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Hydrodenitrogenation of Quinoline over High-Surface-Area Mo_2N

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The reaction pathway for the hydrodenitrogenation of quinoline over Mo_2N has been investigated. Quinoline is found to undergo a rapid hydrogenation to form 1,2,3,4,-tetrahydroquinoline. This product then reacts more slowly to form 2-propylaniline, which, in turn, undergoes hydrogenolysis of the C–N bond in the saturated ring to form propylbenzene. No evidence is found for propylcyclohexane.

INTRODUCTION

The removal of nitrogen from organonitrogen compounds present in petroleum is carried out by hydrodenitrogenation (HDN). The catalysts used most frequently for HDN are sulfided $CoMo/Al_2O_3$ or $NiMo/Al_2O_3$. While effective, these catalysts require complete saturation of all aromatic rings prior to removal of nitrogen, resulting in a consumption of hydrogen that is significantly higher than the minimum required for the removal of nitrogen atoms (*1*). Recent work by Schlatter *et al.* (*2*) has shown that molybdenum carbides and nitrides might offer an interesting alternative to existing HDN catalysts. It was reported that Mo_2C and Mo_2N have HDN activities comparable to that of commercial $NiMo/Al_2O_3$ catalysts, but exhibit much higher selectivities for the formation of aromatic products. The aim of the present study is to elucidate the reaction pathways for nitrogen removal from quinoline over Mo_2N.

EXPERIMENTAL

The fcc phase of Mo_2N was prepared following the procedure of Volpe and Boudart (*3*). MoO_3 powder was pressed, ground, and sieved to yield granules of 30–60 mesh. The granules were placed in a quartz reactor and then 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 over a 2-h period, and finally held at 973 K for 1 h. X-ray diffraction of a freshly prepared sample showed a characteristic pattern for Mo_2N and no evidence of residual MoO_3. The BET area of a freshly prepared sample was typically in excess of 200 m^2/g.

All reactions were carried out in the quartz microreactor used for catalyst synthesis. Hydrogen was purified by passage through a catalytic oxygen remover, and the rate of delivery was set using a mass flow controller. Liquid feeds were delivered to the flow manifold using a syringe pump. To assure complete vaporization of liquid feeds, the portion of the flow manifold located downstream from the point of liquid introduction was maintained at a temperature above 500 K. The flow rate of H_2 was maintained at 110 cm^3/min and the liquid flow rate was 0.1 cm^3/h.

The effluent from the reactor 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 offline by gas chromatography/mass spectrometry.

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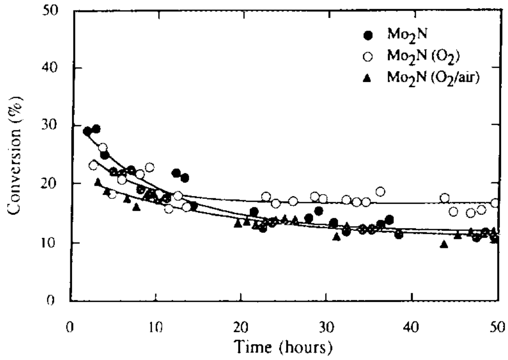

FIG. 1. Quinoline conversion versus time over Mo_2N, $Mo_2N(O_2)$, and $Mo_2N(O_2/air)$; T = 723 K.

RESULTS AND DISCUSSION

The time dependence of the activity of Mo_2N for quinoline HDN was determined for three catalyst samples referred to as Mo_2N, $Mo_2N(O_2)$, and $Mo_2N(O_2/air)$. The first is an as-prepared sample, the second is a sample passivated by exposure to a 1% O_2/He mixture, and the third is a passivated sample that has been air exposed. Figure 1 shows the conversion of quinoline as a function of time at 723 K. The freshly prepared catalyst exhibits the highest initial conversion, but then loses activity over time. The initial activity of $Mo_2N(O_2)$ is less than that of Mo_2N, as is the loss in activity of with time. $Mo_2N(O_2/air)$ is the least active sample at short time and decays to nearly the same activity as the freshly prepared catalyst at longer times. Measurements of the BET surface area before and after 50 h of reaction indicate a decrease from 230 to 145 m^2/g, from which it is concluded that most of the observed loss in activity with time is due to a loss in BET surface area.

