

Selectivity of γ -Al₂O₃ supported vanadium catalysts in the Hydrodemetallisation (HDM) of Ni-TPP and VO-TPP.

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abstract

The HDM reactions of nickel-tetraphenylporphin (Ni-TPP) and vanadyl-tetraphenylporphin (VO-TPP) over sulfided V/γ -Al₂O₃ catalysts have been studied in the liquid phase. Kinetic analysis revealed that both Ni-TPP and VO-TPP are demetallised through a reversible sequential mechanism via hydrogenated intermediate porphinic compounds. For the hydrogenation of the porphins a single site model, in which atomic hydrogen and porphins are adsorbed on the same type of sites, applies with a Langmuir-Hinshelwood type of kinetics for hydrogen. Hydrogenolysis is achieved on a different type of sites.

The HDM reactions of both Ni-TPP and VO-TPP are structure sensitive: increasing the vanadium loading of the catalysts initially results in an increased hydrogenation activity. The presence of crystalline materials on the catalysts suppresses the hydrogenation activity of the catalysts. Hydrogenolysis is not influenced by the presence of crystalline material but decreases almost linearly with increasing vanadium loading of the catalysts.

Introduction

Today's oil refining is facing major changes. The world's supplies of relatively easily refinable petroleum are decreasing whereas demands for clean refinery products (e.g. transportation fuels) are increasing. As a consequence, ever increasing quantities of low quality crude oils have to be processed, resulting in vast amounts of economically invaluable residual oils. The alternative which is rapidly becoming more important is to upgrade the residual oils into the desired products composition. In doing this, not only the C/H ratio of the feed has to be improved but a more thorough removal of hetero-atoms (sulfur, nitrogen and metal compounds) has to be achieved as well in order to protect 'down-stream' catalysts from rapid deactivation and to meet with stricter environmental legislations.

Unlike HDS and HDN, hydrodemetallisation (HDM) generates deposits of metal sulfides (mainly nickel and vanadium sulfides) on the catalysts, leading to an alteration of selectivity and eventually to an irreversible deactivation of the catalysts. Furthermore, the metallic constituents of petroleum tend to concentrate in the heavy fractions which makes the upgrading of residual oils even more cumbersome. In the improvement of existing processes and the development of new processes, kinetic data are highly desirable. Also the development of new types of catalysts with improved selectivity toward demetallisation as well as large metal storage capacity is to a large extent based on kinetics.

The objective of the current investigation is to relate structural aspects and sulfiding behavior of γ -Al₂O₃ supported vanadium catalysts to their activity and selectivity in the HDM of model metal compounds.

Experimental

1) Catalysts.

A listing of the catalysts applied in this study is given in table 1. All catalysts were prepared by pore volume impregnation of a wide-pore, high purity γ -Al₂O₃ support (Rh ne-Poulenc SCM

99XL, specific surface area $156 \text{ m}^2/\text{g}$, pore volume $1.2 \cdot 10^{-6} \text{ m}^3/\text{g}$ and mean pore radius 13 nm). 75-150 μm particles were used. Further details on the preparation of the catalysts are given elsewhere [1].

Table 1. Catalysts applied

catalyst	vanadium loading	
	wt% V	atoms V/nm^2
V(0.9)/Al ₂ O ₃	1.25	0.94
V(1.4)/Al ₂ O ₃	1.79	1.35
V(1.8)/Al ₂ O ₃	2.33	1.77
V(3.0)/Al ₂ O ₃	3.93	2.98

Prior to the activity measurements, the catalysts were sulfided at 673 K in a gas mixture consisting of 15 vol% H₂S in H₂ (total flow rate: 13.67 $\mu\text{mol/s}$). The sulfiding mechanism of the catalysts is discussed in detail elsewhere [2]. The sulfiding procedure was as follows:

- Purging with Ar at 293 K to remove air.
- Isothermal sulfiding at 293 K in H₂S/H₂ for 1.8 ks.
- Temperature programmed heating (0.167 K/s) in H₂S/H₂ to 673 K.
- Isothermal sulfiding at 673 K in H₂S/H₂ for 7.2 ks.
- Purging with Ar at 673 K for 1.8 ks.
- Cooling down to 293 K in Ar.

2) HDM-activity measurements.

