

EVALUATION OF CATALYTIC ROLE OF VANADIUM IN COAL-OIL PROCESSING USING MODEL SYSTEMS

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ABSTRACT

The catalytic activity of vanadium for hydrogenation and heteroatom removal reactions occurring in coal-oil processing was evaluated using model systems. Two-ring aromatics, hydroaromatics and heteroatomic species containing S, N and O were selected as the models representing typical species in coal and oil. Vanadium catalysts generated *in situ* from organic vanadium complexes, such as vanadium acetylacetonate and vanadylacetylacetonate, were activated in the presence of sulfur. Their activity increased as the amount of sulfur present increased. The vanadium catalysts were active for partial saturation of two-ring aromatics to hydroaromatics but far less active for the further saturation to alicyclic compounds. The vanadium catalysts were severely poisoned by organic nitrogen compounds, showing lower activity for N removal than for S and O removal and achieving low amounts of hydrogenation and heteroatom removal of other reactants when nitrogen compounds were present.

INTRODUCTION

Vanadium (V) is one of the most abundant trace metals in petroleum and is more concentrated in the petroleum residuum than in the crude. (1) V sulfides, which are generated from their organic precursors such as V naphthenate, octoate or acetylacetonate in the presence of sulfur, have been used as hydrodesulfurization catalysts in petroleum refining. (2-5) The V indigenous to residuum may form V sulfide and be catalytic under coal-oil processing conditions. These species may influence the reaction pathways and product slates involved in the processing.

The objective of this study is to evaluate the catalytic activity of V sulfide for hydrogenation and heteroatom removal reactions occurring in coprocessing. The activity and selectivity of *in situ* generated V sulfide were evaluated by reacting model hydrocarbon and heteroatomic systems with V precursors, vanadium acetylacetonate and vanadylacetylacetonate, and excess sulfur under coal-oil processing conditions. The activity and selectivity of *in situ* generated V sulfide for the reactions of model compounds were also compared to those of a Mo sulfide catalyst generated *in situ* from Mo naphthenate and sulfur.

EXPERIMENTAL

Chemicals

The model reactants used were naphthalene (99%), indan (97%), indene (99%), benzothiophene (97%), o-cresol (99%), benzofuran (99.5%), quinoline (99%) and indole (99%). n-Hexadecane (99%) was used as a solvent. All of these chemicals were obtained from Aldrich. The V precursors were vanadium(III) acetylacetonate (VAcAc) and vanadyl(IV)acetylacetonate (VOAcAc). VAcAc was obtained from Shepherd Chemical and Aldrich, and VOAcAc was obtained from Aldrich.

Reactions and Analyses

Hydrogenation reactions were conducted in 20 cm³ batch tubing bomb microreactors. Four grams of hexadecane solution containing 2 wt% naphthalene and/or 1 wt% of

each of other reactants were charged to the reactor. The V precursor was introduced at a level of 2850 to 2950 ppm V while always keeping a constant weight ratio of V to reactant. Excess elemental sulfur, 0.034 g S which was three times the stoichiometric amount of sulfur to form V_2S_3 from V precursors, was added to the reaction. Prior to the reaction, 1250 psig H_2 was introduced at ambient temperature. The reactions were conducted at 380°C for 30 minutes with horizontal agitation at 550 cpm. The liquid products were analyzed by gas chromatography using a 30 m fused silica DB-5 column (J & W Scientific) and FID detection with p-xylene as the internal standard. Some of the reaction products were identified by GC/MS equipped with a VG 70EHF mass spectrometer and a Varian 3700 gas chromatograph.

RESULTS AND DISCUSSION

The catalytic activity of V generated *in situ* from VAcAc and VOAcAc was investigated in hydrogenation reactions of hydrocarbons and heteroatomic species individually or in combination under coprocessing conditions. In addition, the effect of sulfur on the activity of V species was determined.

The degree to which hydrogenation and heteroatom removal occurred in each reaction is reported in terms of percent hydrogenation (% HYD), percent hydrodesulfurization (% HDS), percent hydrodeoxygenation (% HDO), and percent hydrodenitrogenation (% HDN). The % HYD is defined as the number of moles of hydrogen used to achieve the final liquid product distribution as a percentage of the moles of hydrogen required to achieve the most hydrogenated liquid product. The % HDS, % HDN and % HDO are the summations of the mole percents of products not containing sulfur, nitrogen and oxygen, respectively. In the calculation of % HYD, the most hydrogenated liquid products defined for the systems used were decalin for naphthalene and tetralin; cyclohexane for indan, indene, benzothiophene, o-cresol, benzofuran, and indole; and n-propylcyclohexane and n-butylcyclopentane for quinoline.

