Catalytic hydrotreating of indole, benzothiophene, and benzofuran over Mo_2N

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The activity of γ-Mo_2N for heteroatom removal from benzofuran, benzothiophene, and indole has been investigated. γ-Mo_2N is found to be an effective catalyst in all three cases. The distribution of products observed as a function of temperature suggests that the reaction mechanism is similar for all three reactants. Rapid hydrogenation of the heterocyclic ring is followed by hydrogenolysis of the X–C bond in the saturated ring and release of the heteroatom as XH_n (X = O, S, N). The product formed in the last step of the sequence is ethylbenzene. Hydrogenation of the benzene ring in ethylbenzene is not observed, but evidence is found for hydrogenolysis and dealkylation of the alkyl group.

Keywords: Hydrotreating; indole; benzofuran; benzothiophene, Mo_2N

1. Introduction

Molybdenum nitride (Mo_2N) and molybdenum carbide (Mo_2C) have been reported recently to exhibit activity for hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) [1–4]. Schlatter et al. [1] have shown that Mo_2N and Mo_2C have activities for quinoline HDN comparable to that of a commercial NiMo/Al_2O_3 catalyst, but exhibit much higher selectivities for the formation of aromatic products. Similar findings are reported by Lee et al. [3]. Their work has shown 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-propylaniline which, in turn, undergoes hydrogenolysis of the C–N bond in the saturated ring to form propylbenzene. HDN of pyridine over a series of Mo_2N catalysts has also been reported recently by Thompson et al. [4]. The aim of the present investigation is to investigate the activity of Mo_2N for heteroatom removed from benzofuran, benzothiophene, and indole, all of which have a similar chemical structure.

2. Experimental

γ-Mo_2N was prepared by temperature-programmed reduction of MoO_3 in a flow of ammonia. A more detailed description of the catalyst preparation procedure may be found in ref. [5]. X-ray diffraction of a freshly prepared sample showed a characteristic pattern for Mo_2N and no evidence of residual MoO_3. The BET surface area of a freshly prepared sample was typically between 208 and 220 m^2/g.

All reactions were carried out in the quartz microreactor used for the catalyst preparation. Each of the organic reactants, indole (Aldrich, 99+%), benzothiophene (Aldrich, 99%), and benzofuran (Aldrich, 99.5%), was 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 downstream 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

Fig. 1 shows the time dependence of the activity of Mo_2N. In each case, 1 g of catalyst was used and the reaction temperature was kept at 723 K. It is immediately apparent that the activity of Mo_2N for heteroatom removed is a function of the feed composition and that the activity decreases in the order benzofuran

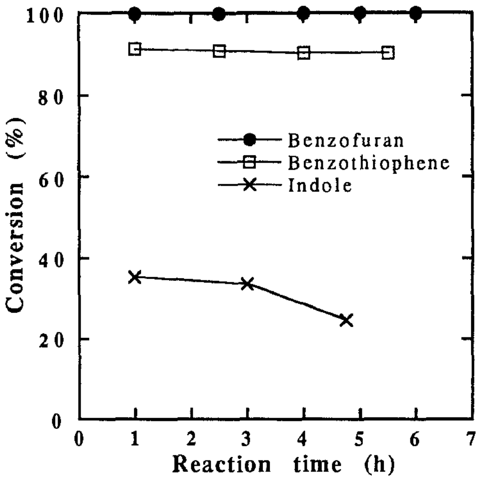
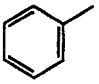
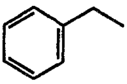
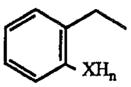


Fig. 1. Conversion of benzofuran, benzothiophene and indole over Mo_2N at 723 K versus time.

Table 1
The distribution of reaction products formed at 723 K[a]

Feed	Product distribution (%)			
				
benzofuran	36.6	30.2	32.5	0.7
benzothiophene	0.4	0.0	99.1	0.6
indole	24.6	57.0	18.4	0.0

[a] $P = 1$ atm; H_2/reactant = 287; $Q_T = 110.4\ cm^3/min$.