Vanadyl-meso-Tetraphenylporphin (VO-TPP) and Nickel-meso-Tetraphenylporphin (Ni-TPP) were used as model metal compounds. The HDM-activity measurements were performed in the liquid phase. The solvent employed in this study was o-Xylene (Janssen Chimica, p.a. grade). Because of the poor solubility of the model compounds at room temperature and their reactivity towards oxygen at elevated temperatures [3], they were dissolved under argon in refluxing o-Xylene for 7.2 ks. The porphin solutions thus obtained contained approximately 0.3 mol/m³ VO-TPP or Ni-TPP and were stored under Ar or used immediately.

HDM-activity measurements of the presulfided catalysts were performed in a $2 \cdot 10^{-4} \text{ m}^3$ stirred batch autoclave. The reactor was equipped with a sampling device from which samples were taken at regular intervals. After thoroughly purging the autoclave with argon, about 100 g of model compound solution was loaded into the reactor. The reactor was then evacuated and approximately 0.1 g of catalyst was introduced from a catalyst loader that had been mounted on the reactor to prevent the presulfided catalyst from contact with air. After purging with H₂ and subsequent evacuation the reactor was pressurised to approximately 0.3 MPa with a gas mixture containing 15 vol% H₂S in H₂. The H₂S/H₂ mixture was used as received. The reactor was further pressurised to 3 MPa with H₂ (99.9 %) which had been prepurified to remove traces of oxygen and water. After completing the loading and pressurising, the autoclave was closed and heated to 573 K while stirring its contents.

With each metalporphin, six runs were carried out at 573 K. In four of these runs the vanadium loading of the catalysts was varied while the liquid phase concentration of hydrogen was kept constant. The effect of the liquid phase concentration of hydrogen at 573 K was evaluated in three runs with the V(1.8)/Al₂O₃ catalyst. An overview of the HDM experiments with Ni-TPP and VO-TPP is given in table 2.

In each run 8-10 liquid samples of approximately 0.5 g were taken at various reaction times from the sampling port and analysed immediately with a Philips PU 8725 rapid scanning UV/VIS spectrophotometer. Porphins and metalporphins are known to have distinct and intense absorption maxima in the visible range. The concentrations of the porphins and their

hydrogenated intermediates were calculated from the UV/VIS spectra by applying Beer's law. The specific absorptions of each compound were corrected for overlap with other absorption bands in the spectra.

Table 2. Overview of HDM experiments with Ni-TPP and VO-TPP over sulfided V/ γ -Al₂O₃ catalysts

catalyst	run	Ni-TPP		run	VO-TPP	
		[H ₂] (mol/m ³)	[H ₂ S] (mol/m ³)		[H ₂] (mol/m ³)	[H ₂ S] (mol/m ³)
V(0.9)/Al ₂ O ₃	Ni-1	365.50	13.17	V-1	396.55	13.63
V(1.4)/Al ₂ O ₃	Ni-2	388.78	13.51	V-2	381.02	13.40
V(1.8)/Al ₂ O ₃	Ni-31	255.87	13.81	V-31	236.30	13.39
V(1.8)/Al ₂ O ₃	Ni-32	381.02	13.40	V-32	404.31	13.73
V(1.8)/Al ₂ O ₃	Ni-33	536.45	13.32	V-33	532.57	13.28
V(3.0)/Al ₂ O ₃	Ni-4	400.43	13.68	V-4	392.67	13.57

In order to check for the presence in the liquid samples of metal compounds not detected by UV/VIS spectrometry, the total metal content of several samples was determined by Graphite Furnace Atomic Absorption Spectrometry (GFAAS, Perkin-Elmer HGA 500/560).

The actual concentrations of H₂ and H₂S at reaction conditions were calculated with the Peng-Robinson equation of state. Binary interaction parameters for H₂ and o-Xylene were obtained from literature [4]. Interaction parameters for H₂-H₂S and for H₂S-Xylene were set to zero. Also the density of the liquid phase at the reaction conditions was calculated with the Peng-Robinson equation of state. This made accurate calculation of the concentration of model compounds at these conditions possible.

3) Kinetic analysis.

Intrinsic kinetic parameters were obtained by evaluation of the concentration versus time curves with a non-linear regression programme (NLS). The objective function, defined as the sum of squares of deviations (residuals) between experimental and calculated concentrations, was minimised by using a combination of the Simplex and Levenberg-Marquardt methods.