Catalytic Activity of V for Aromatic Ring Saturation

The activity of V generated *in situ* from VAcAc and VOAcAc in the presence of excess sulfur was evaluated for hydrogenation of aromatics and alkyaromatics: naphthalene, tetralin, n-butylbenzene, n-propylbenzene, ethylbenzene and toluene. The result was compared to the activity of *in situ* generated Mo sulfide at the same metal loading level for the same systems. The V species from both precursors showed high activity for partially saturating two-ring aromatics to hydroaromatics, but low activity for fully saturating the two-ring aromatics or single-ring alkyaromatics to alicyclics and alkylalicyclics as did the Mo sulfide; only 2-5% of aromatic ring in alkyaromatics was saturated to alkylalicyclics with VAcAc, and only 3-9% was saturated with VOAcAc. However, the V sulfide catalysts showed a slightly higher activity for both the aromatic ring saturation and the ring hydrogenolysis than the Mo sulfide catalyst.

Activity and Selectivity of V Catalyst for Hydrogenation and Heteroatom Removal

The catalytic activity and selectivity of *in situ* generated V for reactions involving hydrogenation, hydrogenolysis and heteroatom removal were evaluated by using individual model systems. The major products and the degree of hydrogenation and heteroatom removal achieved with V catalysts were compared to those from comparable systems reacted with *in situ* generated Mo sulfide at equivalent reaction conditions (Tables 1).

Naphthalene and Tetralin. With V sulfide, both naphthalene and tetralin produced a partially saturated hydroaromatic, tetralin, as the primary product, as the same product with Mo sulfide. V sulfide, especially from VOAcAc, produced more decalin from both reactants, hence achieving higher % HYDs, than did Mo sulfide.

The V sulfide also produced various hydrogenolyzed products.

Indan and Indene. V sulfides showed low activity for saturating the aromatic ring of indan as did Mo sulfide. Indene was completely converted to indan with V catalysts, but only less than 12% of indan was converted further to fully saturated hexahydroindan, predominantly to *cis*-hexahydroindan. Compared to Mo sulfide, V catalysts were relatively more active for saturating the aromatic ring and for hydrogenolyzing the five-membered ring, showing a higher % HYD.

Benzothiophene. VAcAc and VOAcAc without sulfur was nearly inactive for hydrogenation of benzothiophene. But in the presence of excess sulfur, both V precursors almost completely hydrodesulfurized benzothiophene, producing ethylbenzene and ethylcyclohexane as the primary and secondary products, respectively. When compared to Mo sulfide, V sulfides were more active for producing ethylcyclohexane; the mole ratio of ethylcyclohexane to ethylbenzene produced was 6:90 with MoNaph, 23:72 with VAcAc and 23:66 with VOAcAc. Hence, V sulfides yielded higher % HYD than Mo sulfide.

***o*-Cresol.** In the absence of sulfur, VAcAc and VOAcAc did not catalyze the deoxygenation of *o*-cresol. But, in the presence of excess sulfur, *o*-cresol was completely deoxygenated with both precursors. When compared to Mo sulfide, V sulfides removed more oxygen and produced more alkylalicyclics, such as methylcyclohexane, ethylcyclopentane and their isomers, and less alkylaromatics such as toluene, hence yielding higher % HYD.

Benzofuran. With VAcAc and VOAcAc in the absence of sulfur, no oxygen was removed from benzofuran. But in the presence of excess sulfur, both VAcAc and VOAcAc completely converted benzofuran and achieved a high level of oxygen removal, producing ethylcyclohexane and ethylbenzene as the primary and the secondary products, respectively. V catalysts were more active for hydrogenolyzing the five-membered ring and removing oxygen from benzofuran than Mo sulfide.

Quinoline. VAcAc and VOAcAc in the presence of excess sulfur showed a relatively low activity for the hydrodenitrogenation of quinoline. With the *in situ* generated Mo sulfide, quinoline was completely converted, achieving 90% HDN. Propylcyclohexane and butylcyclopentane were the major products. By contrast, only 31% HDN and 36% HDN were achieved with VAcAc and VOAcAc, respectively, and 1,2,3,4-tetrahydroquinoline was the major product. The low activity for nitrogen removal and, thus, the low % HYD achieved suggested that the V sulfides, which were highly active for hydrogenation of aromatics and removal of S and O, might be severely poisoned by organic nitrogen compounds. In the absence of sulfur, V precursors were nearly inactive for quinoline denitrogenation.