>benzothiophene>indole. The catalytic activity of Mo_2N remains constant when benzofuran or benzothiophene are used as the feed, but decreases by 12% over 5 h when indole is used as the feed.

The distribution of reaction products formed from each feed at 723 K is given in table 1. Benzofuran produces nearly equivalent amounts of ethylbenzene, toluene, and benzene. By contrast, benzothiophene produces primarily ethylbenzene and only a small amount of benzene. In the case of indole, toluene is observed as the principal product, together with smaller amount of benzene and ethylbenzene.

Fig. 2 illustrates the effects of temperature on the conversion of benzofuran, benzothiophene, and indole. The distribution of products formed from each of these reactants is presented in figs. 3–5. It is evident from fig. 2 that benzofuran and benzothiophene exhibit comparable reactivities. The conversion of each of these reactants increases rapidly from 500 to 550 K and then more slowly with further increases in temperature. Indole is much less reactive than either benzofuran or benzothiophene.

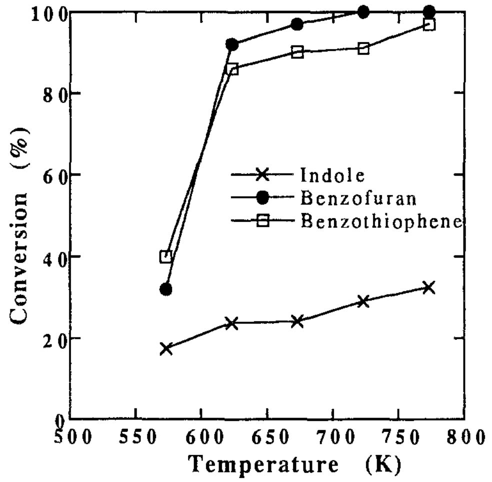


Fig. 2. The effect of temperature on the conversion of benzofuran, benzothiophene, and indole.

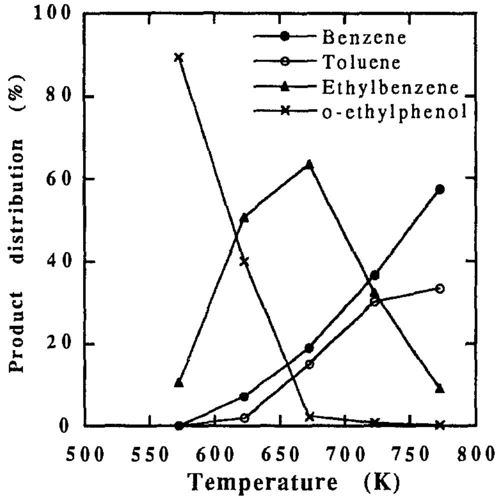


Fig. 3. Benzofuran HDO: product distribution versus temperature.

Fig. 3 shows the change in the distribution of products formed from benzofuran. At low temperatures, the principal products are *o*-ethylphenol and ethylbenzene. As the temperature increases, the selectivity to *o*-ethylphenol decreases monotonically, the selectivity to ethylbenzene passes through a maximum, and the selectivities to toluene and benzene increase monotonically.

The effects of temperature on the distribution of products formed from benzothiophene are given in fig. 4. At the constant temperature investigated, 575 K, *o*-ethylthiophenol and ethylbenzene are the principal products formed. Very small amounts of toluene are also observed. With increasing temperature, the selectivity to *o*-ethylthiophenol decreases rapidly to zero, whereas the selectivity to ethylben-

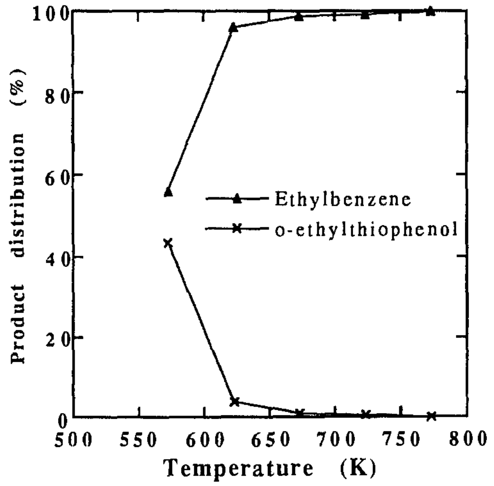


Fig. 4. Benzothiophene HDS: product distribution versus temperature.