With the NLS programme, several reaction mechanisms were tested. A fourth order Runge-Kutta method was used to numerically solve the sets of coupled differential equations for each kinetic model. Zero reaction time was taken at the moment the desired reaction temperature was reached. During the heating of the reactor and its contents some conversion of the reactants already occurred. In order to overcome this problem, concentrations of reactants and intermediates in the sample taken at zero reaction time were used as the initial concentrations in the kinetic analysis of the experiments.

Results

Typical concentration versus reaction time plots for HDM experiments with Ni-TPP and VO-TPP at 573 K are shown in figures 1 (run Ni-32) and 2 (run V-32). The experimentally obtained concentrations of reactants and hydrogenated intermediates are represented by markers. Solid lines represent calculated concentrations.

Ni-TPP has been shown to demetallise through a reversible sequential mechanism via the hydrogenated intermediate species Ni-TPC and Ni-TPiB [5-7]. In analogy with Ni-TPP, VO-TPP appears to demetallise through a similar sequential mechanism. The concentration of VO-TPP as a function of reaction time rapidly drops while the concentrations of VO-TPC and VO-TPiB

build up and then, after reaching a maximum, slowly decline indicating that these hydrogenated species are rather stable intermediates in the course of the HDM reaction of VO-TPP. No other vanadium containing species and metal-free porphins were detected in the liquid samples. Similar trends were observed in all the other HDM-experiments with VO-TPP, irrespective of vanadium-loading of the catalysts, liquid phase concentration of hydrogen and reaction temperature. It can be seen clearly from figures 1 and 2 that VO-TPP is much more reactive than Ni-TPP at the conditions applied. Not only the concentration of VO-TPP drops faster and the concentration levels of hydrogenated intermediate species are much higher, but also the total content of vanadium in the liquid phase decreases faster than is the case with nickel.

Since the concentrations of reactants, reaction intermediates, hydrogen and hydrogen sulfide could be calculated at the reaction conditions applied, detailed kinetic analysis of the HDM reactions of both Ni-TPP and VO-TPP was possible.

Various kinetic models were tested which were all based on sequential reaction mechanisms. The most successful model is depicted in figure 3. In this model, which applies for both Ni-TPP and VO-TPP, the initial porphin is hydrogenated reversibly to its intermediates M-TPC and M-TPiB ($M = Ni, VO$). The intermediate M-TPiB then goes through a series of reactions, leading to the deposit of a metal sulfide on the catalyst and the fragmentation of the porphin macrocycle. The hydrogenolysis process is lumped into one irreversible step, represented by an apparent rate constant k_5 .

It was carefully checked if inhibition by porphinic species occurs. No evidence was found for this at the conditions applied. Also in separate experiments with a flow reactor, in which the initial concentration of reactants as well as reaction temperatures were varied over large intervals, no evidence was obtained for inhibition of the HDM reactions by porphinic species.

Kinetic analysis of the HDM reactions of Ni-TPP and VO-TPP with respect to the liquid phase concentration of hydrogen revealed that both the hydrogenation reactions (1 and 3) and the hydrogenolysis step (5) exhibit fractional orders in hydrogen. The dehydrogenation reactions (2 and 4) appeared to be zeroth order in hydrogen. Similar results were obtained by Van Steenderen et al. [8] for the HDM reactions of Ni-TPP over a sulfided $Mo\gamma/Al_2O_3$ catalyst at 613 K. The kinetic orders with respect to the liquid phase concentration of hydrogen are given in table 3. For comparison, the results obtained by Van Steenderen et al. are included.

Table 3. Kinetic orders with respect to the liquid phase concentration of hydrogen

catalyst	porphin	T (K)	α	β
V(1.8)/Al ₂ O ₃	Ni-TPP	573	0.80	1.89
V(1.8)/Al ₂ O ₃	VO-TPP	573	1.01	1.51
Mo(1.2)/Al ₂ O ₃	Ni-TPP	613	0.73	1.78

The kinetic order in hydrogen of the hydrogenation reactions is represented by α . β represents the order in hydrogen of the hydrogenolysis step.

The fractional orders in hydrogen concentration indicate a Langmuir-Hinshelwood type of kinetics. Two kinetic models were considered based on the fact that no inhibition occurs by porphins and their hydrogenated intermediates or products. In the first model, adsorbed molecular hydrogen reacts with the porphins and their hydrogenated intermediates. In the second model, the porphinic species are thought to react with dissociatively adsorbed hydrogen. In both the models hydrogenolysis was considered to take place on either the same type of sites as

hydrogenation and dehydrogenation or on a different type of sites.

