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INVESTIGATIONS OF HYDRODENITROGENATION OF QUINOLINE OVER MOLYDENUM NITRIDE

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Abstract

An investigation has been carried out of the reaction pathway for the hydrodenitrogenation of quinoline over Mo_2N. Quinoline is found to undergo a 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. No evidence is found for propylcyclohexane.

1. INTRODUCTION

The removal of nitrogen from organonitrogen compounds present in petroleum is carried out by hydrodenitrogenation (HDN). The catalysts most frequently used for this purpose 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. Recent work by Schlatter et al. (1) has shown that molybdenum carbides and nitrides might offer an interesting alternative to existing HDN catalysts. Both Mo_2C and Mo_2N are reported to have HDN activities comparable to that of commercial $NiMo/Al_2O_3$ catalysts, but ehxibit much higher selectivities for the formation of aromatic products. The aim of the present study is to gain some insight into the reaction pathway for nitrogen removal from quinoline over Mo_2N.

2. EXPERIMENTAL

The fcc phase of Mo_2N was prepared following the procedure of Volpe and Boudart (2). 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 reaction were carried out in a quartz microreactor heated by a tube furnace. 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 μm thick film of polydimehylsiloxane. Product identification was carried out by off-line gas chromatography/mass spectrometry.

3. RESULTS AND DISCUSSION

The time dependence of the activity of Mo_2N for quinoline HDN was determined for freshly prepared Mo_2N, Mo_2N passivated by exposure to a 1% O_2/He mixture, and passivated

Mo_2N that had been air exposed. At 723 K, the conversion of quinoline over the freshly prepared sample decreased from 30 % to 10 % in 30 h and then remained constant for an additional 20 h. Passivation and air exposure reduced the initial conversion to about 25 % but did not significantly affect the long-term activity of the catalyst. Measurements of the BET surface area before and after 50 h of reaction indicated a decrease from 230 m^2/g to 145 m^2/g, from which it is concluded that most of the loss in activity with time is due to a loss in the BET surface area of the catalyst. Consistent with this interpretation it is observed that the product selectivity is virtually the same, independent of catalyst pretreatment and duration under reaction conditions.

The dependence of quinoline conversion on temperature over freshly prepared Mo_2N is given in Figure 1. Between 523 and 623 K, the conversion 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, whereas at temperatures 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.

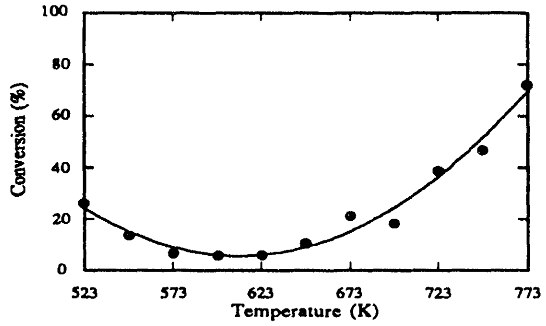

Figure 1. Quinoline conversion versus temperature

The distribution of the principal products is given in Figure 2. In Figure 2, the group of products referred to as analine total is comprised of 2-methylananline (2-MA) and 2-propylanaline (2-PA), whereas the group referred to as benzene total is comprised of benzene, methylbenzene (toluene), ethylbenzene, propylbenzene (PB), and 2,3-dihydroindene. The distributions of individual products in the total analine and total benzene groups are shown in Figures 3 and 4, respectively.

Figure 2 shows that at 523 K, the principal product is 1,2,3,4-tetrahydroquinoline (1-THQ). Experiments conducted with 1-THQ as the feed indicate that for temperatures greater than or equal to 523 K thermodynamic equilibium is attained between quinoline and 1-THQ. Since the hydrogenation of quinoline is an exothermic process, the observed decreases in quinoline conversion as the temperature is increased from 523 to 623 K is attributable to a decrease in the equilibrium conversion of quinoline. Above 623 K, the kinetics of 1-THQ conversion to products other than quinoline is suffcient to to achieve an increase in quinoline conversion with increasing temperature.