Although the conversion of quinoline decreases with time over each catalyst tested, there is virtually no change in the product distribution. The average selectivity over the 50-h reaction period is listed in Table I for each sample. Complete nitrogen removal is achieved from over 70% of the feed in each case. Benzene and toluene are the most abundant products. The selectivity to benzene and toluene is greater over the passivated and passivated/air-exposed samples than over the as-prepared sample. This increase in selectivity is accompanied by a decrease in selectivity to 2,3-dihydroindene and 2-methylindole.

TABLE I

Effect of Catalyst Pretreatment on Distribution of Products Formed at 723 K

Compound	Mo_2N	$Mo_2N(O_2)$	$Mo_2N(O_2/air)$
Benzene	21.5	25.0	25.2
Methylbenzene	23.2	27.1	25.9
Ethylbenzene	5.5	5.0	4.9
Propylbenzene	2.6	2.5	2.4
2,3-Dihydroindene	19.6	14.3	14.9
2-Methylaniline	3.3	3.3	4.0
n-Methylquinoline[a]	5.6	8.3	6.9
2-Methylindole	18.7	14.5	15.9

[a] n = 2, 5, or 6.

The dependence of quinoline conversion on temperature over freshly prepared Mo_2N is given in Fig. 2, whereas the distribution of the principal products is given in Fig. 3. The group of products referred to as analine total is comprised of 2-methylaniline (2-MA) and 2-propylaniline (2-PA), whereas the group referred to as benzene total is comprised of benzene, methylbenzene, ethylbenzene, propylbenzene (PB), and 2,3-dihydroindene. The distributions of individual products in the total aniline and total benzene groups are shown in Figs. 4 and 5, respectively.

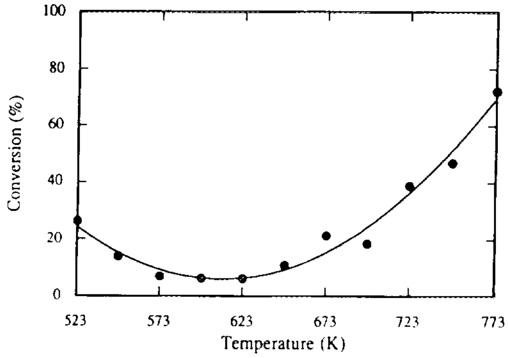

FIG. 2. Effect of temperature on the conversion of quinoline.

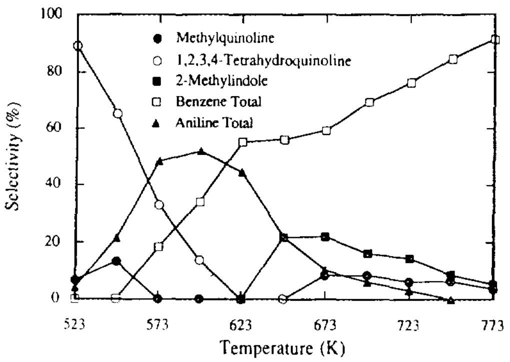

FIG. 3. Effect of temperature on the distribution of products formed during the HDN of quinoline.

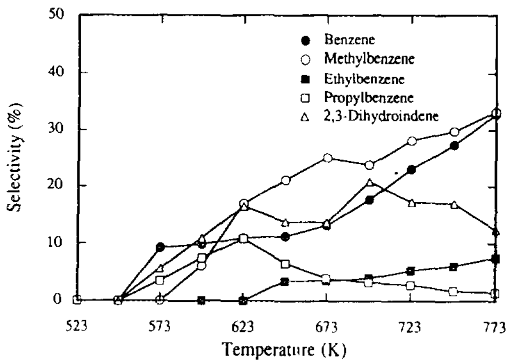

FIG. 5. Effect of temperature on the distribution of benzene compounds formed during the HDN of quinoline.