Although all models considered fitted reasonably well with the experimental data, for both Ni-TPP and VO-TPP the best results were obtained with the model of dissociatively adsorbed hydrogen with different types of sites for hydrogenation/dehydrogenation and hydrogenolysis. With this model, a value of $K_H = 7.49 \cdot 10^{-5} \text{ m}^3/\text{mol}$ was obtained. The hydrogenation and dehydrogenation rate constants were not introduced as variables but the ratios k_1/k_2 and k_3/k_4 were kept constant. They are in fact the equilibrium constants which were estimated from non-catalytic experiments and from various catalytic experiments in which liquid phase concentrations of hydrogen and hydrogen sulfide were widely varied. The estimated equilibrium constants at 573 K are given in table 4.

Table 4. Equilibrium constants of Ni-TPP and VO-TPP at 573 K

	Ni-TPP	VO-TPP
$K_{1,2} = k_1/k_2$	$3.147 \cdot 10^{-3}$	$7.983 \cdot 10^{-3}$
$K_{3,4} = k_3/k_4$	$8.919 \cdot 10^{-4}$	$2.949 \cdot 10^{-3}$

Plots of intrinsic rate constants for the HDM reactions of Ni-TPP and VO-TPP as a function of vanadium content of the catalysts are shown in figures 4 and 5, respectively.

It can be seen from figures 4 and 5 that VO-TPP is much more reactive than Ni-TPP. In both cases, the HDM reactions appear to be structure sensitive. This effect is for both Ni-TPP and VO-TPP most pronounced in the secondary hydrogenation rates (k_3). The (lumped) rate constant of hydrogenolysis (k_5) decreases almost linearly with increasing vanadium loading.

Discussion

The results obtained from the current investigation have demonstrated that the HDM of VO-TPP and Ni-TPP proceed through identical pathways. In both cases the initial porphin is reversibly hydrogenated to its chlorin, which in turn is reversibly hydrogenated to yield a metal-isobacteriochlorin.

Kinetic analysis of the hydrogen dependence of the HDM reactions revealed that both the hydrogenation and hydrogenolysis reactions exhibit fractional orders in the liquid phase concentration of hydrogen (table 3) whereas zeroth order applies for the dehydrogenation reactions. The non-integer orders in hydrogen indicate a Langmuir-Hinshelwood type of kinetics. It was shown that a single site model for hydrogenation and dehydrogenation reactions, in which porphinic species and atomic hydrogen are adsorbed on the same type of sites, fitted best with the experimental data, irrespective of the porphin used. The fact that the value for K_H is very low shows that the HDM reactions of both Ni-TPP and VO-TPP are only slightly inhibited by hydrogen at 573 K.

At present it is not clear whether the metal is removed from the metal-isobacteriochlorin, at which a very unstable metal-free porphinic molecule is formed, or metal removal takes place after destruction of the porphin macrocycle by e.g a combination of hydrogenation and cracking reactions. Fact is however that the hydrogenolysis reactions leading to the removal of metals from Ni-TPP and VO-TPP have fractional orders in hydrogen greater than 1 indicating that demetallisation is achieved via a sequence of reactions.

The HDM reactions of Ni-TPP and VO-TPP over sulfided V/Al_2O_3 catalysts are clearly demanding. Primary as well as secondary hydrogenation rates initially increase with increasing vanadium loading of the catalysts, the effect being most pronounced with the secondary hydrogenation rates. The catalyst with a vanadium loading of 3 atoms/nm² has a significantly lower

activity toward the hydrogenation reactions. Increasing of the vanadium loading of the catalysts has a dramatic impact on the hydrogenolysis step. Whereas hydrogenation rates initially increase with increasing vanadium loading, the hydrogenolysis rate decreases linearly with the vanadium content of the catalysts. This observation nicely confirms the conclusions that hydrogenation and hydrogenolysis are achieved on different types of sites.

It has been reported [1,2] that with V/Al_2O_3 catalysts prepared by pore volume impregnation with vanadium loadings up to 2 atoms/nm² the alumina surface contains an ill defined two-dimensional structure of vanadium oxide. At very low loadings the alumina surface contains species of tetrahedrally coordinated vanadium which, on increasing the vanadium loading, are transformed into octahedrally coordinated species. Further increasing of the vanadium loading is thought to result in an expanding of these relatively small clusters due to polymerisation into larger structures of octahedrally coordinated vanadium with a relatively less intimate interaction with the alumina surface than the former ones. At vanadium loadings exceeding 2 atoms/nm², V_2O_5 crystallites are present on the catalysts.

