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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

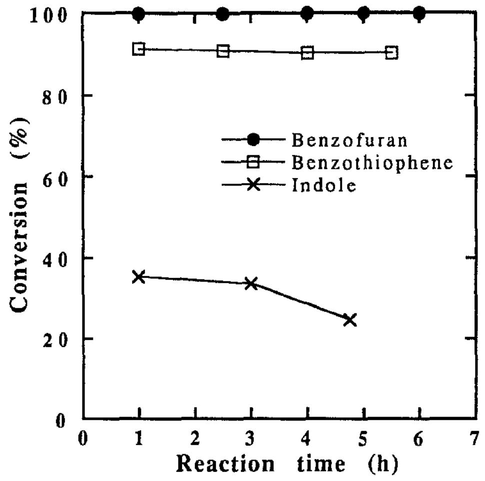

Fig. 1. Conversion of benzofuran, benzothiophene and indole over Mo_2N at 723 K versus time.