The activity of transition metal nitrides for hydrotreating quinoline and thiophene

Hiroshi Abe, Tsz-keung Cheung and Alexis T. Bell

Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley Laboratory
and Department of Chemical Engineering, University of California, Berkeley,
CA 94720-9989, USA

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An investigation has been conducted of the activity of AlN, BN, TiN, VN, Mo_2N, and W_2N as catalysts for quinoline hydrodenitrogenation (HDN). The activity of Mo_2N and VN for thiophene hydrodesulfurization (HDS) and the concurrent hydrotreatment of quinoline and thiophene have also been examined. Bulk AlN, BN, and TiN were obtained with low surface areas and found to be inactive for the HDN of quinoline. Bulk Mo_2N, W_2N, and VN could be obtained with high surface area. Each of these nitrides exhibited high activity for quinoline HDN, the turnover frequency for this reaction decreasing in the order $Mo_2N > W_2N > VN$. Highly dispersed VN supported on SiO_2 was found to have a specific activity for quinoline HDN identical to that of bulk VN. Both bulk Mo_2N and 27% VN/SiO_2 exhibit high activity for the HDS of thiophene. The behavior of these two catalysts for the concurrent hydrotreatment of quinoline and thiophene is also discussed.

Keywords: Metal nitride catalysis; quinoline hydrodenitrogenation; thiophene hydrodesulfurization

1. Introduction

Transition metal nitrides have recently been shown to be active catalysts for hydrotreating nitrogen- and sulfur-containing compounds. Schlatter et al. [1] have reported that Mo_2N has an activity for the hydrodenitrogenation (HDN) of quinoline that is comparable to that of sulfided NiMo/Al_2O_3, but is more selective for the formation of aromatic products. Lee et al. [2] have made similar observations. Studies of the reaction pathway revealed that upon contact with Mo_2N quinoline undergoes rapid hydrogenation to form 1,2,3,4-tetrahydroquinoline. This product then reacts more slowly to form 2-propylanaline which, in turn, undergoes hydrogenolysis of the C–N bond in the saturated ring to form propylbenzene. HDN of pyridine over a series of molybdenum nitride catalysts has been reported by Choi et al. [3]. Mo_2N was found to exhibit higher activity and better C–N bond hydrogenolysis selectivity than sulfided Co–Mo hydrotreatment catalysts. The hydrodesul-

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furization (HDS) of thiophene over Mo_2N was first described by Markel and Van Zee [4]. During reaction, butene originated primarily from C–S bond cleavage of tetrahydrothiophene, formed via the hydrogenation of thiophene, rather than by the direct desulfurization of thiophene. A comparison of the activity of Mo_2N for HDN of indole and HDS of thiophene has recently been reported by Abe and Bell [5]. The catalyst was observed to be much more active for HDS of benzothiophene than HDN of indole, but the reaction pathway for both processes was similar. In both cases, hydrogenation of the heterocyclic ring occurred first followed by cleavage of X–C (X = S or N) bond in the saturated ring and release of the heteroatom as XH_n. The hydrocarbon produced in the last step of the sequence was ethylbenzene. More recently, Nagai et al. [6] have found that alumina-supported Mo_2N is effective in catalyzing the HDS of dibenzothiophene, producing biphenyl as the primary product. In the present study, an investigation was carried out of the activity and selectivity of bulk AlN, BN, TiN, VN, Mo_2N, and W_2N, as well as supported VN, for quinoline HDN. The activity of Mo_2N and VN for thiophene HDS and concurrent hydrotreatment of quinoline and thiophene were also examined.

2. Experimental

Bulk Mo_2N, W_2N, and VN were prepared from the oxide of each metal following the procedure of Volpe and Boudart [7]. Mo_2N (100%) was purchased from Aldrich, WO_3 (99.9994%) was purchased from Strem Chemicals, and V_2O_5 (99%) was purchased from Fisher Scientific. The oxide powder was pressed, ground, and sieved to yield granules of 30–60 mesh. The granules were then placed in a quartz reactor and reduced in flowing NH_3. The reduction temperature was increased from 395 to 623 K over a 3.5 h period, held at 623 K for 1 h, increased to 723 K over a 3 h period, then increased from 723 to 973 K during the course of 1 h, and finally held at 973 K for 1 h. X-ray diffraction of a freshly prepared sample showed the characteristic pattern for the nitride and no evidence of the starting oxide. AlN, BN, and TiN were purchased from Aldrich and renitrided with NH_3 using the heating schedule described above. Supported VN was prepared by dispersing V_2O_5 on either SiO_2 (Cabosil-L90, 90 m^2/g), Al_2O_3 (Degussa C, 100 m^2/g), or TiO_2 (Degussa P25, 50 m^2/g), following the procedure described by Went et al. [8]. The dispersed vanadia was then nitrided using the same procedure used to prepare bulk VN. The total BET surface area of each catalyst was determined by N_2 adsorption at LN_2 temperature, and the concentration of active sites was characterized by NH_3 adsorption at room temperature.