As for the sulfidability of V/Al_2O_3 catalysts, it was shown [2] that catalysts lacking crystalline V_2O_5 are nearly completely sulfided at 673 K whereas the major part of the sulfiding process of crystalline V_2O_5 takes place at temperatures well above 673 K. At temperatures up to 673 K, crystalline V_2O_5 is reduced to V_2O_3 .

The ease with which the catalysts are sulfided and the observed sulfiding mechanism are indicative for the preservation of the characteristics (e.g. dispersion and support interaction) of the active phase. Also the temperature at which the sulfiding of the catalysts was performed is too low for solid state transformations or solid state diffusion processes to occur.

From the above, the impact of the vanadium loading of V/Al_2O_3 catalysts on the HDM of Ni-TPP and VO-TPP reactions can be rationalised as follows. The relatively low hydrogenation activities of $V(0.9)/Al_2O_3$ may be the result of the presence of the active phase in small clusters with a strong interaction with the support. On increasing the vanadium content, these clusters expand to larger structures which have a weaker interaction with the support. Due to this weaker interaction sulfur vacancies, which are thought to be the active sites for porphyrin adsorption and hydrogenation, may be formed with more easily. Also edges of the clusters of the active phase may contribute to the hydrogenation activity of the catalysts. It appears that after reaching a maximum with the $V(1.4)/Al_2O_3$ catalyst, the rate constants of hydrogenation slowly decline. This may be the result of the presence of larger clusters, formed out of small clusters, of the active phase with a relatively lower ratio of edges/mol V. The presence of crystalline material on the $V(3.0)/Al_2O_3$ catalyst results in a lowering of the hydrogenation activity for both Ni-TPP and VO-TPP. From this it is tentatively concluded that crystalline V_2O_3 has no hydrogenation capacity and, through coverage of the active sites, causes a lowering of the hydrogenation activity of V/Al_2O_3 catalysts.

The fact that the hydrogenolysis activity for both Ni-TPP and VO-TPP decreases linearly with increasing vanadium loading of the catalysts indicates that hydrogenolysis is to a large extent independent of the characteristics of the different phases in which the active material is present and supports the idea that hydrogenolysis is achieved on another type of sites.

As in hydrogenation, sites located at the edges of the active phase clusters apparently play an active role in the hydrogenolysis. Upon increasing the vanadium loading of the catalysts small clusters expand through polymerisation to larger clusters with a relatively lower ratio of edges/mol V resulting in a lowering of the hydrogenolysis activity.

Conclusions

- HDM of Ni-TPP and VO-TPP proceeds through a reversible sequential mechanism via hydrogenated intermediate compounds of similar nature: metal-tetraphenylchlorin and metal-tetraphenylisobacteriochlorin. VO-TPP is more reactive than Ni-TPP with respect to hydrogenation which can be seen from the faster decline of the concentration of VO-TPP and the substantially larger amounts of hydrogenated intermediates formed.

- A two-site mechanism is found to apply for the HDM reactions of both Ni-TPP and VO-TPP. In the hydrogenation and dehydrogenation reactions porphins, intermediates and atomic hydrogen are adsorbed on the same type of sites which are thought to consist of sulfur vacancies. Hydrogenolysis is achieved on another type of sites in which hydrogen sulfide is thought to play an important role.
- The HDM reactions of both Ni-TPP and VO-TPP are first order in porphins and hydrogenated intermediates. Hydrogenation reactions are approximately first order in the liquid phase concentration of hydrogen whereas dehydrogenation reactions are zero order in hydrogen. The hydrogenolysis reactions exhibit fractional orders in hydrogen greater than one.
- The fact that for hydrogenolysis, hydrogen orders are greater than one indicates the demetallisation of the porphins to proceed through a sequence of fast reactions.
- The HDM reactions of both Ni-TPP and VO-TPP over sulfided $V_7Al_2O_3$ catalysts are clearly structure sensitive. With increasing vanadium loading of the catalysts hydrogenation rates for both Ni-TPP and VO-TPP increase until, at loadings exceeding 2 atoms V/nm^2 , crystalline V_2O_3 is present on the catalysts. The presence of crystalline V_2O_3 results in a loss of hydrogenation activity probably caused by coverage of active sites by crystalline material. The hydrogenolysis rate is not affected by the presence of crystalline V_2O_3 .