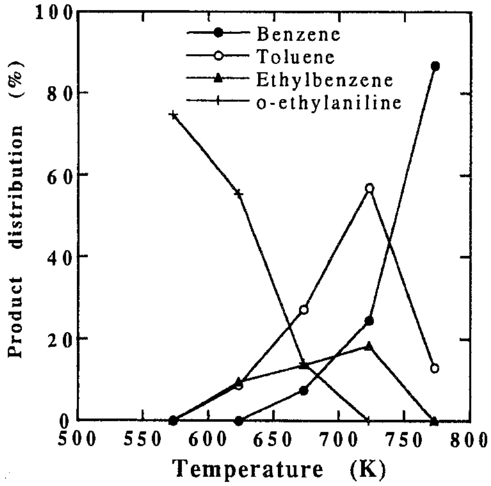


Fig. 5. Indole HDN: product distribution versus temperature.

zene rises to 100%. The selectivities to toluene and benzene are practically zero for temperatures above 600 K.

Fig. 5 shows the influence of temperature on the distribution of products obtained from indole. *o*-ethylaniline and *o*-methylaniline are the principal products observed at 500 K. As the temperature increases, the product distribution shifts first to ethylbenzene and toluene, and then to benzene.

The effect of H_2/feed ratio on feed conversion and product distribution was investigated at 723 K. Fig. 6 shows that at this temperature the conversion of benzofuran is insensitive to feed ratio of H_2/benzofuran, but that the conversion of benzothiophene and indole both increase with increasing proportion of H_2 in the

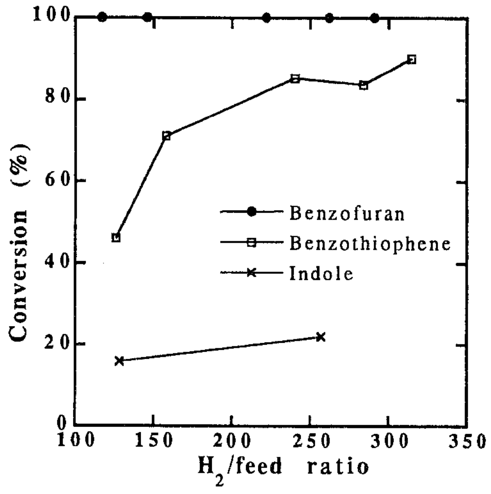


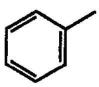
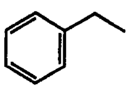
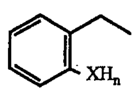
Fig. 6. The effect of hydrogen/feed effect on feed conversion at 723 K.

feed. The ratio of H_2/feed has only a slight effect on the distribution of products in each case, as may be seen in table 2.

The distribution of products formed as a function of reaction temperature suggests the reaction mechanism shown in fig. 7. The first step is rapid hydrogenation of the heteroatom-containing ring. The fact that the product of this reaction is never observed suggests that it is very reactive, so that its concentration at the temperatures utilized in this study is low. Cleavage of the C–X bond in the saturated heterocyclic ring results in the formation of products such as 2-ethylphenol, 2-ethylthiophenol, and 2-ethylaniline. Each of these products then readily undergoes a loss of the heteroatom-containing side group (i.e. OH, SH, NH_2) to form ethylbenzene. Hydrogenolysis of the ethyl group produces toluene, whereas dealkylation of ethylbenzene and toluene leads to benzene.