All reactions were carried out in the quartz microreactor used for the catalyst preparation. Quinoline (Aldrich, 99+%) and thiophene (Aldrich, 99%) were delivered by a syringe pump into a flow of H_2 at 1 atm. To ensure complete vaporization of the liquid feed, the portion of the flow manifold located down stream of the point of liquid introduction was maintained at 500 K. Hydrogen was purified by passage through a catalytic oxygen remover. The flow rate of H_2 was maintained at 110 cm^3/min and flow rate of the liquid feed was 0.1 cm^3/h.

The effluent from the reaction was analyzed by on-line gas chromatography. Products were separated using a 60 m long, 0.25 mm i.d. capillary column coated with a 1 mm thick film of polydimethylsiloxane. Product identification was carried out off-line by gas chromatography/mass spectrometry.

3. Results and discussion

AlN, BN, and TiN exhibited BET surface areas of 5–6 m^2/g. These materials were found to be totally inactive for quinoline HDN at 723 K, and, hence, were not investigated further. By contrast, VN, Mo_2N, and W_2N all exhibited significant HDN activity. Table 1 lists the BET surface area, the NH_3 chemisorption capacity for each of these materials, together with the quinoline conversion observed at 723 K, the rate of quinoline conversion per gram of catalyst, and the turnover frequency for quinoline consumption based on NH_3 chemisorption capacity of each catalyst. The distribution of products formed over each catalyst is given in table 2. It is evident from table 1 that the activity for quinoline conversion to all products decreases in the order $Mo_2N > W_2N > VN$. Similar product distributions were obtained with each of the three catalysts, as may be seen from table 2. However, the extent of quinoline HDN was found to increase with increasing conversion.

The activity of supported VN is compared to that of bulk VN in table 3. After 1 h under reaction conditions the activity of VN/TiO_2 on a per gram basis is more than twice as high as that of VN/SiO_2 or VN/Al_2O_3, and comparable to that of bulk VN. After 2.5 h of use both the VN/TiO_2 and bulk VN exhibit a significant loss in activity, relative to VN/SiO_2 and VN/Al_2O_3. In fact, after 2.5 h under reaction conditions the activities of all four catalysts are roughly comparable.

The effects of VN weight loading on activity per gram of VN for SiO_2-supported VN is presented in fig. 1. The specific activity increases with increasing VN loading

Table 1
BET area, NH_3 chemisorption capacity, quinoline conversion, quinoline HDN activity for bulk Mo_2N, W_2N, and VN[a]

Catalyst	BET area (m^2/g)	NH_3 ads. (μmol/g)	Conv. (%)	R (μmol/g s)	TOF (s^{-1})
Mo_2N	208	60	30	6.8×10^{-2}	1.1×10^{-3}
W_2N	90	26[b]	26	5.7×10^{-2}	9.5×10^{-4}
VN	31	72	12	2.6×10^{-2}	3.7×10^{-4}

[a] Reaction conditions: temperature = 723 K; catalyst weight = 1 g; quinoline flow rate as liquid = 0.1 cm^3/h; H_2 flow rate = 110 cm^3/min; reaction time = 2.5 h.

[b] Calculated on the assumption that the NH_3 uptakes per BET area on W_2N and Mo_2N are identical.

Table 2
Distribution of products formed during quinoline HDN over bulk Mo_2N, W_2N, VN, and 27% VN/SiO_2 [a]

Product (%)	Catalyst			
	Mo_2N	W_2N	VN	27% VN/SiO_2
benzene	23.4	13.1	15.6	7.7
toluene	29.6	17.0	20.6	23.8
ethylbenzene	3.8	5.1	3.8	10.7
propylbenzene	1.3	12.9	2.9	8.4
2,3-dihydroindene	11.3	2.4	12.8	31.7
benzene total	69.4	50.5	53.7	82.3
2-methylaniline	2.4	6.9	5.9	3.3
methylquinoline	9.6	16.0	22.7	5.7
1,2,3,4-THQ	2.8	9.6	6.5	3.8
methylindole	15.7	17.1	9.0	4.9
N-compounds total	30.5	49.6	44.1	17.7
quinoline conv. (%)	30.0	27.0	12.5	39.0