It can be seen from Fig. 2 that up to a temperature of 623 K, the conversion of quinoline decreases with increasing temperature, whereas above 623 K, the conversion increases with increasing temperature. This pattern suggests that at temperatures below 623 K, the reaction is equilibrium limited by an exothermic process, and that above 623 K, the kinetics for converting the products of the equilibrium reaction to other products become sufficiently rapid to give rise to an increase in the conversion of quinoline with increasing temperature. Since 1,2,3,4-tetrahydroquinoline (1-THQ) is the principal product observed at 523 K, and the selectivity to this product decreases monotonically with increasing temperature, it is proposed that the relevant equilibrium process is the hydrogenation of 1-THQ, an exothermic process. To support this hypothesis, experiments were conducted in which 1-THQ was used as the feed. Figures 6 and 7 show that the conversion of 1-THQ and the distribution of products formed are identical to those observed for quinoline over the range of reaction temperatures investigated.

It is evident from Figs. 3–5 that with increasing temperature 1-THQ reacts first to 2-PA and 2-MA. To understand the reaction pathways to 2-MA and the release of nitro-

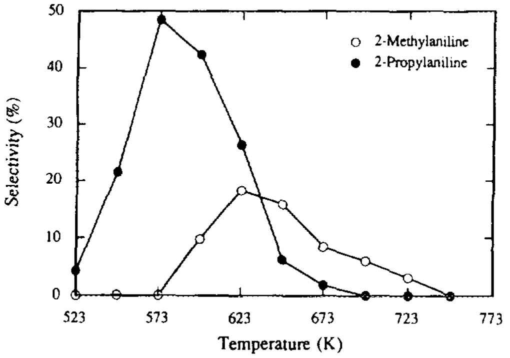

FIG. 4. Effect of temperature on the distribution of aniline compounds formed during the HDN of quinoline.

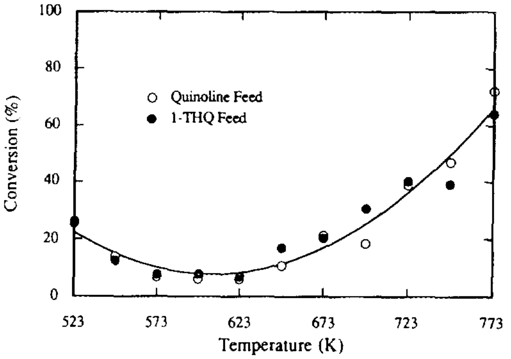

FIG. 6. Effect of temperature on the conversion of quinoline and 1,2,3,4-tetrahydroquinoline (1-THQ). The definition of 1-THQ conversion excludes quinoline as a product.

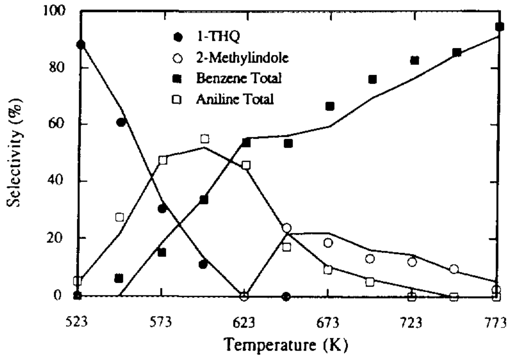

FIG. 7. Effect of temperature on the distribution of products formed during the HDN of quinoline and 1-THQ. Selectivities are defined so as to exclude quinoline as a product. The points indicate data obtained with 1-THQ as the feed and the solid lines are for quinoline as the feed. The data points for quinoline are not shown but are the same as those seen in Fig. 3.

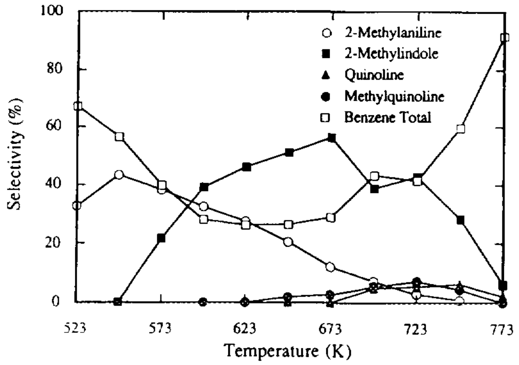

FIG. 9. Effect of temperature on the distribution of products formed during the HDN of 2-propylaniline.