It is significant to note that the reaction sequence presented in fig. 7 is similar to that proposed for quinoline HDN by Lee et al. [3]. In that study, hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline was found to attain equilibrium at temperatures as low as 523 K. Hydrogenation of the five-membered heteroatom-containing ring should be even more facile, since the equilibrium constant for this reaction at 723 K is more than 10^2 times larger than that for quinoline hydrogenation [6]. In the study of quinoline HDN [3], the rate determining step was found to be hydrogenolysis of the C–N bond in 1,2,3,4-tetrahydroquinoline. We may then reasonably postulate that the same type of step will be rate determining in the present case. If this is so, then the observed relative case of heteroatom removal from benzofuran and benzothiophene relative to indole can be readily understood, since the C–N bond is considerably stronger than the C–O or C–S bond. Removal of the heteroatom side group (i.e. OH, SH, NH_2) occurs very rapidly and is complete at temperatures above 700 K.

Table 2
The effect of hydrogen/feed ratio on the product distribution at 723 K[a]

Feed	H_2/feed ratio	Product distribution (%)			
					
benzofuran	291	36.6	30.2	32.5	0.7
	117	37.0	36.2	26.8	0.0
benzothiophene	315	0.4	0.0	99.1	0.6
	126	0.0	0.0	100	0.0
indole	257	24.6	57.0	18.4	0.0
	128	17.7	43.7	23.1	3.8

[a] $P = 1$ atm; $Q_T = 110.4\ cm^3/min$.

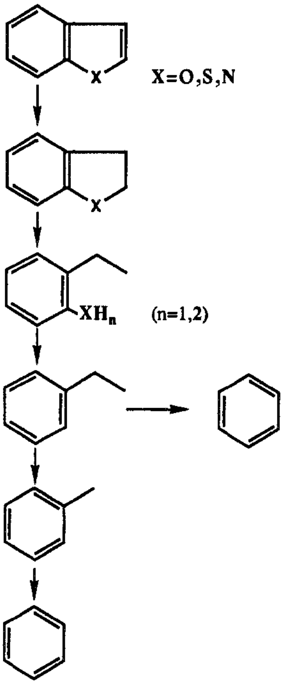


Fig. 7. Proposed reaction mechanism of heteroatom removal over Mo_2N.

In addition to the difference in the extent of reactant conversion at a given temperature, differences are also seen in the extents of alkyl group hydrogenolysis and dealkylation. As can be seen from figs. 3–5, the extent of hydrogenolysis and dealkylation decreases in the sequence benzofuran > indole > benzothiophene. This trend can be attributed to differences in the effects of XH_n ($X = O$, S, N) on the rates of hydrogenolysis and dealkylation. In the study of quinoline HDN, Lee et al. [3] found that NH_3 in the gas phase suppressed the activity of Mo_2N for hydrogenolysis and dealkylation. One may, therefore, project that H_2O, H_2S, and NH_3 will have a similar effect in the present case. Given the relative extents of hydrogenolysis and dealkylation as a function of heteroatom composition, it is inferred that the effectiveness of XH_n ($n = 1, 2, 3$) in suppressing the undesired side reactions decreases in the order $H_2S > NH_3 > H_2O$.

Another significant observation is that for none of the reactants is there any evidence of aromatic ring hydrogenation. This finding is in complete agreement with those of Lee et al. [3] for quinoline HDN over Mo_2N. In that study it was shown, as well, that passage of a feed containing H_2 and either benzene or propylbenzene did not result in hydrogenation of the aromatic ring at temperatures above 500 K. In the case of benzene, partial decomposition to form small hydrocarbon fragments was observed but this process was found to be suppressed when NH_3 was added to the feed. The absence of any evidence for benzene ring decomposition in the present study can, thus, be attributed to the presence of XH_n amongst the products.

In summary, the present study demonstrates that γ-Mo_2N is an effective catalyst for heteroatom removal from benzofuran, benzothiophene, and indole. Each of these molecules appears to react via a similar mechanism, which involves rapid hydrogenation of the heterocyclic ring followed by hydrogenolysis of the X–C bond in the saturated ring and release of the heteroatom as XH_n ($X = O, S, N$). The hydrocarbon produced in the last step of this sequence is ethylbenzene. No evidence is found for hydrogenation of the benzene ring in ethylbenzene, but hydrogenolysis of the alkyl group and dealkylation can occur. These latter two processes are suppressed, however, by the presence of XH_n, the effectiveness of the suppression decreasing in the order $H_2S > NH_3 > H_2O$.

Acknowledgement

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