[a] Reaction conditions: temperature = 723 K; catalyst weight = 1 g; quinoline flow rate as liquid = 0.1 cm^3/g; H_2 flow rate = 110 cm^3/min; reaction time = 2.5 h.

up to a loading of 27%, whereafter the specific activity passes through a maximum and then falls very rapidly towards that characteristic of bulk VN. The increase in specific activity observed for loadings below 27% may be due to incomplete conversion of the dispersed vanadia to VN, as a result of difficulties in NH_3 reduction of the V–O–Si bonds which connect the dispersed vanadia to the support. Curiously, the turnover frequencies based on sites titrated by NH_3 adsorption are nearly the same for 27% VN/SiO_2 and bulk VN. After reaction for 2.5 h under the standard reaction conditions the turnover frequencies were 3.9×10^{-4} s^{-1} for 27% VN/SiO_2 and 3.7×10^{-4} s^{-1} for bulk VN, indicating that the intrinsic activity of supported

Table 3
Comparison of the activities of unsupported and supported VN [a]

Catalyst	Quinoline conversion (%)	
	1 h	2.5 h
VN	22.2	12.0
7% VN/TiO_2	26.0	10.0
7% VN/SiO_2	12.3	11.9
7% VN/Al_2O_3	10.8	8.4

[a] Reaction conditions: temperature = 723 K; catalyst weight = 1 g; quinoline flow rate as liquid = 0.1 cm^3/h; H_2 flow rate = 110 cm^3/min; reaction time = 2.5 h.

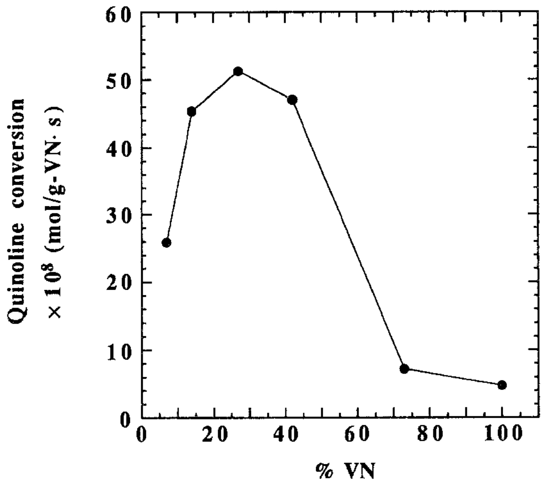

Fig. 1. The effects of weight loading on the specific activity of SiO_2-supported and bulk VN.

VN is identical to that of bulk VN. Based on these findings, we may conclude that the dispersion of VN is essentially 100% for 27% VN/SiO_2. The decline in specific activity observed for VN loadings above 27% may be due to a decrease in the dispersion of VN.

The distribution of products formed over the 27% VN/SiO_2 catalyst is shown in table 2. The higher extent of HDN over this catalyst compared to bulk VN is simply a reflection of the higher per gram activity of the supported catalyst.

The activities of bulk Mo_2N and 27% VN/SiO_2 for the reactions of quinoline and thiophene are compared in table 4. The turnover frequency for quinoline consumption is almost a factor of three higher for Mo_2N than 27% VN/SiO_2, but the turnover frequency for thiophene consumption is a factor of ten higher for Mo_2N than for 27% VN/SiO_2. The only carbon-containing products observed from the

Table 4
Comparison of the activities of Mo_2N and 27% VN/SiO_2 for quinoline HDN and thiophene HDS [a]

Catalyst/feed	Conversion (%)		TOF (s^{-1})	
	thiophene	quinoline	thiophene	quinoline
Mo_2N				
pure	98.0	30.0	3.6×10^{-3}	1.1×10^{-3}
mixed [b]	95.0	27.0	3.5×10^{-3}	9.9×10^{-4}
27% VN/SiO_2				
pure	35.0	39.0	3.5×10^{-4}	3.9×10^{-4}
mixed [b]	68.0	9.0	6.8×10^{-4}	9.0×10^{-4}

[a] Reaction conditions: temperature = 723 K; catalyst weight = 1 g; quinoline (thiophene) flow rate as liquid = 0.1 cm^3/g; H_2 flow rate = 110 cm^3/min; reaction time = 2.5 h.