gen from the benzene ring, studies were conducted with 2-PA as the feed. Figure 8 illustrates the conversion of 2-PA as a function of temperature, whereas Figs. 9 and 10 show corresponding plots of product selectivities. For temperatures below 548 K, PB and 2-MA are the only products observed, indicating that 2-PA readily undergoes loss of the NH_2 group and hydrogenolysis of the $\alpha\beta$ C–C bond of the propyl group. At temperatures above 548 K, 2-PA undergoes ring closure to form significant amounts of 2-methylindole, but above 673 K undergoes hydrodenitrogenation to form alkylbenzenes. The formation of benzene and alkylbenzenes from quinoline occurs above 553 K. Benzene and alkylbezenes are formed by the hydrogenolysis and dealkylation of propylbenzene, and by the deamination of 2-MA.

The results obtained with 1-THQ and 2-PA as the feed suggest that the slow step in the hydrodenitrogenation of quinoline is cleavage of the C–N bond in 1-THQ to form 2-PA. This conclusion is supported by the plot of extent of nitrogen removal vs temperature shown in Fig. 11. It is apparent that the data for quinoline, 1-THQ, and 5-THQ all show nearly the same temperature de-

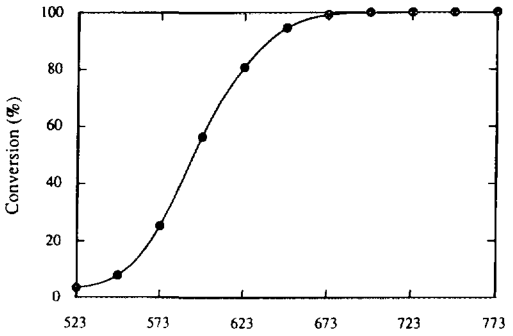

FIG. 8. Effect of temperature on the conversion of 2-propylaniline.

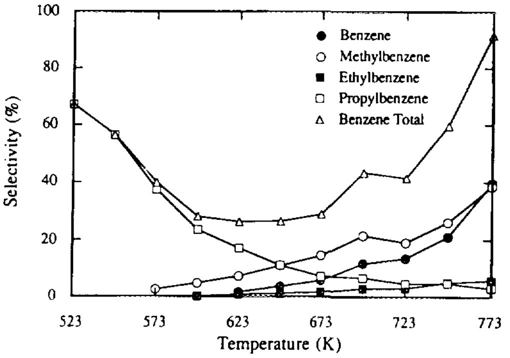

FIG. 10. Effect of temperature on the distribution of benzene products formed during the HDN of 2-propylaniline.

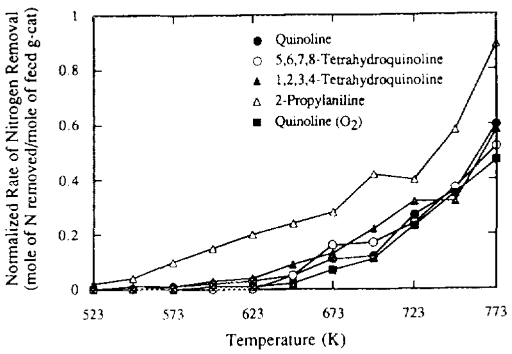

FIG. 11. Effect of temperature on the normalized rate of nitrogen removal from quinoline and various reaction intermediates.

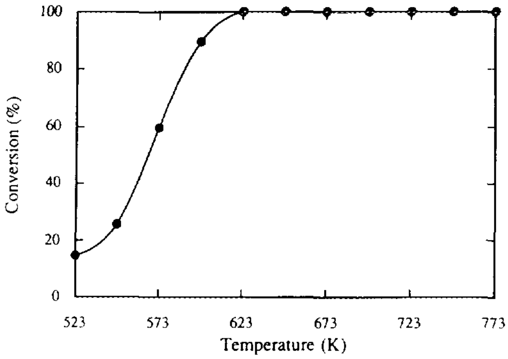

FIG. 12. Effect of temperature on the conversion of propylbenzene.

pendence, whereas the data for 2-PA indicate that nitrogen is removed more readily from this reactant. The apparent activation energy for nitrogen removal from each feed, E_a, is listed in Table 2 for each feed. The value of E_a for 2-PA is seen to be significantly lower than that for quinoline, 1-THQ, or 5-THQ.

