and nickel removal shown in Figs. 5 indicate that a reaction order of 1.5 gives the best fit in correlating kinetic data for HDM reactions. Demetallation kinetic orders varying from 1.0 to 2.0 have been reported by different workers(3). In the case of model compound demetallation studies with pure metalloporphyrins, first order kinetics have been reported for both vanadium and nickel removal. In the present work a reaction order of 1.5 is observed for vanadium removal from Kuwait atmospheric residue. Just as in hydrodesulfurization, several first order reactions with different rates can occur due to the presence of more than one class of metal compounds in the residual oil. This can lead to an apparent order greater than unity.

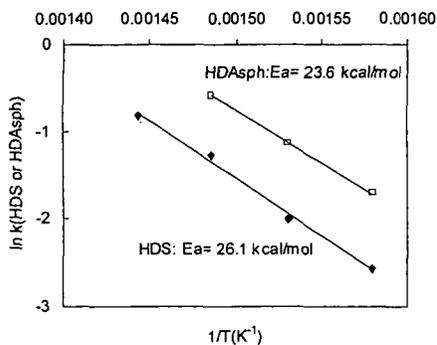


Fig. 4 Arrhenius plot for HDS and HDA sph

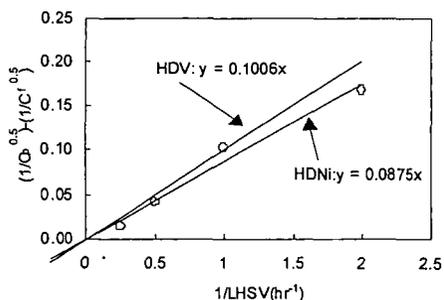


Fig. 5 1.5-order plot of kinetic data HDV and HDNi of Kuwait atmospheric residue

The Arrhenius plots of $\ln k$ vs $1/T$ for both vanadium and nickel removal reactions (Fig. 6) show a sharp increase in the reaction rate at temperatures above 400 °C with two different activation energy values, namely 27.7 and 62.2 kcal/mole for vanadium and 12.5 and 28.9 kcal/mole for nickel.

Apparent activation energy values reported in literature for vanadium removal from residues by HDM reaction range from 10 to 38 kcal/mole depending on the reaction order(3). The discrepancies observed in the activation energy values may reflect differences in crude source resulting in different reactivities of metal containing species and different rate limiting steps. The sharp increase in activation energy for HDM reactions at temperatures above 400 °C is considered to be due to a combination of factors such as improved diffusion and change in reaction mechanism.

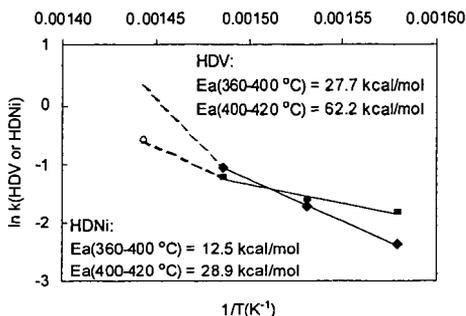


Fig. 6 Arrhenius plots for HDV and HDNi

CONCLUSIONS

Pilot plant studies were conducted to investigate the activity and selectivity of an industrial HDM catalyst for various reactions such as HDS, HDM, HDN, asphaltenes conversion and hydroconversion of residual oil feed to distillates as well as to examine the reaction kinetics in residual oil hydrotreating. The catalyst showed a remarkably high activity for HDM and asphaltenes cracking reactions and a moderate activity for HDS. Its activity for HDN, hydrogenation and hydroconversion reactions was very low. HDS activity increased with time on stream probably because of the promotional effect of nickel deposited on the catalyst surface. Kinetic data analysis showed 2nd order for HDS and asphaltenes cracking and 1.5 order for HDV and HDNi reactions. The apparent activation energies for HDS and asphaltenes cracking reactions were, respectively 26.1 and 23.6 kcal/mole. Arrhenius plots for HDV and HDNi reactions showed a sharp increase of the reaction rate constants at temperatures above 400 °C with two different activation energy values, namely, 27.7 and 62.2 kcal/mole for nickel. The increase in the activation energy of the HDM reactions above 400 °C is considered to be due to a combination of factors such as improved diffusion and change in reaction mechanism.

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