Indole. With VAcAc and VOAcAc in the presence of excess sulfur, indole was completely converted, yielding *o*-ethylaniline as the primary product and ethylcyclohexane as the secondary product. V sulfides were less active for nitrogen removal compared to Mo sulfide. This low activity for indole denitrogenation again suggested that the activity of V catalysts might be severely inhibited by organic nitrogen compounds. Without sulfur, VOAcAc did not catalyze the nitrogen removal from indole.

Reaction Pathway of Heteroatom Removal. Because V sulfides did not actively catalyze the direct hydrogenation of ethylbenzene to ethylcyclohexane (only up to 3-4%) and toluene to methylcyclohexane (5-9%), the large amounts of ethylcyclohexane produced from the hydrogenation of benzothiophene (23% with VAcAc and VOAcAc), benzofuran (66% with VAcAc, 58% with VOAcAc) and indole (26% with VAcAc, 32% with VOAcAc) and methylcyclohexane from *o*-cresol hydrogenation (60% with VAcAc, 55% with VOAcAc) appeared to be produced from heteroatom-

containing intermediates: octahydrobenzothiophene and 2-ethylcyclohexanethiol for benzothiophene, octahydrobenzofuran and 2-ethylcyclohexanol for benzofuran, perhydroindoline and 2-ethylcyclohexylamine for indole, and methylcyclohexanol for o-cresol. Therefore, heteroatom removal with V sulfides was simultaneously achieved through two different pathways as with Mo sulfide. (6) For removal of the heteroatom from benzothiophene, benzofuran and indole, one pathway proceeded through the hydrogenation to dihydro-products, followed by heteroatom removal, producing ethylbenzene, and the other pathway proceeded through the aromatic ring saturation, thereby producing the heteroatom-containing saturated intermediates that later released heteroatoms, producing ethylcyclohexane. For o-cresol, one pathway proceeded through direct oxygen removal from o-cresol, producing toluene, and the other proceeded through aromatic ring saturation, producing methylcyclohexanol, and then followed by oxygen removal, producing methylcyclohexane. When compared to Mo sulfide, V sulfides catalyzed the heteroatom removal principally through the second pathway, which utilized the heteroatom-containing saturated intermediates to produce alkylalicyclics. Hence, the % HYD achieved with V sulfides was higher than that with Mo sulfide in all cases except for the systems containing nitrogen compounds.

Effect of Combined Reactants

The effect of additional hydrocarbon and heteroatomic species on the hydrogenation of other reactants was tested with VOAcAc in the presence of excess sulfur (Table 2). In this experiment, two compounds of naphthalene, indan, benzothiophene, o-cresol, benzofuran, quinoline, indole or pyridine were mixed.

Effect on Naphthalene Hydrogenation. The activity of V sulfide for naphthalene hydrogenation was not affected much by other hydrocarbons, sulfur-compounds or oxygen-compounds. The slightly reduced % HYD of naphthalene was because of possible competitive reactions occurring on the same active sites of the catalyst. When nitrogen-containing compounds were mixed, the activity of V sulfide was tremendously reduced, indicating that organic nitrogen compounds inhibited the activity of V sulfide for hydrogenation of aromatics.

Effect on Benzothiophene Hydrodesulfurization. Nitrogen-containing reactants and products severely inhibited the activity of VOAcAc for sulfur removal from benzothiophene, while hydrocarbons and oxygen-compounds reduced % HYD in a small amount by competitive reactions on the same catalyst.

Effect on the Hydrodeoxygenation of o-Cresol and Benzofuran. The extent of hydrodeoxygenation catalyzed by V sulfides was slightly reduced by additional sulfur-compounds, while not being greatly affected by other hydrocarbons and oxygen-compounds. When quinoline was added, the activity of the V sulfide catalyst for HDO was severely inhibited. Therefore, nitrogen compounds appeared to be the most detrimental to V sulfide catalysts not only for the hydrodenitrogenation of nitrogen-containing reactants but also for other hydrogenation and heteroatom removal reactions.

Effect of Sulfur Amount on the Activity of V Catalyst

The activity of V species was generated in the presence of sulfur. The effect of the amount of sulfur on the activity of *in situ* generated V species was examined using naphthalene hydrogenation (Table 3). Without sulfur, neither V precursors showed any activity for naphthalene conversion. When sulfur was added, catalytic activity of the V species was observed. Addition of more sulfur induced higher conversion of naphthalene to decalin, indicating that the activity of the *in situ* generated V catalyst strongly depended on the amount of sulfur present.