Acknowledgements

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Figure 1. Concentration versus reaction time plot of a HDM experiment with Ni-TPP at 573 K (run Ni-32). Experimental values are represented by markers. Solid lines represent calculated values.

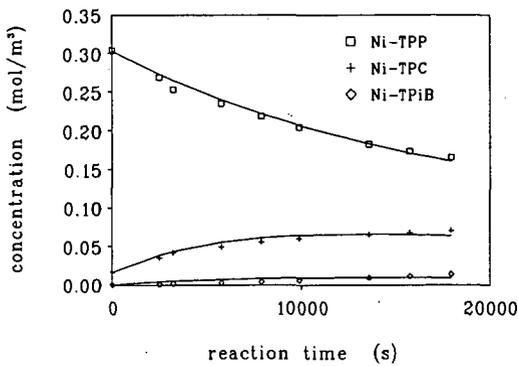


Figure 2. Concentration versus reaction time plot of a HDM experiment with VO-TPP at 573 K (run V-32). Experimental values are represented by markers. Solid lines represent calculated values.

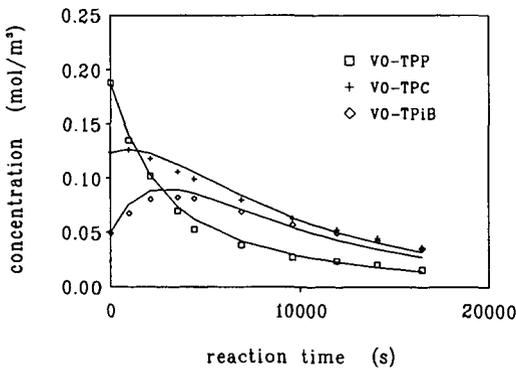


Figure 3. Reversible sequential reaction model for the HDM of M-tetraphenylporphyrins (M=Ni,VO). Deposited metal sulfides are represented by MS_x .

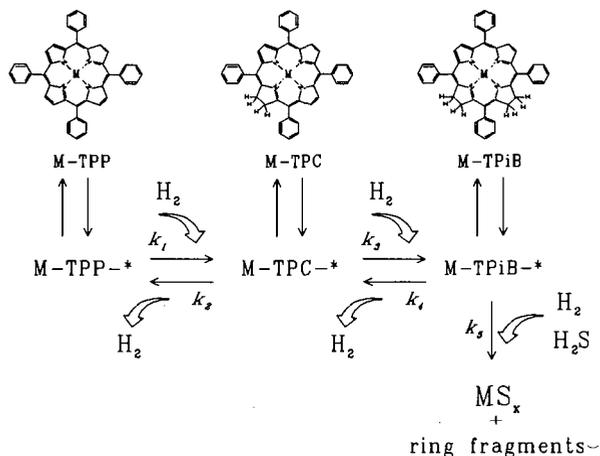


Figure 4. Intrinsic rate constants for the HDM of Ni-TPP at 573 K as a function of the vanadium loading of the catalysts (k_2, k_4 omitted).

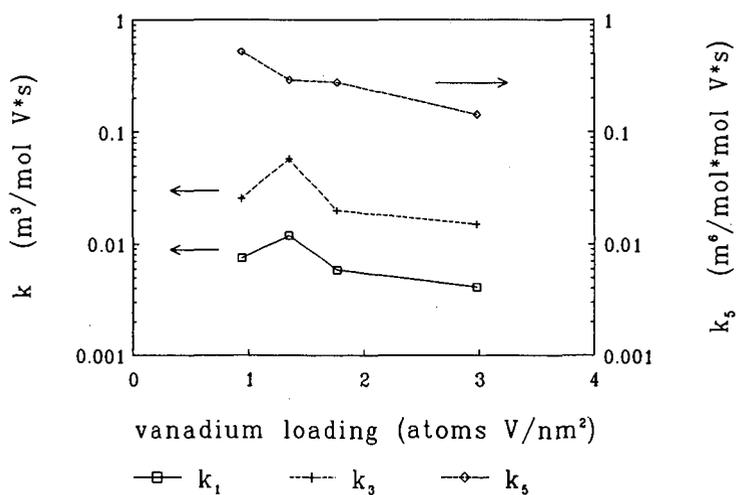


Figure 5. Intrinsic rate constants for the HDM of VO-TPP at 573 K as a function of the vanadium loading of the catalysts (k_2 , k_4 omitted).