It is evident from Figures 2-4, that with increasing temperature 1-THQ reacts first to 2-PA and 2-MA. Studies conducted with 2-PA as the feed indicate that 2-MA is formed by hydrogenolysis of the propyl group. At temperatures above 623 K, 2-PA can undergo ring closure to form 2-methylindole. The formation of benzene and alkylbenzenes from quinoline occurs above 553 K (see Figures 3 and 5). Here again, experiments conducted with 2-PA as the feed indicate that benzene and alkylbezenes are formed by the release of the NH_2 group of 2-PA to form PB and ammonia, and the subsequent hydrogenolysis and dealkylation of PB to form methylbenzene and benzene, respectively.

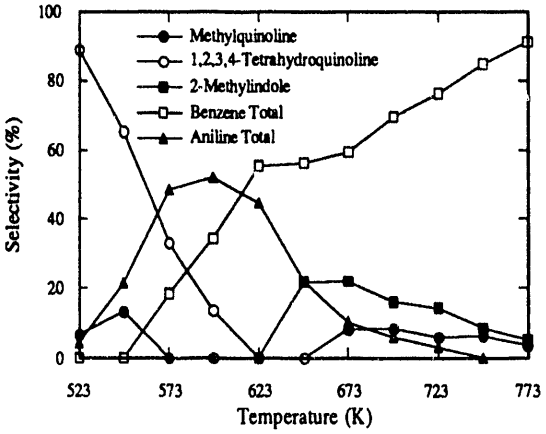

Figure 2. Product selectivity versus temperature

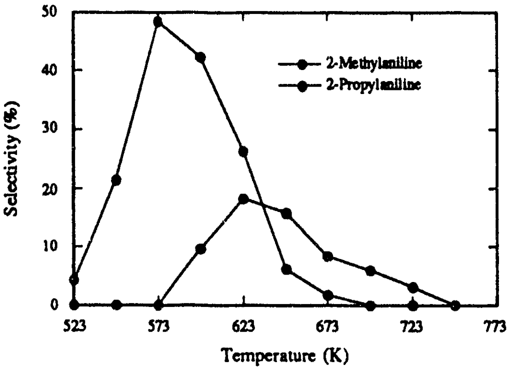

Figure 3. Analine compound selectivity versus temperature

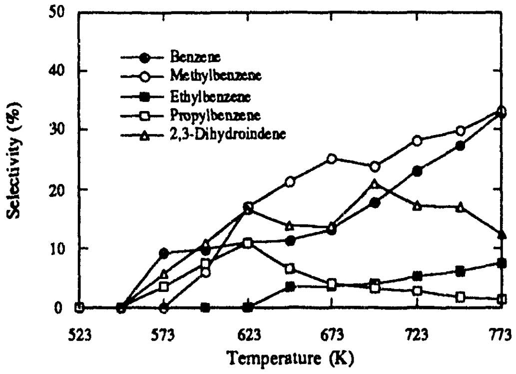

Figure 4. Benzene compound selectivity versus temperature

It is significant to observe that the reaction products contain no evidence of cyclohexane or alkylcyclohexanes. The absence of these products is assumed to be due to a weak interaction of the benzene ring with the catalyst surface. Experiments conducted using benzene or propylbenzene as the feed indicate that at temperatures where these products are formed from quinoline, hyrogenation of the benzene ring occurs to only a very limited degree, and when ammonia is present in the feed stream the hydrogenation activity of Mo_2N is totally suppressed.

4. CONCLUSIONS

The hydrodenitrogenation of quinoline HDN over Mo_2N is initiated by the hydrogenation of quinoline to 1-THQ. This reaction is very rapid and achieves thermodynamic equilibrium already at 523 K. No evidence is found for 5,6,7,-tetrahydroquinoline, even though the Gibbs free energy for forming this compound is significantly greater than that for the formation of 1-THQ. The removal of nitrogen from 1-THQ is initiated by cleavage of the C-N bond in the saturated ring, to form 2-PA. 2-PA then undergoes a loss of the amine group to form PB. Hydrogenolysis of the alkyl group in PB leads to the formation of toulene and ethylbenzene, whereas dealkylation produces benzene. In strong contrast to sulfided $NiMo/Al_2O_3$ [3,4] the standard catalyst for HDN, Mo_2N does not produce decahydroquinoline or propylcyclohexane. This difference is attributable to the weak chemisorption of aromatic rings on Mo_2N.

5. ACKNOWLEDGMENT

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