The effect of sulfur amount on the activity of V catalysts for hydrogenation of aromatics and heteroatom removal was also tested by introducing more sulfur in combined reactions (Table 4). Two different levels of sulfur, three times and

nine times the stoichiometric amount of sulfur required to form V_2S_3 (0.034 g and 0.102 g S, respectively), were added in each reaction set. In the hydrogenation of combined sets of naphthalene-indan, naphthalene-benzothiophene and naphthalene-indole, the higher sulfur amount achieved higher % HYDs of all reactants and also markedly increased the extent of nitrogen removal from indole. However, in the combined reaction of naphthalene and o-cresol, more sulfur increased naphthalene hydrogenation, but it decreased o-cresol deoxygenation and thereby decreased o-cresol hydrogenation. These results indicated that the addition of more sulfur could enhance the activity of V sulfide for aromatic hydrogenation, sulfur removal and nitrogen removal, but that excessive sulfur might reduce the activity of V sulfide for oxygen removal.

SUMMARY

The activity of V sulfide generated *in situ* from VAcAc and VOAcAc was strongly dependent upon the amount of sulfur present. The characteristics of V sulfides in the model hydrogenation and heteroatom removal reactions were somewhat similar to those observed with the *in situ* generated Mo sulfide. In the hydrogenation of aromatics and alkylaromatics, V sulfide was active for the partial saturation of an aromatic ring in multiring aromatics but far less active for the further saturation to alicyclics and for the saturation of single-ring alkylaromatics. The heteroatom removal with V sulfide simultaneously occurred through two pathways as did with Mo sulfide: one pathway for heteroatom removal prior to saturation of the aromatic ring, producing alkylaromatics and the other for heteroatom removal following the saturation of the aromatic ring, producing alkylalicyclics. When compared to Mo sulfide, the V sulfide was more active for the hydrogenation of aromatic rings adjacent to the heteroatom before the heteroatom was removed, producing more heteroatom-containing alkylalicyclics as the intermediates and thus more alkylalicyclics in the final product slates. Therefore, V sulfide achieved higher % HYDs in the hydrogenation of oxygen and sulfur-containing compounds than did Mo sulfide. V sulfide was more active for O removal but less active for N removal than Mo sulfide.

In combined reactions, the activity of V sulfide for hydrogenation and heteroatom removal was only slightly affected by other aromatics, hydroaromatics, organic sulfur compounds, and organic oxygen compounds, but it was severely inhibited by organic nitrogen compounds. A higher content of sulfur enhanced the activity of V sulfide for the hydrogenation of aromatics, hydroaromatics and sulfur- and nitrogen-containing compounds and for the removal of S and N. However, this excessive sulfur slightly inhibited the activity of V sulfide for O removal.

Because coprocessing feed materials contain several percents of indigenous sulfur, the V indigenous to residuum may be converted to V sulfide *in situ* and show a catalytic activity for the aromatic hydrogenation and heteroatom removal reactions involved in coprocessing. However, because the activity of V sulfide can be inhibited by organic nitrogen components indigenous to the feed materials, V sulfide can be far less catalytic in coprocessing than that shown in the model hydrogenation reactions.

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Table 1. Comparison of the Hydrogenation Activity of In Situ Generated V sulfide from VOAcAc and VOAcAc and Mo sulfide from MoNaph in Model Systems^a

Reactant	Hetero atom (A)	Major Products		% H ₂ O ^b		% H ₂ C ^c	
		V sulfide	Mo sulfide	V sulfide VAcAc	Mo sulfide VAcAc	V sulfide VAcAc	Mo sulfide MoNaph
Naphthalene	-	tetralin	tetralin	42.9±0.8	50.8±3.0	42.6±0.4	-
Tetralin	-	tetralin	tetralin	15.3±0.3	26.9±0.8	4.7±0.3	-
Indene	-	indan	indan	17.2±1.3	18.0±0.6	16.0±0.3	-
Indan	-	indan	indan	3.6	6.8±0.2	3.4±0.3	-
Benzothioephene	S	ethylbenzene	ethylbenzene	47.6±1.4	50.3±0.6	40.7±0.7	99.6±0.8
o-Cresol	O	methylcyclohexane	toluene	74.2±0.4	71.6±0.2	36.2±0.2	100.0±0.0
Benzofuran	O	ethylcyclohexane	ethylbenzene	67.4±0.6	69.1±0.2	46.3±0.7	92.4±0.8
quinoline	N	1,2,3,4-THQ ^d	propylcyclohexane	51.9±1.8	54.9±0.1	90.6±1.5	31.0±2.4
Indole	N	o-ethylaniiline	ethylcyclohexane	38.8±0.3	43.8±0.0	70.4±2.2	33.8±0.7

^a The reactions were conducted at 360°C for 30 minutes with 3000 ppm metal loading in the presence of excess sulfur, three times the stoichiometric sulfur to form V₂S₅ and MoS₂ (0.094 g for V, 0.024 g for Mo). Most reactions were at least duplicated, and the amount of hydrogenation and heteroatom removal was summarized as the average value and standard deviation of $\bar{x} \pm \sigma$.

