

## KINETIC MODELING OF DEMETALIZATION REACTIONS OF TOPPED ATHABASCA BITUMEN

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### Abstract

Heavy petroleum fractions contain significant amounts of various metals including nickel and vanadium which could act as poisons for catalysts used in downstream processing. These metals can be removed from heavy fractions as metal sulfides deposited on the surface of hydrodemetalization (HDM) catalysts. In this paper a simple kinetic model is developed for HDM of topped Athabasca bitumen. HDM reactions were conducted in a laboratory scale stirred basket reactor using a fresh and a spent catalyst as well as experiments with no catalysts. The experimental data indicated that HDM reactions were first order with respect to the metal concentration and that the rate of vanadium removal was greater than the rate of nickel removal.

*Keywords:* metal removal, bitumen, kinetic modeling, nickel, vanadium

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### 1. Introduction

Residue oil and heavy petroleum fractions contain high molecular weight species which contain highly condensed aromatic structures to which sulfur, nitrogen, oxygen and metals, mainly vanadium and nickel, are bound. Catalytic hydroprocessing is employed to upgrade the quality of such feedstocks by removal of these heteroatoms and metals [1-3]. Common hydroprocessing catalysts are Co-Mo and Ni-Mo on alumina supports [4]. In catalytic hydrodemetalization processes metals present in the feed deposit as metal sulfides on the inner surface of the porous catalysts. These deposits, though not as active as the original catalytic sites, act as a site for further metal deposition [5]. The accumulation of metal containing deposits within the pores of the catalyst over time cause an irreversible catalyst deactivation as the pore mouths are blocked rendering the inner surface inaccessible for diffusion of feed molecules. In the selection of appropriate catalysts for hydroprocessing of heavy petroleum fractions, it is important to consider the diffusion behavior of large metal containing molecules within the catalyst pores whose pore structures are changing with time on stream as a result of metal deposits. The buildup of metal deposits is believed to be the main cause of the decline in catalytic activity after a short initial period of coke deposition [6-8]. Catalyst pore structure plays an important role in the overall lifetime of the catalyst. Catalysts with smaller pores have higher activity but smaller pores are quickly plugged. On the other hand, catalysts with larger pores have lower initial activity but a longer lifetime [2-7]. Optimum pore diameters depend on the type and size of the reacting molecules. For example the optimum pore size for demetalization of nickel is less than that for vanadium. Kinetic studies on HDM reactions have indicated that increasing hydrogen pressure result in an increase in HDM rate until catalyst surface is saturated with hydrogen. Increasing reaction temperature will also result in an increase in HDM rate. Higher temperatures, however, will also enhance coke formation leading to a loss in catalyst activity. First and second order rate laws in terms of metal concentrations have commonly been used to describe the kinetics of HDM reactions for various feedstocks. The differences are due to the amount of sulfur, nitrogen and metal compounds in the feeds as well as the ratio of porphyrin to non-porphyrin metal compounds [9]. In this study, the HDM of topped Athabasca bitumen was investigated in a

laboratory scale stirred basket reactor using a fresh and a spent commercial catalyst as well as thermal reactions in the absence of any catalysts.

## 2. Methods and Materials

The properties of the feed used in this study are presented in Table 1. Experiments were conducted in a stirred basket reactor. The details of the experimental set up and feed and product analyses are given elsewhere [4]. The following conditions were employed for kinetic studies: temperature in the range of 400 to 450°C, pressure of 13.9 MPa, and space time of 0.5 to 2.0 hours. Three sets of experiments were performed using a) fresh catalysts, b) spent catalysts, and c) no catalyst. Nickel and vanadium content of the liquid products for the above sets of experiments at different space times are presented in Table 2 and Table 3.

Table 1 Properties of topped Athabasca bitumen

Distillation cut	wt. %	Distillation cut	
177-343°C	6.98	Sulfur (wt. %)	4.73
343-524°C	38.06	Nitrogen (wt. %)	0.44
524+°C	54.96	Nickel (ppm)	87.2
		Vanadium (ppm)	138.6

Table 2 Reaction conditions and metal contents of liquid products for experiments at 430°C

a) no catalyst				
Run #	1	2	3	4
Space time (h)	0.41	0.58	0.81	1.49
Nickel (ppm)	64.5	57.2	42.0	34.6
Vanadium (ppm)	160.7	131.7	109.0	100.1
b) spent catalyst				
Run #	1	2	3	4
Space time (h)	0.43	0.56	0.95	2.17
Nickel (ppm)	42.9	36.0	29.6	16.0
Vanadium (ppm)	108.0	85.7	66.0	32.7
c) fresh catalyst				
Run #	1	2	3	4
Space time (h)	0.47	0.92	1.02	1.79
Nickel (ppm)	29.9	12.0	8.5	7.2
Vanadium (ppm)	57.0	20.1	20.9	14.4

Table 3 Reaction conditions and metal contents of liquid products for experiments using spent catalysts

Run #	1	2	3	4	5
Temperature (°C)	410	420	430	440	450
Space time (h)	1.02	0.92	0.60	0.78	0.72
Nickel (ppm)	45.1	40.4	29.6	21.2	10.7
Vanadium (ppm)	108.1	93.9	66.0	40.1	18.2