It is noteworthy that the reaction products produced from both quinoline and 2-PA contain no evidence of cyclohexane or alkylcyclohexanes. The absence of these products is attributed to a weak interaction of the benzene ring with the catalyst surface. To test this hypothesis, experiments were conducted using propylbenzene as the feed. Figure 12 displays the conversion of PB versus temperature, and the distribution of products formed are presented in Figs. 13 and 14. At 523 K propylcyclohexane makes up 63% of the products, but the selectivity to this product decreases rapidly as the temperature increases, due to equilibrium considerations. With increasing temperature the selectivity to benzene increases rapidly. Toluene and ethylbenzene are also produced, but to a lesser extent, and the selectivities to these products pass through a maximum as the temperature is raised above 573 K. Above 698 K benzene undergoes rapid decomposition to form a variety of low molecular weight alkanes.

The results presented in Fig. 14 indicate that when PB is fed alone it undergoes dealkylation, and hydrogenolysis of the alkyl chain at significantly lower temperatures than when PB is derived from quinoline or

TABLE 2

Apparent Activation Energies for HDN

Feed	E_a (kcal/mol)[a]
Quinoline	17.6
1,2,3,4-Tetrahydroquinoline	16.9
5,6,7,8-Tetrahydroquinoline	16.5
2-Propylaniline	10.5

[a] Based on the data presented in Fig. 11.

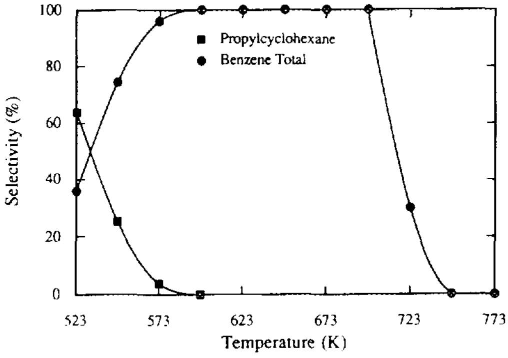

FIG. 13. Effect of temperature on the distribution of products formed from propylbenzene.

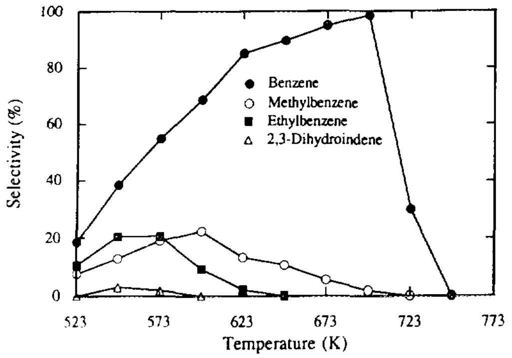

FIG. 14. Effect of temperature on the distribution of benzene products formed from propylbenzene.

2-PA. A second difference is the absence of any evidence of benzene decomposition when this species is produced as a product of quinoline or 2-PA HDN. To determine whether ammonia might suppress the hydrogenolysis and dealkylation of PB, and the decomposition of benzene, experiments were carried out in which ammonia was introduced together with H_2. The results presented in Table 3 indicate that at 673 K, the presence of NH_3 almost completely suppresses the hydrogenolysis and dealkylation activities of Mo_2N, and suppresses the decomposition of benzene to low molecular weight hydrocarbons.