^b The most hydrogenated liquid products used in calculating % H₂O were: decalin for naphthalene and tetralin, and cyclohexane for indan, indene, benzothioephene, benzofuran and o-cresol.

^c % H₂C: Percent heteroatom removal of S, N and O.

^d 1,2,3,4-tetrahydroquinoline.

Table 2. Effect of Multiple Compounds on the V Sulfide-Catalyzed Hydrogenation of Naphthalene, Benzothiophene, o-Cresol and Benzofuran^a

(A) Naphthalene

Additional Compound ^b	Naphthalene	
	% HYD	
None	50.8±3.0	
Indan	43.5±1.2	
Benzothiophene	50.1	
Benzofuran	49.0±2.5	
o-Cresol	48.8±3.9	
Quinoline	5.7±0.6	
Indole	9.1±0.1	
Pyridine	14.4±1.6	

(B) Benzothiophene

Additional Compound ^b	Benzothiophene	
	% HYD	% HDS
None	50.3±0.6	100.0±0.0
Naphthalene	48.2	100.0
o-Cresol	46.7±0.5	100.0±0.0
Quinoline	19.8±0.5	32.3±1.4

(C) o-Cresol and Benzofuran

Additional Compound ^b	Reactant			
	o-Cresol		Benzofuran	
	% HYD	% HDO	% HYD	% HDO
None	71.6±0.2	100.0±0.0	69.1±0.2	98.6±0.1
Naphthalene	69.3±2.3	97.1±2.9	67.4±1.9	95.5±3.5
Benzothiophene	66.0±0.7	92.5±1.2	-	-
Benzofuran	72.7	100.0	-	-
o-Cresol	-	-	69.9	100.0
Quinoline	7.3±0.3	12.8±0.6	26.0±0.1	5.2±0.2

^a Most of the reactions were performed two or three times with VOAcAc and 0.034 g S and the % HYD, % HDS and % HDO were expressed as an average value and a standard deviation in the form of $X \pm \sigma_n$. In calculating % HYD, the most hydrogenated liquid products determined were decalin for naphthalene and cyclohexane for benzothiophene, o-cresol and benzofuran.

^b Each reactant except for naphthalene (2 wt%) was added at 1 wt% level in the hexadecane solution.

Table 3. Effect of Sulfur Amount on the Activity of *In Situ* Generated Vanadium Catalysts in Hydrogenation of Naphthalene

Product, mole %	Sulfur Amount ^a					
	0	1	2	3	5	10
VAcAc % HYD ^b	0.9	5.3±1.5	35.7±1.4	42.9±0.8	50.2±0.8	61.3
t-D/c-D Ratio ^c	-	-	-	1.09±0.08	1.14±0.03	1.37
VOAcAc % HYD ^b	0.7	21.2	40.4	50.8±3.0	57.3±1.1	NP ^d
t-D/c-D Ratio ^c	-	-	-	1.10±0.02	1.13±0.01	

- ^a Multiples of the stoichiometric amount of sulfur required to form V₂S₃.
^b % HYD calculated using decalin as the most hydrogenated liquid product.
^c Approximate ratio of trans- to cis-decalin.
^d NP: not performed.

Table 4. Effect of Sulfur Amount on the V Sulfide-Catalyzed Hydrogenation of Model Compounds^a

Sulfur Amount ^b	Reactants ^c		
	Naphthalene % HYD	Indan % HYD	
Naphthalene/Indan			
	3	43.5±1.2	3.0±0.5
9	55.8±0.3	10.0±0.2	
Naphthalene/Benzothiophene			
	3	50.1	48.2 100.0
9	54.8±0.5	53.9±0.1 100.0±0.0	
Naphthalene/o-Cresol			
	3	48.8±3.9	69.3±2.3 97.1±2.9
9	52.4±3.2	63.7±2.5 89.7±2.9	
Naphthalene/Indole			
	3	9.1±0.1	41.9±0.1 37.1±0.3
9	15.7±0.3	55.3±0.6 58.0±3.6	

- ^a Combined reactions of 2 wt% naphthalene and 1 wt% of other compounds were performed with VOAcAc.
^b The sulfur amount was expressed as multiple times the sulfur required to form V₂S₃.
^c In calculating % HYD, the most hydrogenated liquid products used were decalin for naphthalene and cyclohexane for the other reactants.