## 3. Results and Discussion

Analysis of the data was performed in terms of the continuous stirred tank reactor (CSTR) design equation:

$$-r_A = \frac{m_0 - m_E}{V} \quad (1)$$

where  $m_0$  and  $m_E$  are the mass flow rate of metal compounds in and out of the reactor,  $V$  is the reactor volume, and  $-r_A$  is the rate of metal removal on a mass basis. A simple power law rate expression for HDM reactions can be presented as follows:

$$-r_A = k C_A^\alpha C_{H_2}^\beta \quad (2)$$

where  $\alpha$  and  $\beta$  are the reaction order with respect to metal concentration and hydrogen, respectively, and  $C_A$  is the metal concentration on a mass basis. Since hydrogen pressure was kept constant for all experiments, a pseudo rate expression can be obtained as follows:

$$-r_A = kC_A^\alpha \tag{3}$$

Combining Equations (2) and (3) would result in the following equation for the case where  $\alpha = 1$ :

$$k = \frac{1}{\tau} \frac{X_A}{1 - X_A} \tag{4} \quad X_A = \frac{C_{A0} - C_A}{C_{A0}} \tag{5}$$

where  $X_A$  is the fractional conversion of metal compounds,  $\tau$  is the space time, and  $C_{A0}$  and  $C_A$  are metal concentration in feed and products, respectively.

For first order kinetics ( $\alpha = 1$ ) a plot of  $(C_{A0}-C_A)/C_A$  versus  $\tau$  should result in a straight line through the origin with slope of  $k$ . Figures 1 and 2 represent first order analysis of the data for nickel and vanadium removal, respectively, for fresh, spent, and no catalyst. In all cases, first order rate expressions were found to adequately represent the observed kinetics. For the spent catalysts, first order rate constants were obtained from experiments at different reaction temperatures and the Arrhenius plot of the rate constants for removal of nickel and vanadium using the spent catalyst is presented in Figure 3. Activation energies for nickel and vanadium removal were found to be 207 and 266 kJ/mol, respectively. Comparison of the reaction rate constants for nickel and vanadium removal at 430°C (Table 4) indicated that the rate constants for removal of vanadium were slightly higher than those for nickel removal in the presence of both fresh and spent catalysts. Without a catalyst, however, the rate constant for nickel removal was greater than that for vanadium removal.

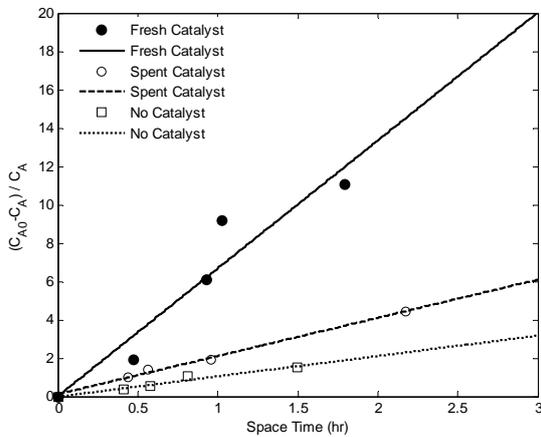


Figure 1: First order analysis of data for nickel removal

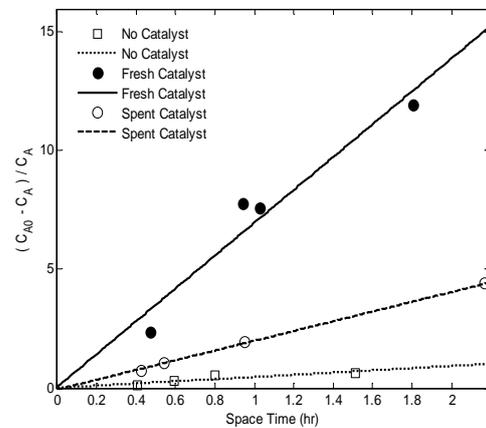


Figure 2: First order analysis of data for vanadium removal

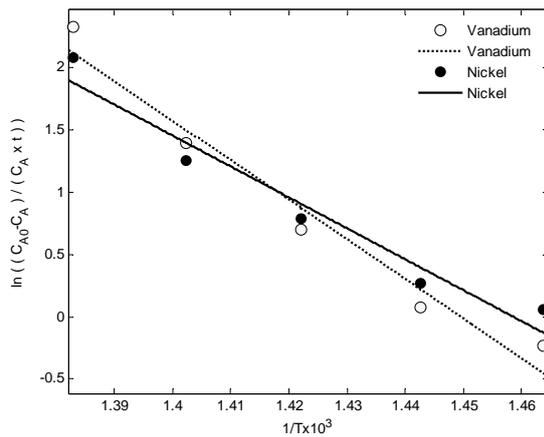


Figure 3: Arrhenius plot of the rate constants for nickel and vanadium removal using spent catalyst

Table 4 Reaction rate constants for nickel and vanadium removal at 430°C

	no catalyst	spent catalyst	fresh catalyst
$k_{\text{nickel}}$	1.1	2.0	6.7
$k_{\text{vanadium}}$	0.7	2.1	7.1

#### 4. Conclusions

Analysis of experimental data indicated that first order kinetics was adequate to represent nickel and vanadium removal in hydroprocessing of topped Athabasca bitumen. The presence of catalysts resulted in slightly enhanced removal rates for vanadium compared with nickel at 430°C and the activation energy was higher for vanadium compared with nickel removal using the spent catalyst.

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