TABLE 3a

Effects of Ammonia on the Dealkylation and Hydrogenolysis of PB at 673 K

Run no.	1	2	3
Feed flowrate			
PB (cm^3/h)	0.1	0.1	1.4
NH_3 (cm^3/min)	0.0	5.0	1.6
H_2 (cm^3/min)	110	110	110
Product comp. (mol %)			
PB	0.0	93.4	94.0
EB	0.0	1.7	1.7
Toluene	7.0	2.8	2.9
Benzene	93.0	0.7	0.8

TABLE 3b

Effects of Ammonia on Benzene Decomposition at 823 K

Run no.	1	2
Feed flowrate		
Benzene (cm^3/h)	0.1	0.1
NH_3 (cm^3/min)	0.0	1.9
H_2 (cm^3/min)	110	110
Conversion of Benzene to HC's (%)	100	67

The overall reaction network for quinoline HDN over Mo_2N deduced from the present study is summarized in Fig. 15. The first reaction is the hydrogenation of quinoline to 1-THQ. This process is very rapid and achieves thermodynamic equilibrium already at 523 K, as indicated by the data presented in Figs. 6 and 7. The removal of nitrogen from 1-THQ is initiated by the cleavage of the C–N bond in the saturated ring, to form 2-PA. The occurrence of this reaction is suggested by the appearance of large quantities of 2-PA when 1-THQ reacts at temperatures above 523 K. 2-PA then undergoes a loss of the amine group to form PB (see Fig. 10). In parallel reactions, 2-PA can react to form 2-methylindole via ring closure or 2-MA via hydrogenolysis of the propyl group (see Figs. 9 and 10). The loss of the amine group from 2-MA leads to toluene. PB reacts, in turn, to form 2,3-dihydroindole via ring closure, ethylbenzene and toluene via hydrogenolysis of the propyl group, or benzene via dealkylation (see Figs. 13 and 14).

The reaction network shown in Fig. 15 is similar to that observed for HDN of quinoline over sulfided $NiMo/Al_2O_3$. Over both Mo_2N and sulfided $NiMo/Al_2O_3$, quinoline undergoes rapid hydrogenation to achieve an equilibrium concentration of 1-THQ. Neither catalyst produces any 5-THQ, even though the equilibrium constant for the formation of this product is nearly six times greater than that for formation of 1-THQ (*4*, *5*). However, in contrast to sulfided NiMo/Al_2O_3, Mo_2N does not catalyze the further hydrogenation of 1-THQ to decahydroquinoline. It is this critical difference that gives rise to the formation of 2-PA, rather than 2-

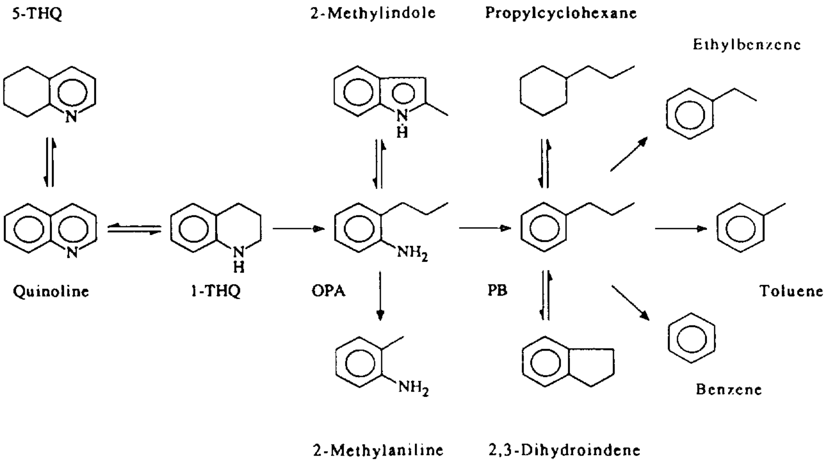

FIG. 15. Proposed reaction network for HDN of quinoline over Mo_2N.

propylcyclohexylamine as the primary product of HDN.

4. CONCLUSIONS

Bulk Mo_2N is an active catalyst for HDN of quinoline. Freshly prepared, passivated, and air-exposed samples exhibit similar activities and selectivities. In all cases, benzene and alykylbenzenes are produced as the final products. A loss in HDN activity with time under reaction conditions, attributable to a reduction in the BET surface area, is observed; however, this change does not affect product selectivity.

HDN is initiated by a rapid, equilibrium conversion of quinoline to 1-THQ. This step is followed by hydrogenolysis of the saturated ring to form 2-PA. The principal reaction of 2-PA involves loss of the amine group to form PB; PB then undergoes dealkylation and hydrogenolysis. Both of these processes are inhibited, though, by the presence of ammonia in the product gases.

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