[b] Quinoline/thiophene = 9/1.

reaction of thiophene were butenes and butane. Thus, while the turnover frequencies of 27% VN/SiO_2 for the reactions of quinoline and thiophene are comparable, the turnover frequency for the reaction of thiophene is about 3.5 times higher than the turnover frequency for quinoline over Mo_2N.

Table 4 also shows the results of experiments in which a 9/1 mixture of quinoline to thiophene was fed to the reactor. In the case of Mo_2N, the activities for the reactions of quinoline and thiophene were affected to only a slight degree, whereas in the case of 27% VN/SiO_2, the activity for the reaction of quinoline deceased significantly, while that for the reaction of thiophene increased by nearly a factor of

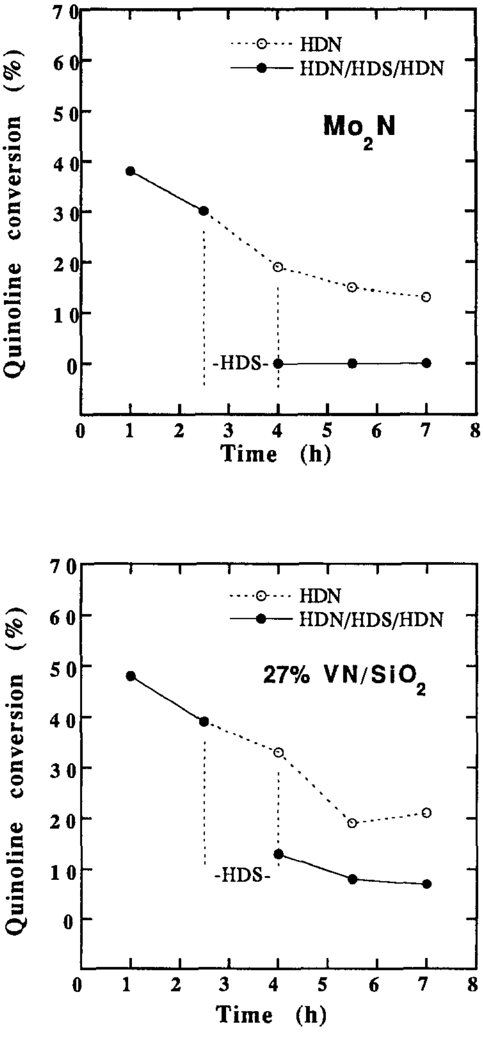

Fig. 2. Comparison of the activities of Mo_2N and 27% VN/SiO_2 for quinoline HDN before and after use of the catalyst for thiophene HDS.

two. It is interesting to compare these results with those shown in fig. 2 for experiments in which Mo_2N and 27% VN/SiO_2 were first exposed to a feed containing quinoline in H_2 for 2.5 h, then to a feed containing thiophene for 1.5 h, and finally to a feed containing quinoline again. In the case of Mo_2N the catalyst is completely deactivated for quinoline HDN after exposure to thiophene but 27% VN/SiO_2, while experiencing significant loss in activity, continues to retain a noticeable activity even after having seen thiophene. These results suggest that H_2S formed during the hydrotreatment of thiophene over Mo_2N is so strongly bound that it blocks the adsorption of quinoline, when hydrotreatment of quinoline is resumed after a brief use of the catalyst for thiophene HDS. By contrast, 27% VN/SiO_2 is presumed to adsorb H_2S less strongly than Mo_2N, and, hence, 27% VN/SiO_2 retains its activity even after use for thiophene HDS. Interpretation of the results obtained when quinoline and thiophene are fed together cannot be readily explained and must await the results of studies currently in progress.

4. Conclusions

Bulk Mo_2N, W_2N, and VN all exhibit catalytic activity for quinoline HDN, whereas AlN, BN, and TiN are inactive. Based on sites titrated by NH_3 chemisorption at room temperature, the turnover frequency for the conversion of quinoline to all products decreases in the order $Mo_2N > W_2N > VN$. The turnover frequency for highly dispersed VN on SiO_2 was found to be identical to that of bulk VN. For identical reaction conditions the turnover frequency for quinoline hydrotreatment is almost a factor of three higher for Mo_2N than for 27% VN/SiO_2, but the turnover frequency for thiophene hydrotreatment is a factor of ten times higher for Mo_2N than 27% VN/SiO_2. The HDN and HDS activities of Mo_2N are unaffected when a 9/1 mixture of quinoline and thiophene are reacted together. By contrast, the HDS activity of 27% VN/SiO_2 increases and its HDN activity decreases when this catalyst is exposed to a mixture of quinoline and thiophene.

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